



University of Zagreb

Faculty of Science
Department of Geology

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**CHANGES IN PHYSIOCHEMICAL
PROPERTIES, TRACE ELEMENTS
MOBILITY AND TOXICITY OF
WEATHERED COAL COMBUSTION
RESIDUES**

DOCTORAL THESIS

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Mentor:
Željka Fiket, PhD

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Sveučilište u Zagrebu

Prirodoslovno-matematički fakultet
Geološki odsjek

Marija Petrović

**PROMJENE U FIZIKALNO-KEMIJSKIM
SVOJSTVIMA, MOBILNOSTI
ELEMENATA U TRAGOVIMA I
TOKSIČNOSTI TROŠENIH OSTATAKA
IZGARANJA UGLJENA**

DOKTORSKI RAD

Mentor:
dr. sc. Željka Fiket

Zagreb, 2026.

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Information about the supervisor

Željka Fiket, PhD is a senior research associate and head of the *Laboratory for Inorganic Environmental Geochemistry and Chemodynamics of Nanoparticles* at the Division for Marine and Environmental Research of the Ruđer Bošković Institute. She holds a PhD in Oceanology from the University of Zagreb and was awarded by the L'Oréal-UNESCO for Women in Science. With her strong research interest in inorganic environmental geochemistry and a wide range of collaborations, she has had the opportunity to be (co-)author of more than 90 scientific papers and 2 book chapters, and to collaborate on or lead various projects. She is also a titular Assistant Professor in the Department of Geology in the Faculty of Science, where she teaches several courses, (co-)organiser of several Environmental Science Schools, and mentor of numerous graduate students, laboratory interns, and 2 PhD students.

Abstract

This dissertation investigates the long-term environmental behavior and impacts of coal combustion residues (CCR), with emphasis on weathering, contaminant mobility, toxicity, and source tracing. The research combined mineralogical, geochemical, radiological, ecotoxicological, and isotopic approaches to evaluate CCRs from historical disposal sites in Croatia and active coal regions in Bosnia and Herzegovina. Results showed that CCRs undergo substantial physicochemical transformation during decades of natural weathering, including mineral alteration, pH decline, and early pedogenic development, but remain environmentally reactive. Leaching experiments demonstrated selective mobilization of elements, while ecotoxicological assays confirmed persistent phytotoxic and genotoxic effects despite long-term weathering. Isotopic and radiological characterization showed that CCRs possess distinct geochemical fingerprints that can support environmental source attribution. Application to surface waters revealed site-specific CCR-related impacts rather than a universal contamination signature, with isotopic tracers providing the clearest evidence of source influence where conventional hydrochemistry was ambiguous. The findings demonstrate that weathered CCRs remain dynamic environmental materials and provide tools for assessing their long-term ecological and hydrogeochemical impacts.

Keywords

coal combustion residues; weathering; trace element leaching; phytotoxicity; Technosols; genotoxicity

Sažetak

Ova disertacija istražuje dugoročno ponašanje i utjecaj ostataka izgaranja ugljena (CCR) u okolišu, s naglaskom na procese trošenja, mobilnost onečišćivala, toksičnost i utvrđivanje izvora onečišćenja. Istraživanje je obuhvatilo mineraloške, geokemijske, radiološke, ekotoksikološke i izotopne analize CCR materijala s povijesnih odlagališta u Hrvatskoj te područja eksploatacije ugljena u Bosni i Hercegovini. Rezultati su pokazali da CCR tijekom desettljeća prirodnog trošenja prolazi kroz značajne fizikalno-kemijske promjene, uključujući mineralne transformacije, snižavanje pH vrijednosti i razvoj ranih pedogenetskih procesa, ali pritom ostaje okolišno reaktivan materijal. Pokusi izluživanja pokazali su selektivnu mobilizaciju elemenata, dok su ekotoksikološka ispitivanja potvrdila postojanu fito- i genotoksičnost unatoč dugotrajnom trošenju. Izotopna i radiološka karakterizacija pokazala je da CCR posjeduje prepoznatljive geokemijske otiske korisne za utvrđivanje izvora onečišćenja. Primjena ovih pristupa na površinskim vodama pokazala je prostorno specifične utjecaje povezane s CCR-om, pri čemu su se izotopni pokazatelji pokazali posebno korisnima u razlikovanju izvora onečišćenja kada sama hidrogeokemijska analiza nije bila dovoljna.

Ključne riječi

ostaci izgaranja ugljena; trošenje; ispiranje elemenata; fitotoksičnost; Technosoli; genotoksičnost

Extended abstract (*in Croatian*)

Ugljen je tijekom posljednjih stoljeća predstavljao jedan od najvažnijih izvora energije te je značajno pridonio industrijskom razvoju i proizvodnji električne energije. Unatoč postupnom povećanju udjela obnovljivih izvora energije, termoelektrane na ugljen i dalje sudjeluju u proizvodnji značajnog dijela svjetske električne energije, pri čemu se svake godine proizvede više od milijardu tona ostataka izgaranja ugljena (engl. *coal combustion residues*, CCR). Ti materijali, koji uključuju lebdeći pepeo, šljaku, boilerski pepeo i produkte odsumporavanja dimnih plinova, predstavljaju jedan od najvećih izvora industrijskog otpada na globalnoj razini. Iako se dio proizvedenih ostataka koristi u građevinskoj industriji, znatne količine i dalje završavaju na odlagalištima, gdje mogu predstavljati dugotrajan izvor onečišćenja okoliša.

Za razliku od svježe proizvedenih ostataka izgaranja ugljena, koji su predmet brojnih istraživanja, znatno je manje poznato kako se njihova svojstva mijenjaju tijekom desetljeća prirodnog trošenja. Nakon odlaganja materijal je kontinuirano izložen djelovanju oborinskih voda, atmosferskih utjecaja, promjenama oksidacijsko-redukcijskih uvjeta te biološkoj aktivnosti biljaka i mikroorganizama. Posljedica tih procesa su postupne mineraloške, fizikalne i kemijske promjene koje mogu značajno utjecati na mobilnost potencijalno toksičnih elemenata, njihovu biodostupnost i ukupni okolišni rizik. Unatoč tome, procjena rizika od ostataka izgaranja ugljena još se uvijek u velikoj mjeri temelji na istraživanjima svježeg materijala, dok su dugoročne promjene na povijesnim odlagalištima nedovoljno istražene.

Poseban izazov predstavljaju povijesna, često neuređena odlagališta nastala u razdoblju kada zaštita okoliša nije bila zakonski regulirana u današnjem obliku. Takva odlagališta najčešće nemaju sustave zaštite podzemnih voda niti sustavni okolišni monitoring, zbog čega mogu desetljećima predstavljati difuzni izvor onečišćenja tla, površinskih i podzemnih voda. Istodobno, tijekom vremena u

njima dolazi do razvoja procesa pedogeneze, odnosno postupnog nastanka tla. Ovi procesi mijenjaju mineralni sastav materijala, vrijednost pH, sadržaj organske tvari i sorpcijska svojstva, čime izravno utječu na ponašanje elemenata u tragovima u okolišu. Razumijevanje tih procesa nužno je za pouzdanu procjenu dugoročnog okolišnog rizika te planiranje sanacije i budućeg upravljanja takvim lokacijama.

Dosadašnja istraživanja pokazala su da su u ostacima izgaranja ugljena prisutni brojni elementi u tragovima. Međutim, njihov okolišni utjecaj ne ovisi isključivo o ukupnim koncentracijama, nego prvenstveno o njihovoj mobilnosti i biodostupnosti. Upravo zbog toga ispitivanja izluživanja predstavljaju jedan od najvažnijih alata za procjenu potencijalnog onečišćenja okoliša. Dodatno, sama kemijska karakterizacija često nije dovoljna za procjenu stvarnog rizika, budući da biološki organizmi reagiraju na ukupni učinak svih prisutnih onečišćivala. Stoga se za procjenu rizika za biotu često primjenjuju ekotoksikološki testovi.

Osim procjene mobilnosti i toksičnosti, jedan od važnih izazova predstavlja i pouzdano određivanje izvora onečišćenja. Povišene koncentracije elemenata u prirodnim vodama ili sedimentima mogu biti posljedica različitih prirodnih i antropogenih procesa, zbog čega sama kemijska analiza često nije dovoljna za razlikovanje izvora onečišćenja. Posljednjih godina sve se više primjenjuju izotopni pokazatelji koji omogućuju prepoznavanje karakterističnog geokemijskog potpisa ostataka izgaranja ugljena te njihovo razlikovanje od ostalih mogućih izvora. Kombinacija klasičnih geokemijskih metoda s izotopnim pristupom predstavlja jedan od najučinkovitijih načina praćenja širenja onečišćivala u okolišu.

Polazeći od navedenih spoznaja, ova je doktorska disertacija usmjerena na istraživanje dugoročnog ponašanja ostataka izgaranja ugljena u okolišu, s posebnim naglaskom na procese trošenja, promjene fizikalno-kemijskih

svojstava, mobilnost elemenata u tragovima, ekotoksikološke učinke te mogućnosti određivanja izvora onečišćenja primjenom izotopnih i radioloških metoda. Istraživanje je provedeno na povijesnim odlagalištima ostataka izgaranja ugljena u Hrvatskoj, koja predstavljaju primjer materijala izloženog približno pedesetogodišnjem prirodnom trošenju, kao i na aktivnim ugljenokopnim područjima Bosne i Hercegovine, čime je omogućena usporedba dugoročno trošenih i svježih ostataka izgaranja ugljena. Rezultati istraživanja doprinose boljem razumijevanju procesa koji određuju okolišno ponašanje ostataka izgaranja ugljena te pružaju znanstvenu podlogu za procjenu rizika, praćenje onečišćenja i planiranje budućih aktivnosti sanacije i upravljanja ovim specifičnim vrstama industrijskog otpada.

Glavni cilj ove doktorske disertacije bio je utvrditi kako dugotrajno prirodno trošenje utječe na fizikalno-kemijska svojstva, mobilnost elemenata u tragovima i ekotoksikološka svojstva ostataka izgaranja ugljena te procijeniti njihov dugoročni utjecaj na okoliš. Poseban naglasak stavljen je na procese koji se odvijaju tijekom višedesetljetnog izlaganja atmosferskim i pedogenetskim uvjetima, budući da su upravo takva odlagališta najzastupljenija u mnogim dijelovima Europe, ali su istodobno znatno slabije istražena od svježih ostataka izgaranja ugljena. Uz istraživanje trošenih materijala, cilj rada bio je i procijeniti okolišni utjecaj svježih ostataka izgaranja ugljena na području aktivne eksploatacije ugljena u Bosni i Hercegovini te ispitati mogućnosti primjene geokemijskih, radioloških i izotopnih pokazatelja u određivanju izvora onečišćenja.

Istraživanje je provedeno kroz pet međusobno povezanih cjelina koje zajedno obuhvaćaju pregled postojećih spoznaja, eksperimentalna istraživanja te procjenu okolišnog utjecaja ostataka izgaranja ugljena. Prvu cjelinu čini pregledni znanstveni rad kojim su objedinjene dosadašnje spoznaje o mehanizmima otpuštanja onečišćivala, ekotoksikološkim učincima i metodama praćenja

onečišćenja povezanog s ostacima izgaranja ugljena. Na temelju identificiranih nedostataka u literaturi definirane su istraživačke hipoteze i eksperimentalni pristup koji je primijenjen u nastavku rada.

Eksperimentalni dio istraživanja obuhvatio je dvije različite vrste istraživanih područja. Prvi dio odnosio se na povijesna odlagališta ostataka izgaranja ugljena Štrmac i Plaški u Hrvatskoj, koja predstavljaju primjer materijala izloženog približno pedeset godina prirodnog trošenja. Na tim su lokacijama prikupljeni uzorci različitog stupnja razvijenosti, uključujući trošene površinske slojeve bez vegetacije, površine obrasle vegetacijom te razvijena tla nastala na odlagalištima. Takav pristup omogućio je praćenje promjena koje nastaju tijekom sukcesije i razvoja tla. Drugi dio istraživanja proveden je na području ugljenokopa i termoelektrana Tuzla, Gacko i Stanari u Bosni i Hercegovini, gdje su analizirani svježi ostaci izgaranja ugljena te površinske vode pod mogućim utjecajem odlagališta.

Za karakterizaciju uzoraka primijenjen je širok spektar analitičkih metoda kojima su obuhvaćena fizikalna, kemijska, mineraloška, radiološka i ekotoksikološka svojstva materijala. Fizikalno-kemijska karakterizacija uključivala je određivanje pH vrijednosti, električne vodljivosti, sadržaja organske tvari, granulometrijskog sastava te drugih osnovnih svojstava važnih za procjenu procesa trošenja i razvoja tla. Mineraloški sastav određen je primjenom rendgenske difrakcije, dok je kemijski sastav analiziran određivanjem glavnih i elemenata u tragovima spektrometrom masa uz induktivnu spregnutu plazmu.

Kako bi se procijenila stvarna mogućnost prijelaza elemenata iz čvrste faze u okoliš, provedeni su standardizirani pokusi izluživanja. Dobiveni eluati korišteni su za određivanje mobilnosti elemenata u tragovima, ali i kao podloga za provedbu ekotoksikoloških ispitivanja. Time je omogućena usporedba kemijski procijenjenog okolišnog rizika s biološkim odgovorom testnih organizama.

Ekotoksikološka procjena obuhvatila je ispitivanje fitotoksičnosti i genotoksičnosti primjenom standardiziranih biljnih testova, pri čemu su analizirani pokazatelji klijavosti, rasta korijena i diobe stanica kao osjetljivi indikatori prisutnosti biološki dostupnih onečišćivala.

Kako bi se procijenila mogućnost razlikovanja onečišćenja uzrokovanog ostacima izgaranja ugljena od ostalih prirodnih i antropogenih izvora, u istraživanje su uključene i radiološke te izotopne analize. Primjenom stabilnih i radiogenih izotopa te određivanjem aktivnosti prirodnih radionuklida ispitana je mogućnost korištenja karakterističnog geokemijskog potpisa ostataka izgaranja ugljena za određivanje njihova doprinosa sastavu površinskih voda. Takav integrirani pristup omogućio je povezivanje rezultata mineraloških, geokemijskih, ekotoksikoloških i izotopnih istraživanja u jedinstvenu procjenu dugoročnog okolišnog ponašanja ostataka izgaranja ugljena.

Rezultati provedenih istraživanja pokazali su da ostaci izgaranja ugljena ni nakon približno pedeset godina prirodnog trošenja ne predstavljaju inertan materijal, već prolaze kroz kontinuirane fizikalno-kemijske i mineraloške promjene koje određuju njihovo dugoročno ponašanje u okolišu. Usporedba netrošenih i trošenih materijala pokazala je da tijekom vremena dolazi do razvoja pedogenetskih procesa, promjene kemijskog sastava i mineralogije te postupnog razvoja Tehnosola, pri čemu se istodobno mijenja i mobilnost elemenata u tragovima te njihov potencijalni okolišni utjecaj. Dobiveni rezultati potvrđuju da se procjena okolišnog rizika ne može temeljiti isključivo na karakteristikama svježih ostataka izgaranja ugljena, već mora uzeti u obzir i procese koji se odvijaju tijekom dugotrajnog trošenja.

Jedna od najizraženijih posljedica dugotrajnog trošenja bila je promjena fizikalno-kemijskih svojstava materijala. Tijekom prirodnog izlaganja atmosferilijama dolazi do otapanja lako topljivih mineralnih faza, nastanka sekundarnih minerala

te postupnog smanjenja alkalnosti materijala. Istodobno se povećava sadržaj organske tvari zbog razvoja vegetacije i aktivnosti mikroorganizama, čime započinje razvoj tla na antropogenom supstratu. Dobiveni rezultati pokazuju da se na istraživanim odlagalištima razvijaju obilježja karakteristična za Tehnosole, pri čemu vegetacija ima ključnu ulogu u ubrzavanju pedogeneze i transformaciji početnog materijala. Time je potvrđena prva postavljena hipoteza da višedesetljetno trošenje značajno mijenja fizikalno-kemijska svojstva ostataka izgaranja ugljena.

Iako se tijekom trošenja mijenjaju fizikalna i kemijska svojstva materijala, rezultati pokusa izluživanja pokazali su da određeni elementi u tragovima zadržavaju izraženu mobilnost. Posebno se to odnosi na elemente koji u okolišu tvore oksianione, poput molibdena, selena, vanadija i arsena, čije ponašanje uvelike ovisi o pH vrijednosti i mineralnom sastavu materijala. S druge strane, za dio kationskih elemenata uočeno je smanjenje mobilnosti tijekom razvoja sekundarnih mineralnih faza i povećanja sorpcijskog kapaciteta tla. Rezultati potvrđuju da se dugotrajnim trošenjem mijenja način otpuštanja elemenata u okoliš, ali ne dolazi do potpunog gubitka potencijala za njihovu mobilizaciju. Drugim riječima, trošenje ne uklanja okolišni rizik, već ga mijenja.

Važan doprinos ove disertacije predstavlja povezivanje rezultata kemijskih analiza s ekotoksikološkim ispitivanjima. Pokazalo se da kemijski sastav sam po sebi nije dovoljan pokazatelj stvarnog okolišnog rizika jer biološki odgovor organizama ovisi o biodostupnosti onečišćivala i njihovom zajedničkom djelovanju. Ekotoksikološki testovi provedeni na eluatima pokazali su da pojedini uzorci, unatoč dugotrajnom trošenju, i dalje mogu izazvati fitotoksične i genotoksične učinke. Time je potvrđeno da dugotrajno prirodno trošenje ne dovodi nužno do potpune detoksifikacije materijala, nego okolišni rizik ostaje prisutan, iako se njegov intenzitet i mehanizmi djelovanja mijenjaju tijekom vremena. Dobiveni rezultati naglašavaju važnost uključivanja bioloških testova u

procjenu okolišnog rizika, budući da oni pružaju informacije koje nije moguće dobiti isključivo kemijskom analizom.

Osim istraživanja povijesnih odlagališta, disertacija je obuhvatila i procjenu utjecaja svježih ostataka izgaranja ugljena na području aktivne eksploatacije ugljena u Bosni i Hercegovini. Rezultati su pokazali da utjecaj odlagališta na sastav površinskih voda nije moguće jednoznačno procijeniti samo na temelju koncentracija elemenata, budući da na njihov kemijski sastav istodobno utječu prirodni geološki procesi, rudarske aktivnosti i drugi antropogeni izvori. Upravo zbog toga u istraživanje su uključeni izotopni i radiološki pokazatelji koji omogućuju razlikovanje pojedinih izvora onečišćenja. Pokazalo se da pojedini izotopni sustavi predstavljaju osjetljiviji alat za utvrđivanje utjecaja ostataka izgaranja ugljena od konvencionalnih hidrogeokemijskih pokazatelja, osobito u slučajevima kada su razlike u kemijskom sastavu površinskih voda male ili prikrivene prirodnim varijacijama.

Jedan od važnijih zaključaka proizlazi iz usporedbe različitih istraživanih lokaliteta. Rezultati pokazuju da okolišno ponašanje ostataka izgaranja ugljena nije univerzalno, nego u velikoj mjeri ovisi o sastavu matičnog ugljena, mineralogiji pepela, klimatskim uvjetima, hidrološkim prilikama i stupnju razvijenosti pedogenetskih procesa. Zbog toga nije moguće primijeniti jedinstveni model procjene okolišnog rizika na sva odlagališta. Umjesto toga, svaku lokaciju potrebno je promatrati kao zaseban geokemijski sustav u kojem se dugoročno isprepliću procesi trošenja, razvoja tla, transporta onečišćivala i biološke aktivnosti.

Dobiveni rezultati također imaju šire značenje u kontekstu upravljanja napuštenim industrijskim odlagalištima. Velik broj takvih lokacija u Europi nastao je tijekom razdoblja intenzivne uporabe ugljena te danas više nije pod sustavnim monitoringom. Rezultati ove disertacije pokazuju da dugotrajno trošenje može

značajno promijeniti svojstva ostataka izgaranja ugljena, ali istodobno potvrđuju da oni i desetljećima nakon odlaganja mogu predstavljati aktivan izvor potencijalno toksičnih elemenata. Stoga procjena njihova okolišnog utjecaja zahtijeva kombinaciju mineraloških, geokemijskih, ekotoksikoloških i izotopnih metoda kako bi se dobila cjelovita slika procesa koji određuju njihovo ponašanje u okolišu.

Znanstveni doprinos ove disertacije očituje se u boljem razumijevanju procesa koji određuju dugoročnu transformaciju ostataka izgaranja ugljena nakon odlaganja te u povezivanju procesa trošenja, razvoja tla, mobilnosti elemenata u tragovima i ekotoksikoloških učinaka u jedinstveni koncept okolišnog ponašanja ovih materijala. Dobiveni rezultati doprinose unapređenju metodologije procjene okolišnog rizika na povijesnim odlagalištima te predstavljaju vrijednu znanstvenu podlogu za buduća istraživanja, planiranje sanacije i razvoj učinkovitijih strategija upravljanja lokacijama onečišćenima ostacima izgaranja ugljena.

1. INTRODUCTION

1.1. Formation and global relevance of coal combustion residues

Coal has been one of the dominant energy sources and still accounts for ~38–40% of global electricity production (World Coal Association, 2020). Despite the recent rise of renewables and environmental policies limiting fossil fuel use, coal consumption remains significant, especially in China, India, and the United States (Benalcazar et al., 2017; BP, 2020; International Energy Agency, 2020). Combustion of coal generates vast quantities of by-products, approximately 1.1 billion tons of coal combustion residues (CCR) annually, with half of this amount being disposed of in ash ponds (wet storage) and landfills (dry storage) (Figure 1) (Harris et al., 2019; Zhang, 2014).

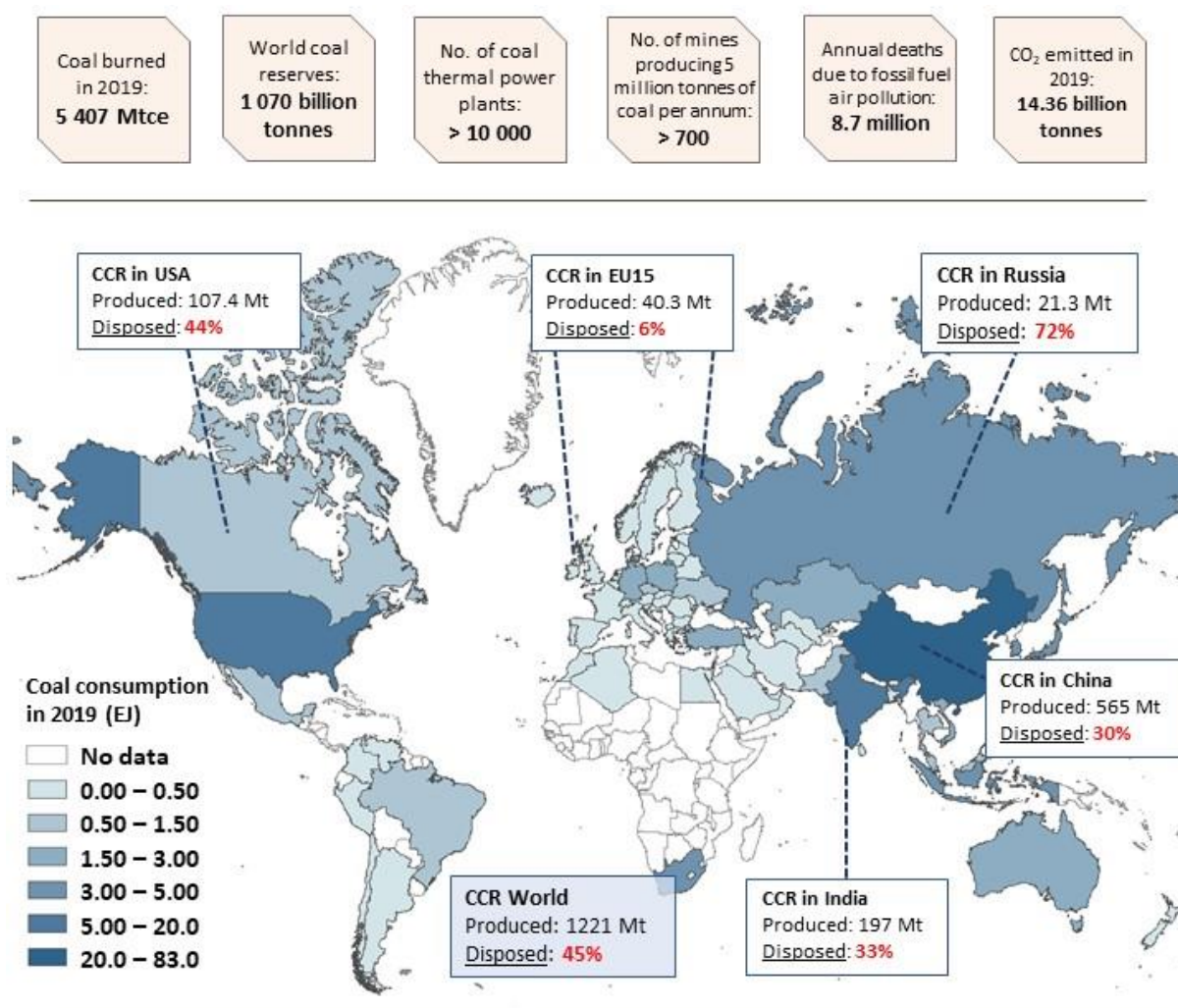


Figure 1. Coal consumption and CCR production and disposal in the world (Petrović and Fiket, 2022).

CCR is a joint name for four by-products that form during and after combustion. During combustion, the organic fraction of coal is volatilized while the inorganic, mostly mineral, fraction remains but undergoes a series of transformations (Hower et al., 2017). Therefore, based on the characteristics of the by-product, CCR are divided into (Figure 2) (Harris et al., 2019; Li et al., 2018):

1. *Fly ash* – fine, powdery particles typically composed of aluminosilicate glass with variable amounts of unburned coal particles. They are either carried by flue gas or captured by electrostatic precipitators or bag filters. Due to its small size and high surface area, fly ash is typically the dominant and most harmful CCR fraction.
2. *Bottom ash* – a coarse, granular material that accumulates at the bottom of the boiler. Compared to fly ash, it is heavier, more crystalline, and less readily mobilized into the environment.
3. *Boiler slag* – a vitrified, glassy slag that forms in certain wet-bottom furnaces. Molten bottom ash from the boiler is quenched with water, producing a hard, glass-like material. Boiler slag is a less common fraction of CCR, limited to specific furnace designs.
4. *Flue gas desulfurization (FGD) residues* – typically a sludge that consists of calcium sulfite or gypsum characterized by crystalline morphology. They are formed from processes designed to remove SO₂ from flue gases, most commonly through wet scrubbing with limestone or lime.

Together, these by-products represent one of the largest industrial waste streams globally (Harris et al., 2019). The heterogeneity of the parent coal strongly influences the composition of CCR. For example, coal rank¹ plays a key role: low-rank coals such as lignite generally contain higher proportions of calcium, magnesium, and sulfur-bearing minerals, whereas higher-rank coals produce ash dominated by silica, alumina, and iron oxides (Finkelman et al., 2019; Gamage et al., 2013). Consequently, the mineralogy, leaching potential, and overall environmental behavior of CCR are intrinsically linked to the geochemical characteristics of the coal from which they are derived.

¹ Coal rank refers to the degree of coalification, the natural process by which plant material is transformed into coal under increasing temperature and pressure over geological time. It reflects the maturity of the coal, progressing from peat to lignite (brown coal), sub-bituminous, bituminous, and to anthracite, with higher ranks having more carbon, higher energy content, lower moisture, and lower volatile matter.



Figure 2. A) Physical appearance and B) particle morphology obtained by SEM of four types of coal combustion residues (CCR) (DAE Pumps, 2021).

Although fly ash is increasingly reused in construction materials (cement, concrete, road fill), utilization rates vary widely. While countries like the Netherlands and France reuse nearly 100% of fly ash, in others such as India, China, or the rest of the Europe, less than 60% is utilized (Kruger, 2017). As a result, massive amounts of CCR remain stored in landfills worldwide (Zhang, 2014).

A major challenge in coal ash global risk assessment is the absence of comprehensive inventories. A recent evaluation of coal ash landfills in the United States reports that more than 1,000 CCR disposal sites exist, with approximately 450 unlined (Earthjustice, 2021). For the rest of the world, such evaluations have not yet been conducted, as many landfills have been abandoned following the decline of the coal industry. These legacy sites are often undocumented, unlined, and unmonitored, yet they can continue to impact surrounding ecosystems for decades after disposal. In Croatia, for example, the Štrmac landfill was abandoned decades ago but still influence soils, water, and biota (Medunić et al., 2018). Similar long-lasting effects have been reported in Poland, Serbia, India, and the U.S. (Brandt et al., 2018, 2017; Lemly, 2018; Madan and Hussain, 2014; Pacwa-Płociniczak et al., 2018; Verma et al., 2016). These legacies highlight CCR as a persistent but underestimated source of diffuse pollution. Only recently have regulators begun addressing them; for instance, in 2024 the U.S. EPA extended federal monitoring and cleanup requirements to previously unregulated “legacy” coal ash ponds and landfills (NRDC, 2025), a move aimed at preventing ongoing contamination from older sites.

1.2. Coal Combustion Residue Pollution Pathways

1.2.1. Types of contaminants released from coal combustion residues

When coal combustion residues are disposed of in the environment (whether in engineered landfills, surface impoundments, or as uncontrolled fills), they have the potential to release a complex mixture of contaminants. These pollutants can migrate through air, surface water, groundwater, and soil, creating multiple pathways of exposure to ecosystems and human populations (Harkness et al., 2016; Petrović and Fiket, 2022; Radić et al., 2018). The following sections outline the types of contaminants found in CCR and how they enter the environment, as well as their biological effects and the factors controlling their release.

1.2.1.1. Organic contaminants

Although the inorganic fraction dominates coal ash, a variety of organic pollutants can also be present. The most important among them are aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) (Kalaitzoglou et al., 2004).

Aliphatic hydrocarbons

Aliphatic hydrocarbons are compounds composed solely of carbon and hydrogen, connected by single (alkanes), double (alkenes), or triple (alkynes) covalent bonds (Peters et al., 2004). The specific type of aliphatic hydrocarbons found in coal ash depends largely on the combustion temperature of the parent coal. For example, in Portuguese coal, short-chain alkanes (C₁₄–C₁₅) were dominant prior to combustion, but after burning at 1300–1400 °C, their concentration decreased while long-chain alkanes (C₁₉–C₃₃) increased, indicating thermally induced transformation of *n*-alkanes (Ribeiro et al., 2014). In contrast, fly ash samples from Greece showed a higher proportion of short-chain alkanes, likely reflecting the lower coal rank from which those ashes were derived (Figure 3) (Kalaitzoglou et al., 2004).

Although aliphatic hydrocarbons can occur in coal ash, their concentrations and environmental risks have been studied far less extensively than those of PAHs.

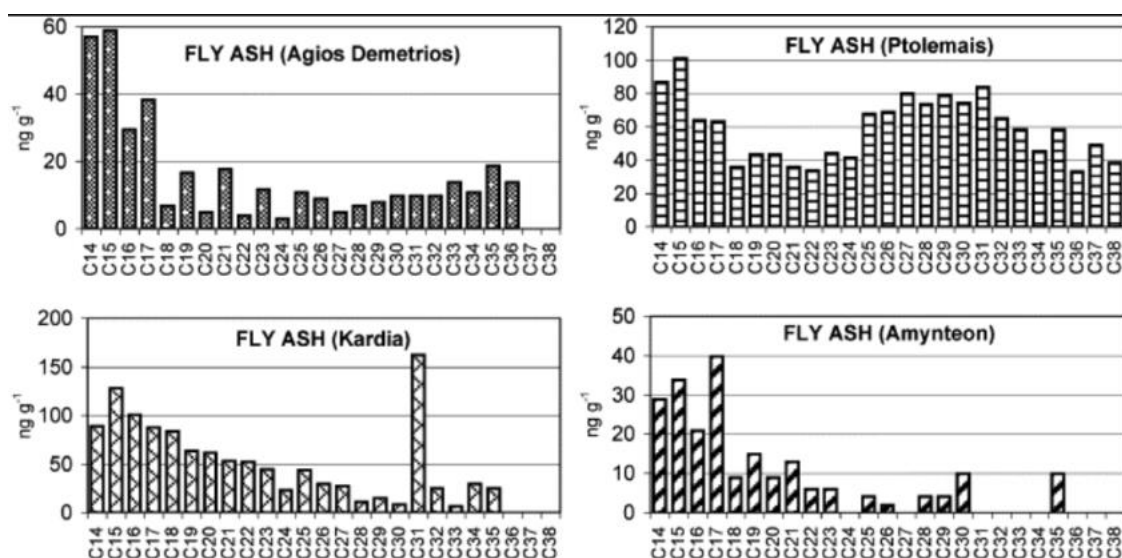


Figure 3. Alkanes concentrations in Greek fly ash mostly had a higher proportion of short-chain alkanes (Kalaitzoglou et al., 2004).

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) represent a large group of organic compounds composed of two or more fused aromatic rings. Their name derives from the characteristic odor (aroma) of many compounds in this class (Rogers et al., 2002). PAHs are lipophilic and therefore easily absorbed from the gastrointestinal tract of mammals, rapidly distributing into various tissues and tending to accumulate in body fat. Owing to these properties, many PAHs are toxic, mutagenic, and carcinogenic (Peters et al., 2004).

PAHs occur naturally in coal, crude oil, and petroleum products, and they are released during combustion or through volcanic activity. Once emitted, they deposit onto soil surfaces, leading to elevated concentrations (Jakovljević et al., 2022; Medunić et al., 2016a; Mizwar and Trihadiningrum, 2015; Thavamani et al., 2012).

During coal combustion, PAHs are either emitted directly into the atmosphere or become associated with fly ash and bottom ash. The concentration and composition of PAHs in a particular ash type depend on combustion conditions, particularly temperature and residence time, which influence thermal transformation pathways (Košnář et al., 2016; Ruwei et al., 2013). For instance, in fly ash from China, total concentrations of 16 PAHs ranged from 0.93 to 2.08 $\mu\text{g g}^{-1}$, while in bottom ash they ranged from 2.83 to 5.32 $\mu\text{g g}^{-1}$ (Ruwei et al., 2013). In contrast, lower concentrations were observed in Indian fly ash (0.03 $\mu\text{g g}^{-1}$) and bottom ash (0.01 $\mu\text{g g}^{-1}$) (Verma et al., 2015).

In Croatia, elevated concentrations of PAHs, sulfur, and trace elements have been documented in the Labin-Plomin region, historically associated with mining and the combustion of high-sulfur Raša coal. Elevated concentrations of PAHs, sulfur, and trace elements were detected in soils and fly ash around the Plomin thermal power plant, indicating persistent contamination from coal combustion residues and atmospheric deposition (Medunić et al., 2016a). Total PAH concentrations in ash samples ranged from 1.03 to 2.64 $\mu\text{g g}^{-1}$, while nearby soils contained up to 0.64 $\mu\text{g g}^{-1}$, with the highest levels occurring downwind of the power plant. The contamination pattern corresponded with prevailing wind directions and with increased concentrations of arsenic, cadmium, lead, and sulfur, confirming the combined influence of historical and ongoing emissions from coal combustion. The PAH assemblages were dominated by four- and five-ring compounds (fluoranthene, pyrene, benzo[a]anthracene, chrysene), typical of high-temperature combustion processes.

Subsequent measurements in 2021 confirmed the persistence of PAH contamination in soils and sediments from the wider Labin region, with total concentrations of 11 PAHs in soils ranging from 0.25 to 14.29 $\mu\text{g g}^{-1}$ (the control soil contained 0.03 $\mu\text{g g}^{-1}$) (Jakovljević et al., 2022). In 11 of 14 locations, the concentrations exceeded Croatian regulatory limits, indicating a widespread legacy of coal-derived pollution. The elevated levels were mainly attributed to historical emissions from the Plomin coal-fired power plant, with minor contributions from traffic.

PAHs generally occur at much lower concentrations than inorganic constituents in CCRs and are typically adsorbed to unburned carbon or fine particles in fly ash, which reduces their immediate leachability (Saeedi et al., 2018). Therefore, this dissertation focuses primarily on inorganic contaminants, as they represent the dominant and more mobile fraction in coal combustion residues.

1.2.1.2. Inorganic contaminants

The primary environmental concern from CCR arises from the inorganic contaminants, especially trace elements, which dominate leachate profiles and are key determinants in site risk assessments. The distribution and behavior of trace elements in CCR are largely inherited from the original coal but can be altered by high-temperature combustion processes (Finkelman et al., 2019; Izquierdo and Querol, 2012; Vejahati et al., 2010). In raw coal, trace elements occur in three principal forms (Figure 4):

1. Bound organically within macerals, associated with functional groups (e.g., carboxylic, phenolic, and amino groups) and occurring as organometallic complexes or chelates,
2. Bound inorganically within mineral matter, either as discrete mineral phases (e.g., sulphides such as arsenopyrite and galena) or incorporated into mineral structures through isomorphic substitution and/or adsorption onto mineral surfaces (e.g. clay minerals),
3. Occurring as fine-grained mineral particles dispersed within the organic matrix.

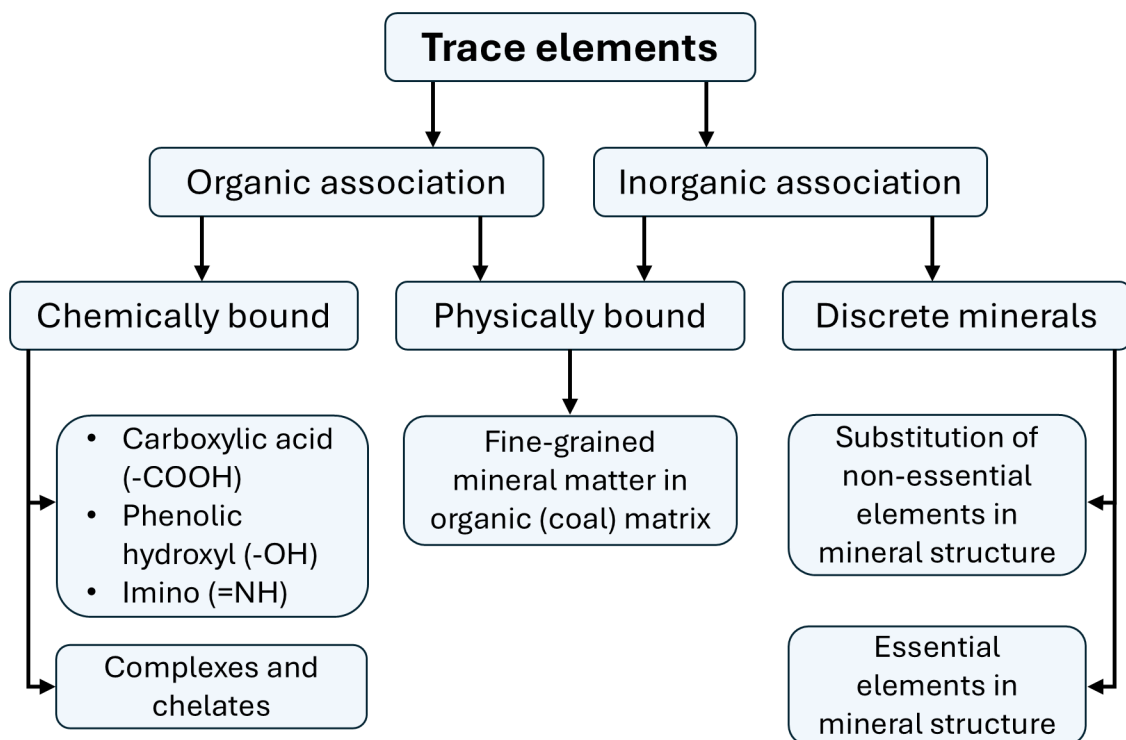


Figure 4. Schematic representation of the modes of occurrence of trace elements in coal, illustrating their association with organic matter and mineral phases. Modified after Clarke and Sloss (1992) and Vejehati et al. (2010)

The high temperatures of combustion ($>1000^{\circ}\text{C}$) break down these associations. Many volatile elements vaporize and then condense onto cooler ash particles, whereas others remain in solid solution or form new mineral phases in the ash. The result is that trace elements in CCR exist in a variety of chemical forms with differing solubilities and environmental mobilities (Izquierdo and Querol, 2012; Vejehati et al., 2010).

Trace elements in CCR can be classified based on their volatilization behavior and post-combustion occurrence modes as :

1. *Volatile and surface-enriched elements* (e.g., Hg, As, Se, Sb, Cd, Pb, Mo): These elements volatilize at boiler temperatures and condense onto the surface of fine fly ash particles. Their enrichment on particle surfaces makes them highly available for leaching, especially under oxidizing and alkaline conditions (Izquierdo and Querol, 2012; Kim et al., 2017)
2. *Refractory and mineral-bound elements* (e.g., Zr, Th, U, Ti, and rare earth elements): These elements remain mostly within resistant crystalline minerals such as zircon, monazite, and apatite or become occluded in amorphous aluminosilicate glass. Due to their chemical inertness, they show very low solubility under typical environmental conditions (Querol et al., 1996).
3. *Intermediate (semi-volatile) elements* (e.g., Cr, Ni, Cu, V, Zn): These elements exhibit mixed behavior, undergoing partial volatilization followed by condensation, while also partitioning into the glassy and crystalline phases of ash. Their mobility is more context-specific, influenced by pH, redox state, and complexation reactions (Querol et al., 1996).

This variability in occurrence and partitioning behavior is one of the factors controlling the release of trace elements during leaching of CCR. In addition, not all trace elements pose equal threats. Among the most environmentally significant are arsenic, selenium, mercury, cadmium, and lead (Shah et al., 2008; Wang et al., 2022; Wu et al., 2016). In addition to elemental chemical properties, the release of trace elements from CCR, and thus their environmental impact, is governed by a combination of intrinsic and extrinsic factors.

1.2.3. Factors controlling trace element release from CCR

One of the primary pathways by which coal ash contaminants migrate into the environment is the percolation of water through ash deposits which dissolves and carries away soluble constituents (i.e., leaching) (Sloot et al., 2009). Elements that leach into the water have the potential to contaminate adjacent soils or disperse into groundwater or surface water bodies. Understanding the leaching behavior of CCR is therefore crucial for predicting long-term pollution risks. The actual release of elements from CCR is governed by a complex interplay of both the intrinsic properties of the ash and extrinsic environmental factors (Kosson et al., 2019; Sloot et al., 2009). Key factors include pH, redox conditions, liquid-to-solid ratio, and hydrology, as well as intrinsic ash properties such as mineralogy, glass, and organic matter content.

pH of the system

The pH of the water/ash system is one of the most important factors controlling the leaching behavior of coal combustion residues (Kosson et al., 2014). Fresh coal ash is typically neutral to strongly alkaline (pH ~8–12), although variability in composition may result in lower pH values. In general, ashes rich in calcium exhibit strongly alkaline behavior due to the presence of Ca-bearing phases such as lime (CaO), portlandite (Ca(OH)₂), and other basic oxides formed during combustion. In contrast, ashes dominated by aluminosilicate phases (Si and Al) tend to show lower alkalinity, as these phases are relatively inert and do not significantly contribute to pH buffering (Wang et al., 2022).

Therefore, depending on the ash composition, leachate pH can fall into three broad categories (Izquierdo and Querol, 2012; Kosson et al., 2019, 2014):

- a) strongly alkaline (pH > 11) if free lime or sodium oxide is abundant (typical of low-rank and high-Ca coal ashes),
- b) moderately alkaline (pH 8–10) often governed by gypsum or carbonate equilibria, or
- c) acidic (pH < 7) due to oxidation of pyrite in the ash which produces acidity (more common in mine-fill scenarios).

Because the solubility of most trace elements is strongly pH-dependent, leaching behaviors can be classified into several characteristic pH-dependent types (Figure 5) (Izquierdo and Querol, 2012; Kosson et al., 2019, 2014):

1. *Soluble salts*. Readily soluble constituents (Na⁺, K⁺, Cl⁻, NO₃⁻, borates) dissolve rapidly in the first flush of water, showing little pH dependence.
2. *Cationic metals*. Elements such as Cd, Ni, Mn, and Pb exhibit low solubility at high pH due to precipitation as hydroxides or sorption onto mineral surfaces. However, their solubility increases markedly under neutral to acidic conditions as these hydroxide and carbonate phases dissolve.
3. *Oxyanions*. Elements such as As, Se, Mo, Cr(VI), V, and Sb form anionic species (e.g., arsenate AsO₄³⁻, selenate SeO₄²⁻) that typically reach maximum solubility in the neutral to mildly alkaline range (pH 7–10). At very high pH they may adsorb to calcium phases or precipitate as Ca-salts, while at low pH they may co-precipitate with Fe/Al oxides.

4. *Amphoteric elements*. Metals such as Al, Zn, and Pb display U-shaped solubility curves, soluble at both low and high pH, but least mobile under circumneutral conditions.

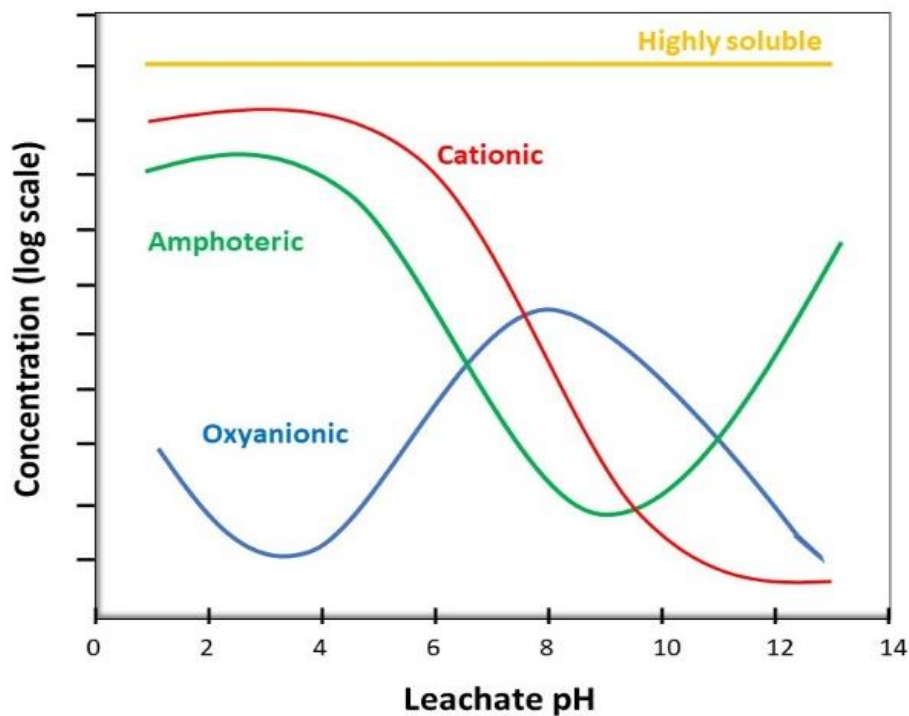


Figure 5. Characteristic pH-dependent leaching curves. Adapted and modified after Kosson et al. (2019)

Redox conditions

The oxidation-reduction environment (often linked to whether the ash is water-saturated or exposed to air) affects the valence state and thus mobility of certain elements (Romero et al., 2007; Sloot et al., 2009). For example, arsenic and chromium are far more mobile and toxic in their oxidized forms (As^{5+} as arsenate, Cr^{6+} as chromate) than in reduced forms (As^{3+} , Cr^{3+}). Selenium is more mobile as selenate (Se^{6+}) than selenite (Se^{4+}) or elemental Se (Plant et al., 2013; Shah et al., 2008). Coal ash basins that become anaerobic at depth (due to microbial consumption of residual organics) might promote reduction of these elements, potentially immobilizing As and Cr by precipitating them as sulfides or sorbing them onto newly formed iron sulfides (Liu et al., 2016). Conversely, if previously waterlogged ash is drained and oxygen enters, reduced species can oxidize and release, for instance converting relatively immobile Se^0 into soluble selenate. Redox also controls the stability of iron-bearing sorbents: under reducing conditions, iron(III) oxides that bind arsenic may dissolve, releasing arsenic into solution (Liu

et al., 2016). Thus, any changes in water table or oxygenation at ash sites can trigger pulses of contaminant release.

Liquid-to-solid ratio and hydrology

The volume of water interacting with coal combustion residues (CCRs) and the residence time of that water are key determinants of leaching intensity and contaminant transport (Kosson et al., 2002; Sloat et al., 2009). In arid environments or during dry seasons, limited infiltration restricts leaching, whereas high rainfall or elevated groundwater levels can lead to extensive flushing of pore water and mobilization of dissolved constituents (Bagwell et al., 2025; Choi et al., 2002; Hayes et al., 2009; Mendez and Maier, 2008; Xu et al., 2025).

The hydrological setting also differentiates leaching behavior between wet and dry disposal systems. In ash ponds, continuous water saturation sustains dissolution processes and enables the migration of solutes through seepage and surface outflow (Able et al., 2023; Boche et al., 2025). In contrast, dry landfills experience intermittent water infiltration, and intense rainfall following prolonged dry periods can produce short-term leachate pulses with elevated solute concentrations, the so-called “first-flush” effect (Akinyemi et al., 2011; Xu et al., 2025).

The flow rate and hydraulic connectivity of groundwater or percolating water further control leaching dynamics. Slow flow conditions promote near-equilibrium reactions and the formation of secondary minerals that can attenuate contaminant release (e.g., ettringite or Fe(III) hydroxides), whereas rapid flow enhances advective transport but limits contact time for dissolution–precipitation equilibria to establish (Bateman et al., 2022; Dijkstra et al., 2006; Kosson et al., 2014; Zhang et al., 2026). These hydrological parameters collectively dictate the temporal and spatial patterns of element mobility in ash deposits.

Intrinsic ash properties

The mineral composition of coal combustion residues (CCRs) strongly influences how elements are released into solutions (Figure 6) (Akinyemi et al., 2011; Schwartz et al., 2018; Wang et al., 2023, 2022). Different minerals dissolve at different rates, and each controls the solubility of specific ions. For instance, ashes containing anhydrite (CaSO_4) readily release sulfate until the mineral is exhausted, keeping sulfate concentrations close to the gypsum solubility limit. If the ash contains lime (CaO) or calcium aluminate phases, leachate pH can exceed 11 due to the formation of portlandite (Ca(OH)_2). Such strongly alkaline conditions favor the release of

hydroxide and certain oxyanion-forming elements (e.g., As, Mo, Se) until these reactive minerals are depleted (Wang et al., 2022).

More stable crystalline phases, such as feldspars, spinels, and magnetite, tend to retain metals within their crystal structures and therefore contribute little to leaching (Garcia et al., 2026; Izquierdo and Querol, 2012; Vassilev and Vassileva, 1996; Wang et al., 2025). In contrast, the amorphous glassy phase, which makes up a large part of most fly ashes, reacts slowly with water in a process similar to cement hydration. As it weathers, it can release alkalis and trace elements but also promote the formation of secondary minerals (e.g., ettringite, clays) that may later capture metals from solution (Garcia et al., 2026; Hower et al., 2017; Izquierdo and Querol, 2012; Wang et al., 2022).

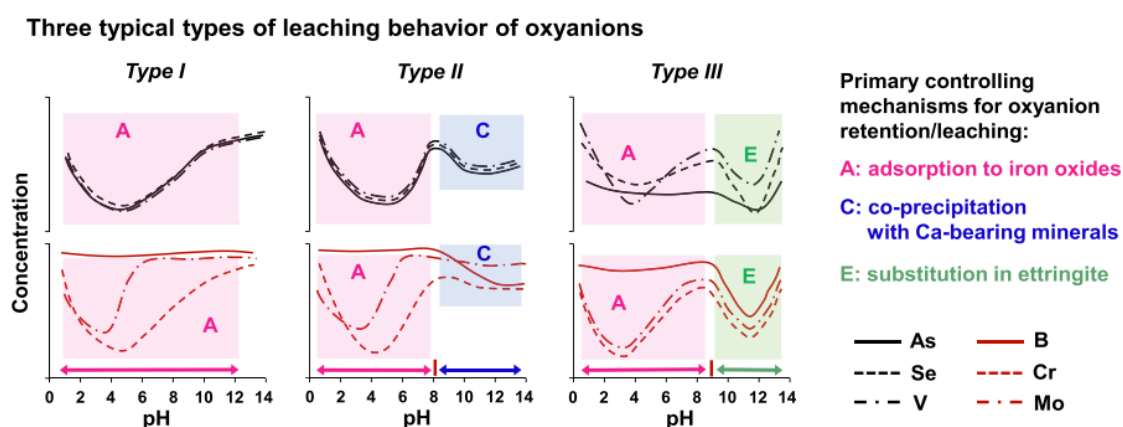


Figure 6. Schematic of pH-dependent leaching of oxyanion-forming elements in CCR, illustrating the role of intrinsic ash properties. The three patterns reflect differences in ash mineralogy: (Type I) adsorption to iron oxides, (Type II) adsorption and co-precipitation with Ca phases, and (Type III) incorporation into secondary minerals (e.g., ettringite) (Wang et al., 2022).

Physical properties further affect how fast these reactions occur (Jones et al., 2012; Kostova et al., 2013; Van Dyk et al., 2009; Zikeli et al., 2004). Fine-grained fly ash has a larger reactive surface and therefore leaches faster than coarse bottom ash, which is less reactive but more permeable (Liu et al., 2024; Tang et al., 2021; Z. Zhang et al., 2022). High porosity increases water-solid contact and facilitates flow-through but can also trap pore water, extending reaction time (Liu et al., 2024). Altogether, the mineralogy, glass content, and physical texture of CCRs determine both their initial leaching behavior and long-term environmental reactivity.

1.2.2. Biological effects and toxicity

Coal combustion residues (CCR) exert a wide range of toxic effects on organisms, spanning from plants and invertebrates to vertebrates and humans. Toxicity most likely arises from the combined presence of trace metals, metalloids, organic pollutants, and naturally occurring radionuclides, making CCR complex in terms of predicting the biological impact (Brandt et al., 2017; Chakraborty et al., 2009; Chen et al., 2024; Lemly, 2018).

Phytotoxicity

Plants are among the most frequently used test organisms in CCR toxicity studies. Coal ash has been shown to inhibit seed germination and radicle elongation in a variety of plant species, including *Vicia faba*, *Brassica parachinensis*, and *Brassica chinensis* (Mehra et al., 1998; Rahmawati et al., 2020; Shakeel et al., 2021; Singh et al., 2016, 1997; Vallejo Vallejo et al., 2024; Wong and Wong, 1989). The degree of inhibition often depends on seed coat protection, with reduced sensitivity prior to germination but significant impairment of root growth afterwards. For this reason, germination tests are often paired with radicle elongation measurements to provide a more complete assessment (Luo et al., 2018).

In addition to growth inhibition, CCR exposure induces cytotoxic and genotoxic effects in plants. These include mitotic abnormalities such as chromosome stickiness, chromosome breaks, laggards, and an overall reduction in the mitotic index (Kaya et al., 2023). Genotoxic damage can be quantified through comet assays (DNA strand breaks) or by measuring oxidative stress markers such as lipid peroxidation (Fiket et al., 2020; Wu et al., 2016). Such cyto- and genotoxic effects have been consistently observed across multiple bioassay species, including *Allium cepa* and *Allium ascalonicum* (shallot), as well as aquatic plants such as *Lemna minor* (Chakraborty et al., 2009; Fiket et al., 2020; Jana et al., 2017; Radić et al., 2018).

Toxicity to invertebrates

While phytotoxicity dominates literature, studies have also examined the effects of CCR on soil invertebrates, particularly earthworms, which are widely recognized as indicators of soil health (Alvarenga et al., 2008; Bartz et al., 2024; Kooch et al., 2025). Even at relatively low concentrations, fly ash leachates have been shown to induce oxidative stress, destabilize lysosomal membranes, and cause DNA damage in earthworms (Markad et al., 2016, 2012).

Such responses suggest disruption of fundamental physiological processes that underpin soil functioning, nutrient cycling, and ecosystem services.

Effects on vertebrates and higher organisms

The impacts of CCR extend to higher trophic levels. Amphibians, due to their permeable skin and aquatic life stages, are particularly vulnerable (Chen et al., 2024; Hughey et al., 2016). Toads inhabiting ash ponds have been observed with oral deformities, reduced ability to graze, impaired swimming performance, altered metabolic rates, and decreased predator avoidance capacity (Hopkins et al., 1998; Rowe et al., 1998, 1996). Similarly, fish exposed to CCR-contaminated waters showed skeletal deformities (Figure 7) (Lemly, 2018; Lohner et al., 2001), while mercury bioaccumulation has been documented in cattle grazing near power plants (Mahajan et al., 2012). Birds and small mammals are also at risk when nesting or foraging around ash ponds (Crnić et al., 2022; Hernández et al., 2017; Meyer et al., 2015; Rowe et al., 2002). The potential for bioaccumulation and biomagnification, especially of selenium and mercury, raises additional ecological concerns (Johnson et al., 2020; Meyer et al., 2015).



Figure 7. Example of CCR toxicity expressed as developmental deformities of fish (largemouth bass, *Micropterus salmoides*) living in a coal ash pond (Lemly, 2018). The upper individual shows pronounced spinal curvature (scoliosis), a typical teratogenic effect associated with selenium originating from CCR, while the lower individual represents normal morphology.

Cellular and human health effects

At the cellular level, CCR exposure has been associated with both cytotoxicity (cell death, reduced proliferation) and genotoxicity (DNA damage, chromosomal aberrations) in a wide range of organisms, including mammalian cell lines and human peripheral blood cells (Chakraborty and Mukherjee, 2009; Chen et al., 2024; Dwivedi et al., 2012; León-Mejía et al., 2016; Matzenbacher et al., 2017; Medunić et al., 2016a; Sambandam et al., 2015). Workers at coal-fired power plants or remediation sites, as well as residents living near unlined ash ponds, face heightened risks (Celik et al., 2007; Chen et al., 2024; Hagemeyer et al., 2019; Turhan et al., 2010; X. Wang et al., 2021). Epidemiological studies suggest increased rates of cancer, cardiovascular and respiratory diseases among affected populations and neurobehavioral problems in affected children (Karavuş et al., 2002; Sears and Zierold, 2017; C. H. Zhang et al., 2022). In addition, the U.S. Environmental Protection Agency has estimated that individuals living within one mile of an unlined coal ash pond have a 1 in 50 lifetime risk of developing cancer from contaminated drinking water (U.S. Environmental Protection Agency, 2007).

Factors influencing toxicity

The toxicity of CCR cannot be predicted from total element concentrations alone, as biological effects depend on the extent to which contaminants are available to interact with living organisms. Therefore, materials with similar chemical compositions may exhibit different toxic responses. These differences arise from variations in contaminant speciation and bioavailability, which control whether elements can be taken up by biological systems (Chen et al., 2024; Gupta et al., 2019; McNally D et al., 2012; Mtisi and Gwenzi, 2019). In addition, toxicity is inherently organism-dependent, as different species, and even different developmental stages, vary in their sensitivity, uptake mechanisms, and ability to tolerate contaminants (Chakraborty and Mukherjee, 2009; Mathews et al., 2020; Radić et al., 2018; Stevenson et al., 2017).

In addition, environmental conditions and ongoing transformations within the ash can therefore either enhance or limit toxic effects over time. Aging and pedogenetic processes may alter contaminant speciation and accessibility, potentially changing their mobility and biological effects. Despite growing recognition of the importance of weathering processes in controlling contaminant behaviour, relatively few studies have examined their implications for CCR toxicity (Bandarra et al., 2020; Kostić et al., 2018) As a result, CCR toxicity should be viewed

as a dynamic property that reflects the interaction between the material, its environment, and the exposed organism.

1.3. Weathering of CCR and soil formation

One of the most overlooked aspects of industrial waste disposal is the fact that waste materials do not remain inert. When exposed to atmospheric and hydrological processes, materials such as coal combustion residues undergo rapid mineralogical, chemical, and biological transformations (Konstantinov et al., 2020; Leguédois et al., 2016; Uzarowicz et al., 2018b). These transformations drive the development of soil-like systems from initially barren waste deposits.

In response to these material transformations and anthropogenic influence on soils, the World Reference Base for Soil Resources (WRB) recognized two new soil groups created predominantly through human activity (FAO, 2014; IUSS Working Group WRB, 2022; Konstantinov et al., 2020; Séré et al., 2010):

1. *Anthrosols*, soils altered by human activity but not derived directly from artificial material.
2. *Technosols*, developed on human artefacts such as slag, ash, and mining by-products and containing $\geq 20\%$ of these artefacts.

By 2010, more than 4% of European soils were already classified as artificial (Hayes et al., 2009; Leguédois et al., 2016). Their relevance is increasing in parallel with global trends in urbanization, industrialization, and land reclamation, yet they remain understudied. As this thesis examines soils derived from CCR, the focus is put on Technosols.

1.3.1. Accelerated pedogenesis in Technosols

Unlike natural soils, which require centuries to millennia to develop, Technosols form over mere decades. This accelerated pedogenesis results from the strong thermodynamic disequilibrium between the freshly deposited industrial waste and the surrounding environment (Coussy et al., 2017; Séré et al., 2010). Early-stage processes, such as oxidation, root penetration, and organic matter accumulation, are often evident within the first few years of deposition. A-horizons thicker than 5 cm have been observed within three years in some

Technosols, whereas such development may take centuries in natural systems (Daniell and van Deventer, 2018).

Due to their rapid formation, Technosols often lack well-developed horizons. Therefore, indicators of pedogenesis include changes in organic matter content, mineral composition, and the appearance of microbial and plant communities rather than horizon differentiation alone (Legu  dois et al., 2016; Uzarowicz et al., 2018a; Watteau et al., 2025). These properties challenge conventional models of soil formation, where time is typically a central factor.

1.3.2. Mineral transformation and biological inputs

The parent material plays a central role in shaping both the physical (e.g., porosity, density) and chemical (e.g., pH, CaCO_3 content) attributes of Technosols (Tarnawczyk et al., 2025; Uzarowicz et al., 2017; Watteau et al., 2025).

Fresh CCR is typically highly alkaline ($\text{pH} > 12$), owing to the presence of reactive phases such as portlandite, gypsum, and free lime. Upon exposure to meteoric water, these compounds dissolve, neutralizing the system and triggering the precipitation of secondary minerals (Uzarowicz et al., 2018b; Uzarowicz and Zagorski, 2015).

The formation of secondary minerals varies with composition. For example, Ca- and S-rich CCR favor the formation of secondary carbonates (e.g., calcite, vaterite) and sulfate-bearing phases such as ettringite and basanite (Figure 8), whereas Fe-rich CCR promotes the formation of secondary iron oxides and oxyhydroxides (e.g., goethite, lepidocrocite, and ferrihydrite) (Colombo et al., 2014; Hayes et al., 2009; Uzarowicz and Zagorski, 2015).

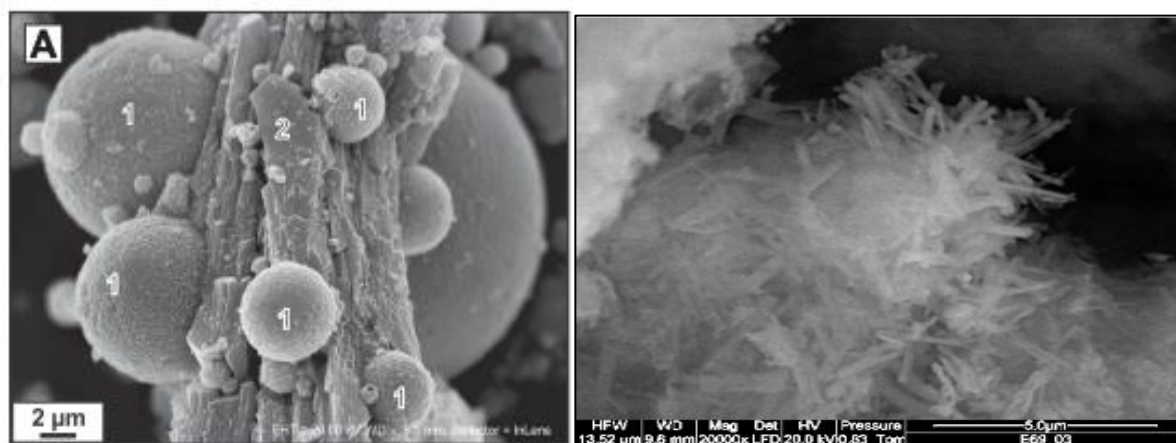


Figure 8. Example of pedogenesis and transformation of minerals in Technosols formed on coal ash. Left: ash particle covered with (1) secondary Si-Al phases and (2) secondary calcium carbonate (Uzarowicz et al., 2018b). Right: Ettringite on soil particles (Uzarowicz and Zagorski, 2015)

As these abiotic weathering processes progress, they create conditions that facilitate biological colonization. Pioneer plants, fungal hyphae, and microbial consortia alter redox dynamics, contribute organic acids, and form symbiotic networks that accelerate weathering. The cumulative effect of these biological processes leads to lower pH, increased organic matter, and the formation of incipient soil horizons (Kostić et al., 2018; Ugolini et al., 2020; Watteau et al., 2025).

Together, these abiotic and biotic processes drive the progressive evolution of CCR Technosols, which can be broadly described through four stages, from CCR formation to advanced soil development (Uzarowicz et al., 2018b):

1. **Fresh ash:** Ash is generated during the combustion of coal, and its properties depend on the parent coal and combustion conditions. Following transport and deposition, fresh CCR typically exhibits high alkalinity (often exceeding pH 12 in Ca-rich systems, although pH varies with composition). Mineralogy closely reflects the parent material (e.g. dominated by portlandite, lime, and glassy aluminosilicates). Vegetation is absent.
2. **Abiotic weathering:** Initial transformation is governed by physicochemical processes, including dissolution of reactive phases and leaching of soluble salts. Secondary minerals such as calcite and gypsum begin to precipitate, and metastable phases may form. pH decreases to approximately 9-10, while biological colonization remains limited. Surface cementation may reduce infiltration and increase susceptibility to erosion.
3. **Early pedogenesis:** As weathering progresses, conditions become favorable for biological colonization. Pioneer vegetation establishes, contributing organic matter and organic acids, while microbial communities and soil fauna further modify substrate chemistry. pH continues to decline toward near-neutral values (6-8), and pedogenic processes such as aggregation, humus accumulation, and clay neoformation begin. Horizon differentiation may occur within years. For example, initial horizon development was observed 3-11 years after revegetation of lignite fly ash deposits in Serbia (Kostić et al., 2018).

4. **Advanced pedogenesis:** Over decades, CCR substrates develop more distinct soil profiles, including Ah and Bw horizons. Depending on vegetation cover, climate, and substrate composition, Technosols may evolve toward more developed soil types such as Cambisols or Phaeozems. Well-established vegetation stabilizes the surface, reduces erosion, and enhances organic matter cycling.

In practice, the progression of these stages is composition-dependent, with mineralogical transformations differing between CCR types, as illustrated by the evolution of bituminous and lignite ashes (Figure 9).

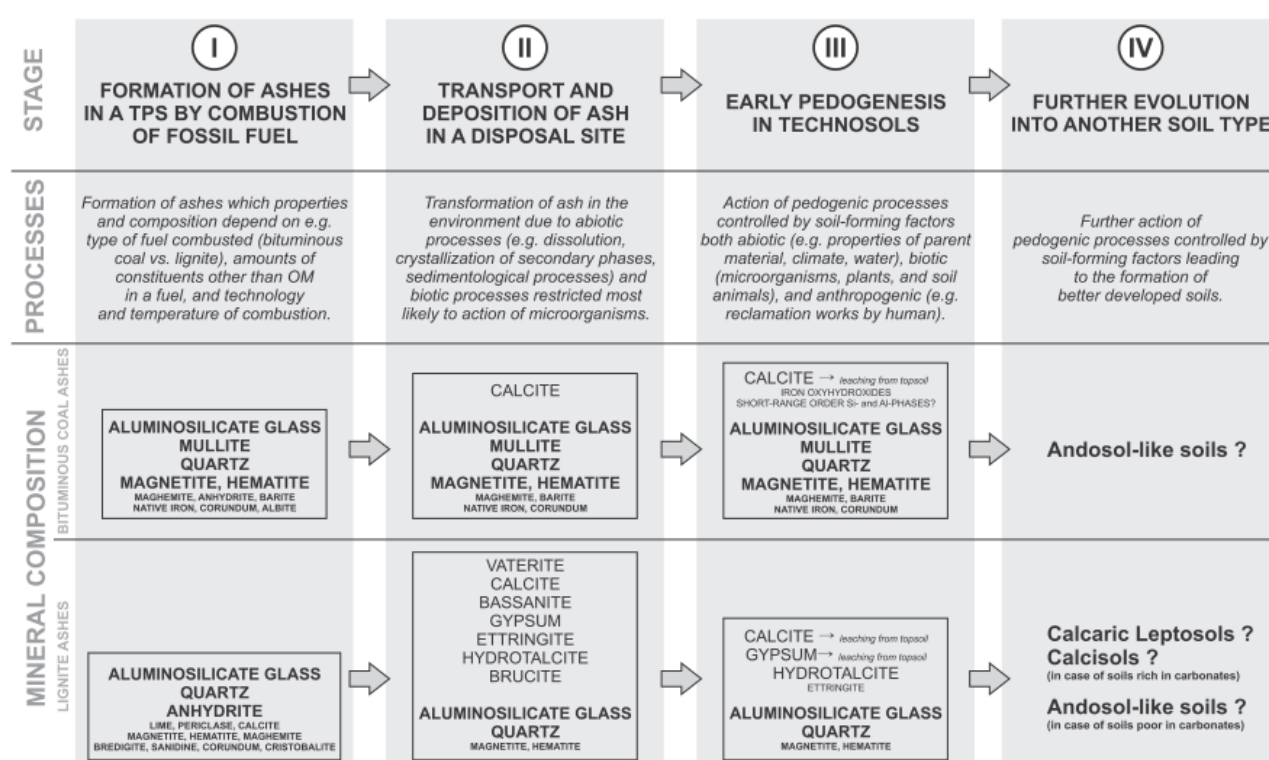


Figure 9. Proposed evolution of Technosols developed on lignite and bituminous CCR.
(Uzarowicz et al., 2018b)

1. 3. 3. Environmental relevance of pedogenesis in coal ash deposits

The transformation of coal combustion residues (CCR) into soil-like materials has important implications for the mobility and long-term fate of contaminants. Processes such as pH decline, secondary mineral formation, organic matter accumulation, and changes in particle surface properties modify sorption capacity, solubility, and contaminant speciation, thereby influencing contaminant mobility (Kostić et al., 2018; Marques et al., 2021).

Only a limited number of studies have examined the mobility in context of pedogenesis. For instance, Kostić et al. (2018) reported decreased concentrations and mobility of elements such as As, B, Cr, Cu, Mn, Ni, and Zn following 3-11 years of revegetation, attributing this to the formation of secondary minerals and increased sorption. However, such trends are not consistent across all elements. Oxyanion-forming elements, including Mo, Se, and V, may remain mobile or even exhibit enhanced release under near-neutral to mildly alkaline conditions typical of weathered CCR (Wang et al., 2022). Despite their environmental relevance, these elements are comparatively underrepresented in the literature, which has largely focused on more traditionally studied cationic heavy metals.

In addition, relatively few studies have addressed the toxicity of weathered CCR. For example, Bandarra et al. (2020) evaluated its toxicity using a range of bioassays, including plant-based tests (e.g., germination and root growth in *Lepidium sativum* and *Vicia faba*), aquatic organisms such as *Daphnia magna* and *Lemna minor*, and microorganisms including algae (*Raphidocelis subcapitata*) and bacteria (*Aliivibrio fischeri*). Overall, weathered CCR exhibited low to moderate toxicity across most test organisms, with *Daphnia magna* showing the highest sensitivity.

Despite these findings, the current understanding remains limited, reflecting the relatively small number of studies focused on weathered CCR. As a result, it is still unclear how pedogenetic transformations control both the mobility of different contaminant groups and their associated biological effects. Consequently, it remains uncertain which elements persist as environmentally relevant over time and whether, and to what extent, CCR continues to exert toxic effects.

More broadly, these gaps highlight the complexity of assessing environmental contamination associated with CCR.

1.4. Tracing the CCR pollution

Assessment of environmental pollution caused by CCR is most commonly based on determining trace element concentrations in environmental media. However, concentration-based approaches are often insufficient, particularly in regions influenced by multiple anthropogenic activities (Figure 10) (Harkness et al., 2017; Wang et al., 2019; Z. Wang et al., 2021). Elevated trace element concentrations in groundwater, surface water, or sediments may originate not only from CCR disposal sites, but also from industrial emissions, natural

weathering processes, or legacy contamination. For instance, strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) have been used to demonstrate that elevated Cr(VI) concentrations near ash disposal sites were both of natural (ophiolitic rock weathering) and CCR origin (Vengosh et al., 2016), while elevated Mo originated mostly from geogenic weathering (Harkness et al., 2017).

Therefore, elemental concentrations alone cannot reliably distinguish between pollution sources or confirm CCR as the primary contributor. In contrast, isotopic compositions provide source-specific “fingerprints” that are largely independent of concentration effects and often remain preserved during dilution, transport, and environmental transformation (Vengosh et al., 1994). As a result, isotope tracing has become a powerful tool for identifying CCR-derived contamination (Harkness et al., 2017; Wang et al., 2019; Z. Wang et al., 2021).

A wide range of isotope systems has been successfully applied in CCR studies, including both stable isotopes (e.g., $\delta^{11}\text{B}$, $\delta^{34}\text{S}$, $\delta^7\text{Li}$, $\delta^{18}\text{O}$, δD) and radiogenic isotopes (e.g., $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{207}\text{Pb}$). Their usefulness is related to their enrichment in coal ash, mobility during leaching, and the relative stability of isotope ratios during combustion and environmental transport. Among these, boron and strontium isotopes are the most widely used tracers of CCR-derived contamination (Harkness et al., 2016; Ruhl et al., 2014; Voltaggio et al., 2015).

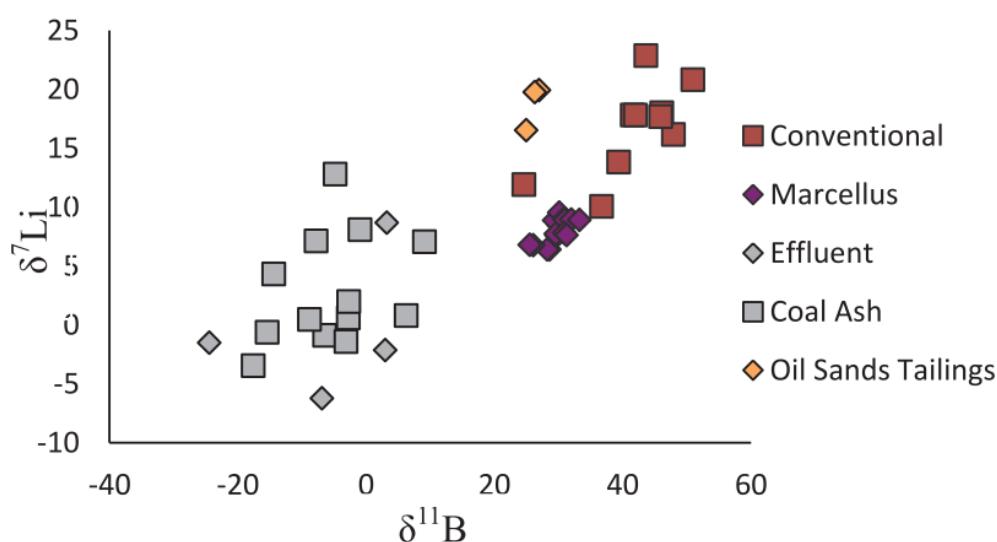


Figure 10. Boron and lithium isotope compositions of coal and CCR leachates and effluents compared with other fossil fuel-associated waters, illustrating the isotopic distinction between different anthropogenic contamination sources (Harkness et al., 2015).

Boron isotopes ($\delta^{11}\text{B}$) are among the most applied tracers of CCR pollution because coal ash leachates are typically enriched in boron and often exhibit isotopically distinct signatures compared with natural waters (Davidson and Bassett, 1993; Harkness et al., 2016; Ruhl et al., 2014; Vengosh et al., 1994). In most cases, CCR leachates display negative $\delta^{11}\text{B}$ values, whereas natural groundwater and surface waters generally show positive values. Therefore, mixing between contaminated and uncontaminated waters produces measurable isotopic shifts toward lower $\delta^{11}\text{B}$ values, allowing the identification of CCR influence. Boron isotopes have been successfully used to trace coal ash leachates in groundwater systems and to distinguish CCR-derived contamination from other anthropogenic and natural boron sources (Davidson and Bassett, 1993; Vengosh et al., 1994). More recently, $\delta^{11}\text{B}$ was used to identify groundwater affected by coal ash pond leachates and to demonstrate that ash disposal sites can remain sources of boron contamination long after their closure (Ruhl et al., 2014).

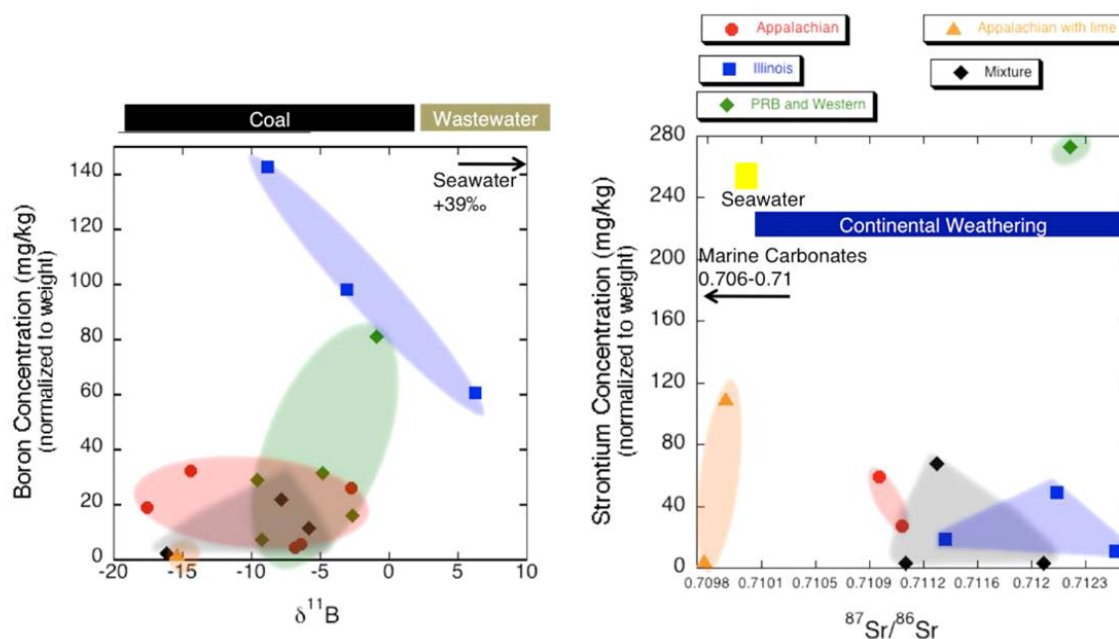


Figure 11. Ranges of elemental boron and strontium concentrations, together with $\delta^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values, measured in effluents on coal samples from major U.S. coal basins. The figure demonstrates that different coal types and associated wastewaters exhibit distinct isotopic and elemental signatures (Ruhl et al., 2014).

Radiogenic strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) are among the most widely used tracers in CCR pollution studies because their ratios are primarily controlled by the geological origin of the source material and are not significantly altered during low-temperature environmental processes (Campbell et al., 2008; Chandler et al., 1997; Hurst et al., 1991; Voltaggio et al.,

2015). Numerous studies have successfully applied Sr isotopes to trace groundwater contamination near coal ash ponds and disposal sites (Figure 11) (Harkness et al., 2016; Hurst et al., 1991; Vengosh et al., 2019; Wang et al., 2020). Strontium isotopes have also been explored as biogenic tracers of CCR contamination (Brandt et al., 2018). Studies of fish otoliths from lakes affected by CCR effluents showed that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in otoliths closely matched contaminated sediment pore waters and were more stable than those measured in surface waters. Because otoliths continuously incorporate Sr during growth, they can preserve long-term records of contamination and may provide a more robust tracer of CCR pollution than temporally variable surface water signatures (Brandt et al., 2018).

Because individual isotope systems may sometimes overlap with background environmental signatures, multi-isotope approaches are increasingly employed. The combined application of boron and strontium isotopes ($\delta^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) has proven particularly effective because the probability of simultaneous overlap in both isotope systems is significantly reduced (Figure 11) (Harkness et al., 2017; Ruhl et al., 2014). A large-scale investigation of groundwater and surface water surrounding 22 coal ash ponds identified CCR contamination in 65 out of 165 groundwater wells using this dual-isotope approach (Harkness et al., 2016). One of the contaminated sites had been closed for 13 years, demonstrating that ash ponds may remain long-term sources of groundwater pollution even after closure.

Other isotope systems have also been investigated in CCR studies, although they are generally less widely applied than boron and strontium isotopes. Sulfur isotopes ($\delta^{34}\text{S}$) can provide information on the origin of sulfate released from coal ash. Strongly positive $\delta^{34}\text{S}$ values (+6.1‰ to +12.9‰) are typically associated with organically bound sulfur in low-sulfur (<1 wt%) coals, whereas negative values (−2.7‰ to −3.2‰) generally reflect pyritic sulfur (FeS_2) (Miljević and Golobočanin, 2007; Puig et al., 2008; Smith and Batts, 1974). However, interpretation of sulfur isotopes is often complicated by multiple sulfur sources and by microbial sulfate reduction processes that can alter isotopic compositions in the environment (Haefner, 2001).

Lithium isotopes ($\delta^7\text{Li}$) have also shown potential as supplementary tracers because CCR leachates may exhibit isotopic compositions distinct from those of natural waters (Figure 10) (Harkness et al., 2015). Lead isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$) have likewise been proposed as tracers of CCR contamination, as coal combustion residues can display isotopic signatures different

from other anthropogenic Pb sources, such as leaded gasoline and paints, while remaining relatively resistant to environmental fractionation (Wang et al., 2019).

3. OBJECTIVES AND HYPOTHESES

Despite decades of research on coal combustion residues (CCR), significant uncertainties remain regarding their long-term environmental behavior. Most risk assessments have focused on freshly produced ash in countries with high coal production and consumption, whereas the fate of CCR after decades of natural weathering remains poorly understood. Four key knowledge gaps can be identified:

1. Pedogenesis within CCR deposits has rarely been investigated, and the resulting changes in physicochemical properties remain largely unexplored.
2. Long-term mobility of trace elements, especially oxyanion-forming species (e.g., As, Mo, Se, V, Sb, U), is insufficiently represented in predictive models. Although freshly generated CCR is known to release contaminants, it remains unclear how prolonged weathering alters these leaching behaviors over time.
3. The toxicity of aged CCR has not been systematically assessed. Chemical characterization alone cannot fully capture ecological risk, and bioassay-based studies at legacy sites remain scarce.
4. Geographical bias in CCR research persists. Research on CCR pollution is heavily concentrated in countries with high coal consumption (e.g., the U.S., India), whereas regions with lower but locally significant coal use remain underrepresented in the literature.

Addressing these gaps requires an integrated approach that combines pedological, geochemical, and ecotoxicological perspectives. By bridging these approaches, this thesis seeks to enhance understanding of CCR legacies and provide a scientific basis for improved risk assessment, site rehabilitation, and the sustainable management of disposal sites.

The main objectives of this study are therefore to:

1. Characterize changes in the physical and chemical properties of CCR after ~50 years of weathering.
2. Evaluate the leaching behavior of trace elements in weathered CCR, with particular emphasis on oxyanion-forming species.
3. Assess the ecotoxicological impacts of weathered CCR eluates using plant-based bioassays.

4. Evaluate the environmental impact of fresh CCR disposal sites in less-studied regions (e.g., Bosnia and Herzegovina).

In line with these objectives, this study tests the following hypotheses:

1. Weathering over ~50 years significantly alters the physical and chemical properties of CCR.
2. The leaching potential of trace elements and the associated toxicity of CCR decrease after ~50 years of natural weathering.
3. The environmental impact of fresh high-Ca CCR is not as severe as the impact of high Al-Si CCR

4. METHODOLOGICAL APPROACH

This research was designed in five phases, each addressing specific hypotheses about the weathering, pedogenesis, contaminant mobility, and toxicity of coal combustion residues (CCR). The approach integrates field sampling, laboratory analyses, standardized leaching protocols, and bioassays, enabling a multi-dimensional evaluation of CCR transformation and its environmental risks.

4.1. Literature synthesis and conceptual integration (Phase 0; Review paper)

In addition to experimental investigations, this dissertation includes a critical review paper focused on the environmental impacts of coal combustion residues (CCR) and the methodologies commonly used for assessing associated environmental risks. The review synthesizes published research on CCR behaviour in environmental systems, with emphasis on contaminant mobility, groundwater contamination, isotope tracing, and ecotoxicological effects.

Particular attention was given to factors controlling contaminant release, including pH, liquid-to-solid ratio, mineralogical composition, redox conditions, and long-term weathering processes. Commonly used leaching protocols were evaluated with respect to the environmental conditions they simulate and the type of information they provide on contaminant mobility.

The review further examines the application of isotope tracers for identifying CCR-derived contamination in groundwater and surface waters. In addition, studies investigating the ecological and toxicological effects of CCR exposure on plants, aquatic organisms, wildlife, and human health were reviewed. Together, the reviewed approaches provide the conceptual background for the experimental phases of this dissertation and support the selection of analytical methods applied in subsequent chapters.

4.2. Sampling and sample preparation (Phase I; All experimental papers)

To investigate the transformation of coal combustion residues (CCR) and test the first two hypothesis, samples were collected from two unlined weathered CCR landfills in Croatia: Štrmac (Istrian Peninsula) and Plaški (Lika region) (Figure 12). These sites were selected as CCR at both sites were exposed to environmental conditions for ~50 years and contain both

naturally vegetated areas and bare areas. This allows for direct comparison between abiotic and biotic weathering influences on pedogenesis.

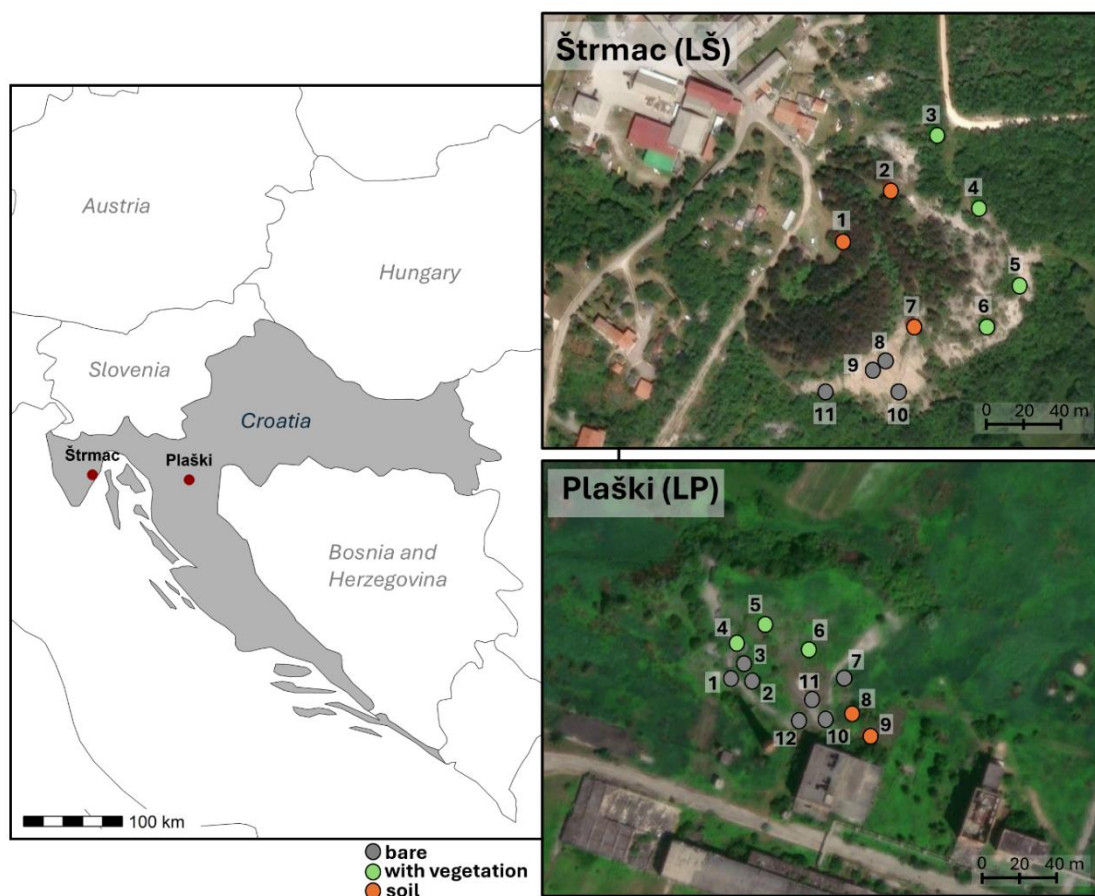


Figure 12. Study area showing the locations of the investigated coal combustion residue (CCR) landfills in Croatia and the sampling locations within each site (Petrović et al., 2023).

The two sites also differ in the type of coal historically combusted. The Štrmac landfill, located on the Istrian Peninsula, contains bottom ash and slag disposed of during the 1960s by a local foundry that combusted Raša coal, a high-sulfur superhigh-organic-sulfur coal (Medunić et al., 2016b). The Plaški landfill, located in the Lika region, contains fly and bottom ash generated by a sulfate pulp factory that operated between 1965 and 1991 (Oreščanin et al., 2012). Differences in coal type and ash composition provide an additional basis for evaluating how parent material influences weathering processes, element mobility, and soil formation in CCR deposits.

Sampling was conducted at multiple surface points and depths of up to 70 cm, targeting both vegetated and non-vegetated zones. In the laboratory, bulk CCR material was subdivided based on analytical requirements:

- For granulometric analyses, fresh untreated samples were used.
- For most other analyses, samples were air-dried, sieved to <2 mm to exclude coarse fragments, and homogenized. Cemented material was carefully disaggregated to preserve mineralogical integrity.
- Where analytical techniques required high homogeneity (e.g. XRD, ICP-MS, NMR), samples were finely ground using an agate mill.

To test the third hypothesis, fresh CCR was collected at three thermal power plants in Bosnia and Herzegovina (Tuzla, Stanari, and Gacko) (Figure 13). Fresh ashes were only dried and, as they are already fine, no other processing is needed. Water samples (streams) were collected upstream and downstream in the rivers and streams flowing in the vicinity of these three power plants, filtered (0.45 μm), acidified (2% supra pur HNO_3) and stored in the refrigerator.

The investigated thermal power plants combust predominantly low-rank coals from local Bosnian coal basins but differ in operational history and coal characteristics. TPP Tuzla, the largest coal-fired power plant in Bosnia and Herzegovina, has operated since the 1960s and combusts lignite and brown coal from the Kreka and Banovići coal basins (Nežirović, 2019). The plant disposes fly ash and bottom ash in nearby ash landfills.

TPP Stanari began commercial operation in 2016 and combusts lignite from the nearby Stanari basin. In contrast to the more Ca-rich ashes typical of some Balkan lignites, Stanari fly ash is characterized by relatively high Si and Al contents and is collected by bag filters during combustion (Bušatlić et al., 2025).

TPP Gacko has operated since 1983 and combusts locally mined lignite/brown lignite from the Gacko coal basin in eastern Herzegovina. The associated CCR consists of fly ash and bottom ash produced from combustion of sulfur- and carbonate-bearing lignite, with disposal historically occurring both at dedicated ash ponds and in mined-out areas of the open pit (Savić et al., 2018).

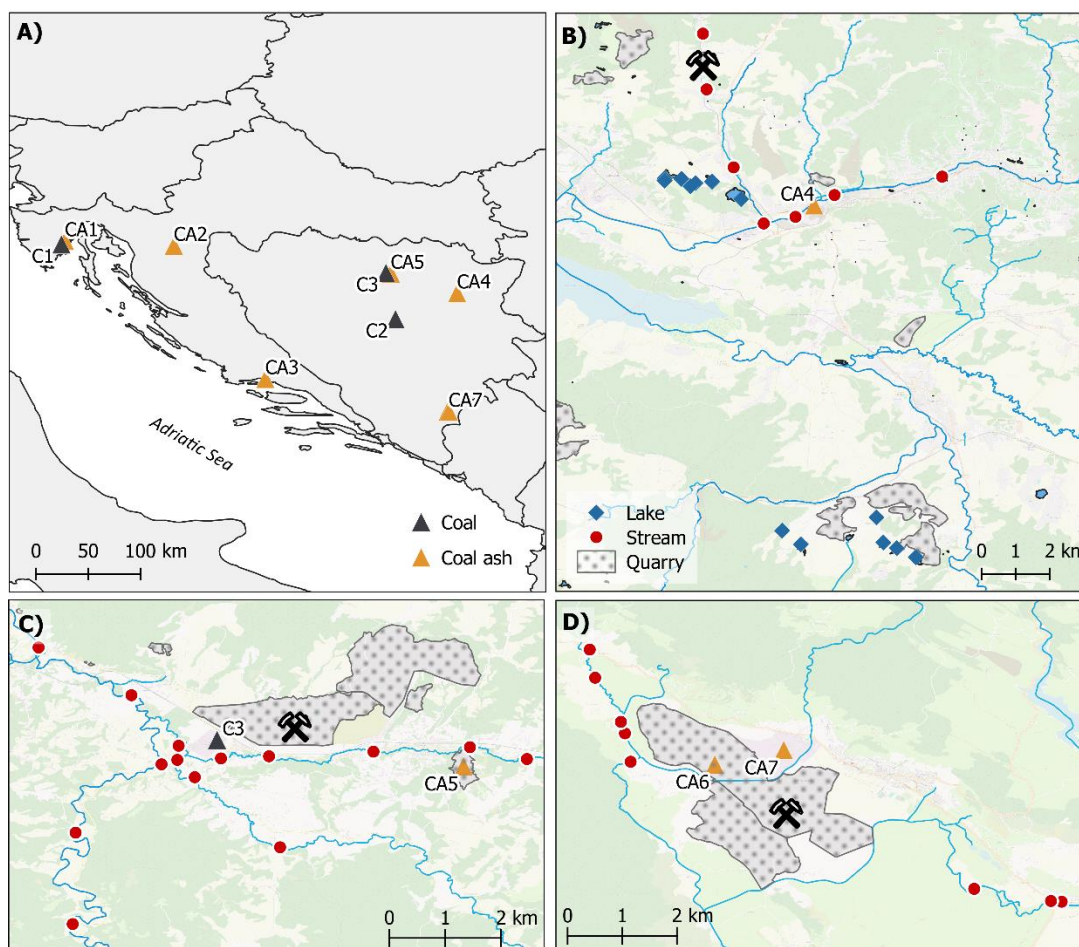


Figure 13. Locations of the investigated thermal power plants (TPPs) in Bosnia and Herzegovina (Tuzla, Stanari, and Gacko) and associated water sampling sites. (A) Coal and coal combustion residue (CCR) samples from Croatia and Bosnia and Herzegovina used for radiological and isotope analyses. Locations of coal, ash, and natural water sampling at (B) Tuzla, (C) Stanari, and (D) Gacko thermal power plants (Petrović et. al., *manuscript*).

4.3. Physicochemical properties of weathered CCR (Phase II; Paper II)

The second phase of this research focused on identifying indicators of pedogenesis in CCR deposits and the key properties controlling trace element mobility. Rather than treating CCR as a static material, this phase approaches it as a dynamic system undergoing transformation toward soil-like conditions. To capture this progression, a suite of complementary physicochemical parameters was analyzed, including pH, mineralogical composition, organic and amorphous phases, particle size distribution, and surface-related properties (cation exchange capacity and specific surface area) (Figure 14). Together, these parameters provide insight into both the degree of weathering and the capacity of CCR to retain or release contaminants.

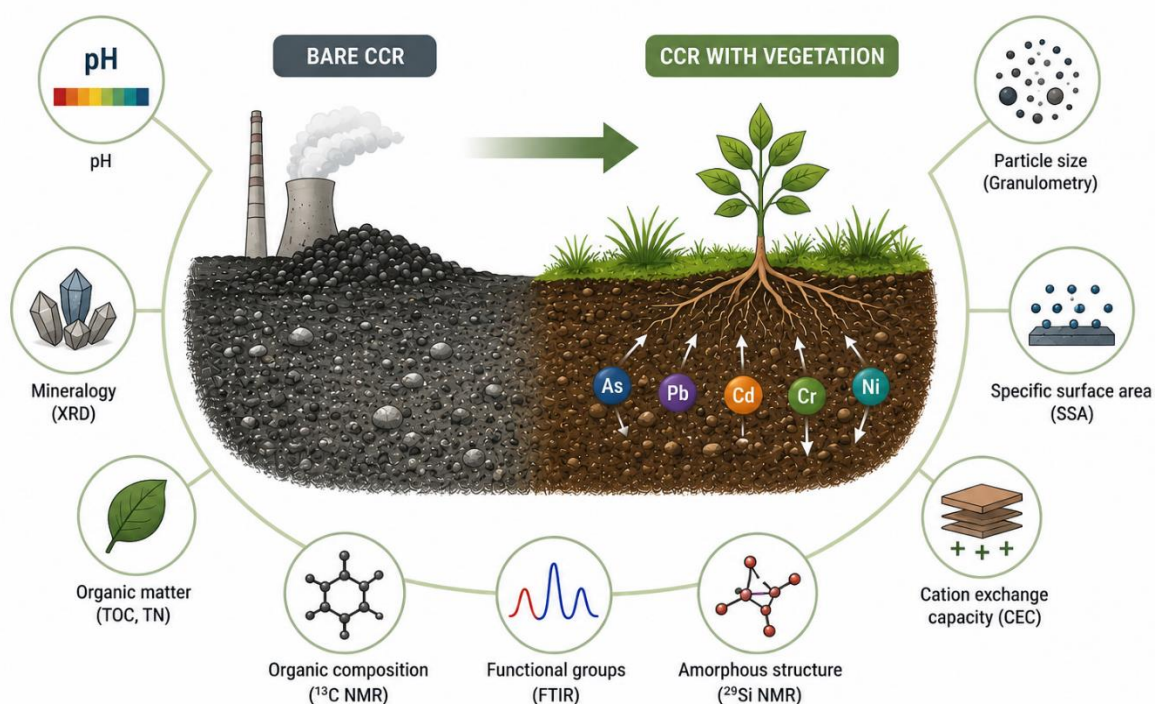


Figure 14. Schematic overview of the physicochemical parameters and analytical methods used to characterize weathered CCR and assess pedogenic development.

pH

pH is a key parameter controlling mineral solubility, chemical speciation, and contaminant mobility (Fleming et al., 1996). If fresh CCR is highly alkaline ($\text{pH} > 12$), the mobility of many contaminants is limited (Garrabrants et al., 2012; Neupane and Donahoe, 2013; Zhang et al., 2019). In that case, progressive weathering may reduce pH toward neutral values, potentially inducing changes in mineral phases and increasing the mobility of certain contaminants.

Measuring pH therefore provides insight into the degree of transformation of CCR toward soil-like features, as well as potential shifts in contaminant leaching behavior. The pH of CCR samples was determined in a 1:5 solid-to-Milli-Q water suspension following 30 minutes of equilibration.

X-ray Diffraction (XRD)

Mineralogical composition provides a direct record of both inherited and newly formed phases during CCR weathering (Uzarowicz et al., 2018b; Uzarowicz and Zagorski, 2015). X-ray diffraction (XRD) was used to identify crystalline mineral phases based on their characteristic

diffraction patterns. Analyses were performed using a Philips PW3710 diffractometer with CuK α radiation.

Organic matter (TOC, TN)

The accumulation and transformation of organic matter represent a key step in the pedogenic development of CCR (Zikeli et al., 2002). The development of organic matter supports microbial activity, enhances nutrient cycling, and contributes to contaminant complexation (Watteau et al., 2018). However, CCR often contains relatively high total organic carbon due to the presence of unburned coal particles, making it difficult to distinguish between inherited and newly formed organic matter (Dick et al., 2006; Uzarowicz et al., 2018a; Zikeli et al., 2004, 2002).

To address this, the C:N ratio was used as an indicator of organic matter origin. Because nitrogen is relatively scarce in coal-derived material, an increase in nitrogen content, and a corresponding decrease in the C:N ratio, indicates the accumulation of newly formed, biologically derived organic matter (Zikeli et al., 2002). Total organic carbon (TOC) and total nitrogen (TN) were measured using an Elementar Vario Micro cube CHNS/O analyzer.

Organic composition (^{13}C NMR)

While bulk TOC and TN provide quantitative information, understanding the *quality* of organic matter requires structural characterization. Solid-state ^{13}C CPMAS NMR was applied to selected samples to identify carbon functional groups (alkyl, aromatic, carboxyl, O-alkyl) (Dick et al., 2006).

This method detects different carbon functional groups (alkyl, aromatic, carboxyl, O-alkyl), providing information on the composition and stability of organic matter.

Functional groups (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the functional groups present in both mineral and organic components of CCR. This technique is based on the absorption of infrared radiation by molecular vibrations, producing characteristic spectra that reflect specific chemical bonds and structural features (Liu et al., 2019).

FTIR provides complementary information to XRD and NMR by enabling the identification of mineral phases, as well as functional groups associated with organic matter (Dick et al., 2006; Uzarowicz et al., 2018b). In the context of CCR weathering, FTIR could allow for the tracking of mineral transformations (e.g., carbonation, sulfate formation) and changes in organic matter composition.

Amorphous structure (^{29}Si NMR)

In addition to crystalline phases, CCR contains a substantial amorphous aluminosilicate fraction that could play a key role in long-term ash reactivity (Hemmings and Berry, 1987; Xu et al., 2021). ^{29}Si NMR was used to assess the degree of polymerization of silicate glass through the identification of Q^0 – Q^4 species.

The connectivity of SiO_4 tetrahedra reflects the reactivity of the glass phase: more depolymerized structures are more susceptible to dissolution (Hemmings and Berry, 1987). As glass alteration progresses, it can release both major and trace elements, making this analysis useful for understanding the long-term geochemical evolution of CCR.

Granulometric Analysis

Particle size distribution influences both physical and geochemical behavior, including water infiltration, erosion susceptibility, and surface reactivity (Kostić et al., 2018; Nikova and Tsoleva, 2017; Van Dyk et al., 2009; Zikeli et al., 2004). Granulometric composition was determined by laser diffraction using a Beckman Coulter LS 13320 particle size analyzer.

Samples were dispersed in deionized water and ultrasonicated to prevent aggregation. Results were classified into sand ($>63\text{ }\mu\text{m}$), silt ($2\text{--}63\text{ }\mu\text{m}$), and clay ($<2\text{ }\mu\text{m}$) fractions. Finer fractions are particularly important, as they exhibit higher surface area and tend to host elevated concentrations of trace elements (Kostić et al., 2018).

Specific Surface Area (SSA)

Specific surface area (SSA) reflects the availability of reactive sites for sorption and chemical interaction. Weathering processes, particularly the formation of secondary minerals and finer particles, generally increase SSA (Jones et al., 2012; Kostova et al., 2013). This enhances the

capacity of CCR to retain metals and organic contaminants, making SSA a key parameter linking physical transformation to geochemical behavior (Kostova et al., 2013).

SSA was determined using nitrogen adsorption via the Brunauer-Emmett-Teller (BET) method on a Micromeritics FlowSorb II 2300 instrument (Kostova et al., 2013).

Cation Exchange Capacity (CEC)

Cation exchange capacity (CEC) integrates the effects of mineralogy and organic matter on the ability of CCR to retain cationic species. It was determined using ammonium acetate extraction and quantified with an ammonium-selective electrode (Ivanić et al., 2020).

CEC is typically low in fresh CCR but increases with pedogenesis due to the formation of clay minerals and the accumulation of organic matter. As such, it serves as an important indicator of the developing sorptive capacity of CCR and its potential to attenuate contaminant mobility (Zikeli et al., 2004).

4.4. Mobility of oxyanions from weathered CCR (Phase III; Paper III)

The third phase of the study assesses trace element mobility from weathered CCR using four standardized batch leaching procedures: TCLP, EN 12457-2, LEAF 1313, and LEAF 1316. These tests simulate contaminant release under controlled conditions to evaluate environmental risk (Garrabrants et al., 2012).

Each method involves mixing a defined mass of CCR with an extraction fluid, agitating the mixture, filtering the solution, and analyzing the resulting eluate. While procedures are similar, the tests simulate different geochemical environments and yield complementary data (Garrabrants et al., 2012; Kosson et al., 2002; Thorneloe et al., 2009).

- **TCLP (Toxicity Characteristic Leaching Procedure)** uses an acetic acid buffer (pH ~4.5) simulating natural infiltration and localized acidification in vegetated landfill zones (USEPA, 2015).
- **EN 12457-2** employs deionized water as the leachant, allowing the CCR's inherent chemistry to dictate the resulting pH (CEN, 2023).

To explore element behavior under a wider range of environmental conditions, two methods from the Leaching Environmental Assessment Framework (LEAF) were applied (Kosson et al., 2019):

- **EPA 1313** investigates pH-dependent leaching by equilibrating samples across a wide pH range (2–13). This provides leaching profiles that reflect the chemical speciation and solubility of trace elements (USEPA, 2015).
- **EPA 1316** evaluates the effect of varying liquid-to-solid (L/S) ratios, simulating hydrological variability such as infiltration and dilution. Low L/S ratios reflect near-field solubility control, while high L/S ratios simulate conditions of extended leaching under high water availability (Figure 15) (USEPA, 2017).

This combined approach, using both regulatory (TCLP, ASTM) and mechanistic (LEAF 1313, 1316) tests, provides a robust framework for understanding how weathering and pedogenesis affect the environmental behavior of trace elements in CCRs under realistic field conditions.

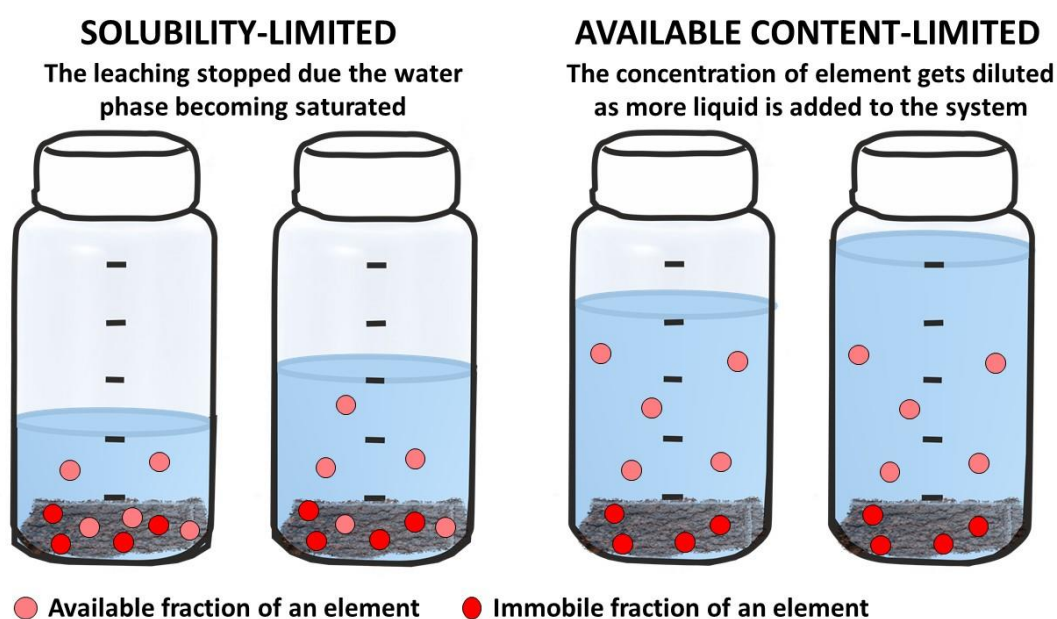


Figure 15. Differences between the solubility-limited and available content-limited leaching highlighting the importance of testing under different L/S ratios.

Multi-element composition (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the concentrations of major and trace elements in all solid samples and eluates. This technique is

based on ionization of the sample in a high-temperature argon plasma, followed by separation and detection of ions according to their mass-to-charge ratio, enabling sensitive multi-element analysis over a wide concentration range (Thomas, 2001).

Multi-element analysis provides information on the bulk geochemical composition of CCR, the mobility of environmentally relevant elements during leaching, and the chemical characteristics of impacted waters. In this study, analyses were performed using Thermo Scientific Element 2 HR-ICP-MS and Agilent 8900 ICP-QQQ-MS at the Ruđer Bošković Institute (Croatia) (Fiket et al., 2016), while for the Paper V, the analysis were performed by a Thermo Fisher XSeries II quadrupole ICP-MS at Duke University (United States).

4.4. Toxicity of weathered CCR (Phase IV, Paper IV)

The fourth phase evaluated the toxicity of weathered CCR eluates, linking geochemical changes during pedogenesis to their potential biological effects. The assumption is that even though chemical analyses and leaching tests indicate contaminant presence and mobility, they cannot predict actual biological outcomes. To address this, two complementary standardized bioassays were used: a seed germination and radicle elongation test and the *Allium* cytogenetic assay (Figure 16) (Fiskesjö, 1993; Luo et al., 2018). These methods assess both physiological and genotoxic responses, offering a broader picture of ecological risk.

Eluate Preparation

Eluates were prepared according to EN 12457-2, using a liquid-to-solid ratio of 10:1 (CEN, 2023). Because some eluates had high pH values (>11), which could independently inhibit biological activity, they were neutralized prior to testing. This allowed for the isolation of toxicity effects attributable to ash-derived contaminants (e.g., trace metals, metalloids, organics), rather than alkalinity alone.

Seed Germination and Radicle Elongation Test

This phytotoxicity test, using *Lactuca sativa* seeds, was conducted under controlled conditions (Luo et al., 2018; Mtisi and Gwenzi, 2019). After four days, two endpoints were measured:

- Germination rate – sensitivity to initial stress
- Radicle elongation – root growth, often more responsive to contaminants

Together, these parameters should indicate sub-lethal toxicity relevant to plant establishment and soil recovery on CCR-affected sites.

Allium Cytogenetic Assay

The *Allium* bioassay (using *Allium ascalonicum* bulbs) evaluates genotoxic effects via microscopic analysis of root tip cells exposed to CCR eluates (Fiskesjö, 1985). Two endpoints were evaluated:

- **Mitotic index (MI)** – expressed as the percentage of dividing cells and used as an indicator of cytotoxicity.
- **Chromosomal aberrations (CA)** – expressed as the frequency of aberrant cells and used as indicators of genotoxic stress (e.g., bridges, laggards, micronuclei, and other mitotic abnormalities).

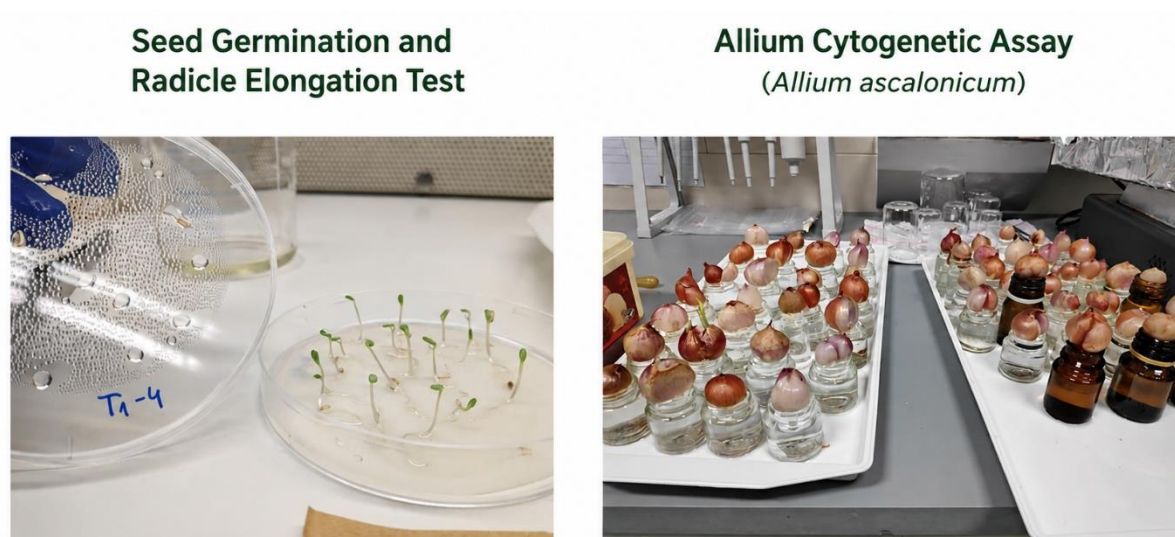


Figure 16. Plant-based bioassays used to evaluate the toxicity of CCR eluates.

Rationale for Bioassay Selection

Plants are primary colonizers of CCR deposits, making plant-based tests ecologically relevant for evaluating restoration potential. The seed germination test offers a rapid, cost-effective, and sensitive tool for detecting physiological stress. The *Allium* test complements this by detecting genetic damage, offering high resolution without animal testing requirements.

Together, these assays assess toxicity at both organismal and cellular levels, providing a comprehensive and multi-tiered evaluation of the environmental risks posed by weathered CCR materials.

4.5. Radiological characterization and isotope tracing of CCR (Phase V; Paper V (unpublished))

The final phase of this research investigates the radiological properties of coal combustion residues (CCR) and the application of isotope tracers for assessing CCR-derived contamination in Southeast Europe. This phase focuses on radionuclide activities and isotope signatures in coal and CCR from Croatia and Bosnia and Herzegovina, and associated waters from Bosnia and Herzegovina.

Gamma spectrometry

Gamma spectrometry was used to determine the activity concentrations of radionuclides belonging to the uranium and thorium decay series, including ^{238}U , ^{226}Ra , ^{210}Pb , ^{232}Th , and ^{228}Ra . Measurements were performed using a high-purity germanium (HPGe) gamma-ray detector following sample drying, homogenization, and equilibration in sealed containers to ensure secular equilibrium between parent and daughter radionuclides (Lauer et al., 2015).

Thermal ionization mass spectrometry (TIMS)

To further investigate contaminant sources and environmental pathways, strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) and boron ($\delta^{11}\text{B}$) isotope ratios were analysed in selected CCR and water samples using thermal ionization mass spectrometry (TIMS). Prior to analysis, samples were digested and Sr was separated using ion-exchange chromatography (Ruhl et al., 2014).

5. ORIGINAL SCIENTIFIC PAPERS

5.1. Paper I (Critical review article; Appendices I)

Name:

Environmental damage caused by coal combustion residue disposal: A critical review of risk assessment methodologies

Authors:

Marija Petrović, Željka Fiket

Journal: *Chemosphere*

Year: 2022

DOI: [10.1016/j.chemosphere.2022.134410](https://doi.org/10.1016/j.chemosphere.2022.134410)

This paper critically reviews the environmental impacts of coal combustion residue (CCR) disposal and evaluates commonly used methodologies for assessing associated environmental risks. It integrates findings from leaching studies, groundwater investigations, isotope tracing, and ecotoxicological assessments to provide an overview of CCR behaviour in the environment. Particular emphasis is placed on factors controlling contaminant mobility, including pH, liquid-to-solid ratio, mineralogical composition, and aging, as well as the limitations of current leaching protocols and risk assessment approaches.

The paper highlights widespread groundwater contamination near coal ash disposal sites and discusses advanced source identification techniques, especially boron ($\delta^{11}\text{B}$) and strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) isotopes, for distinguishing CCR-derived contamination. It also summarizes ecological and toxicological effects on plants, aquatic organisms, wildlife, and human health.

The main contributions are (1) a critical synthesis of current methodologies and a proposed integrated framework for CCR risk assessment combining geochemical, isotopic, mineralogical, and toxicological approaches; (2) identification of key knowledge gaps and methodological inconsistencies, including the lack of standardized leaching protocols, limited comparability among groundwater assessment methods, inadequate source attribution, and poor representation of long-term field conditions in laboratory-based risk assessments.

5.2. Paper II (Research article; Appendices II)

Name:

Physiochemical and mineral characteristics of soil materials developed naturally on two ~50-year-old coal combustion residue disposal sites in Croatia

Authors:

Marija Petrović, Maja Ivanić, Neda Vdović, Matej Dolenc, Branko Čermelj, Primož Šket, Gordana Medunić, Željka Fiket

Journal: *Catena*

Year: 2023

DOI: [10.1016/j.catena.2023.107338](https://doi.org/10.1016/j.catena.2023.107338)

This paper investigated pedogenic processes occurring at two approximately 50-year-old CCR disposal sites in Croatia and evaluated how long-term weathering alters the physicochemical and mineralogical properties of coal combustion residues.

The results showed clear evidence of pedogenesis, reflected in decreasing pH, accumulation of clay fractions, changes in C:N ratios, and formation of secondary minerals such as calcite, ettringite, gypsum, and hydrotalcite. Differences between the two sites indicated that mineralogical composition strongly influenced landfill evolution. The Plaški landfill exhibited higher clay content, SSA, and CEC values, suggesting greater capacity to retain water, nutrients, and contaminants and more advanced pedogenic development.

The main scientific contribution of this paper lies in demonstrating that CCR deposits undergo measurable pedogenic transformation over decadal timescales and should therefore be considered dynamic evolving systems rather than chemically inert waste materials. The study further contributes by integrating conventional physicochemical analyses with advanced spectroscopic techniques (^{13}C and ^{29}Si NMR), providing novel insight into the evolution of organic matter and amorphous aluminosilicate phases during CCR weathering. In addition, the work highlights the importance of clay mineral formation in controlling the retention of water, nutrients, and contaminants in ash-derived Technosols.

5.3. Paper III (Research article, Appendices III)

Name:

Changes in the mobility of oxyanions from coal combustion residues after 50 years of natural weathering

Authors:

Marija Petrović, Antonela Ninčević Grassino, Jasmina Lapić, Senka Djaković, Martina Furdek Turk, Gordana Medunić, Željka Fiket

Journal: *Waste Management*

Year: 2026

DOI: [10.1016/j.wasman.2026.115450](https://doi.org/10.1016/j.wasman.2026.115450)

This study investigates how approximately 50 years of natural weathering and early pedogenesis alter the mobility of oxyanion-forming contaminants in coal combustion residues (CCR) from two unlined Croatian disposal sites. Using standardized leaching protocols, supported by FTIR, SEM-EDS, and geochemical analysis, the behaviour of As, Cr, Mo, P, S, Se, Sb, U, and V was evaluated under varying pH and liquid-to-solid conditions.

The novelty of this study lies in examining naturally weathered CCR under real long-term field conditions, whereas most previous leaching studies focus on fresh ash or short-term laboratory simulations. This allows direct assessment of how decades of pedogenesis modify contaminant mobility. The study demonstrates that weathering fundamentally changes the mechanisms controlling oxyanion release, shifting retention from Ca-bearing alkaline phases (ettringite, portlandite, gypsum) toward sorption-controlled processes involving Fe/Al oxyhydroxides, clays, calcite, and pedogenic organic matter. It further shows, through EPA 1313 and EPA 1316 testing, that pedogenesis changes both pH-dependent leaching behaviour and the dominant release mechanism of key contaminants such as As, V, and P, shifting them from available-content-limited to solubility-controlled release.

This is scientifically important because it provides mechanistic evidence that the environmental behaviour of legacy CCR differs substantially from fresh materials, meaning conventional risk assessments based on fresh ash may not accurately predict long-term contaminant mobility.

5.4. Paper IV (Research article, Appendices IV)

Name:

Phytotoxicity of coal ash after 50 years of weathering: seed germination and *Allium ascalonicum* L. bioassay and multielement analysis of weathered coal ash effluents

Authors:

Marija Petrović, Željka Vidaković-Cifrek, Gordana Medunić, Željka Fiket

Journal: *Environmental Science: Processes & Impacts*

Year: 2025

DOI: [10.1039/d5em01010a](https://doi.org/10.1039/d5em01010a)

This paper investigates the long-term toxicity of coal combustion residues (CCR) after approximately 50 years of natural weathering at two historical unlined Croatian disposal sites, by integrating multielement geochemical characterization with biological toxicity assays. Using seed germination and *Allium* cytogenetic tests alongside chemical analysis of CCR eluates, the study evaluated whether long-term weathering and natural revegetation reduce phytotoxic and genotoxic effects and identified potential toxic drivers.

The key novelty of this work lies in providing one of the first systematic assessments of real-world long-term toxicity in naturally weathered CCR, whereas most previous studies focus on fresh ash or short-term laboratory exposures. Unlike concentration-based studies, this work directly compares chemical contamination with biological responses and demonstrates that contaminant concentrations alone are poor predictors of actual toxicity. Despite decades of weathering and partial pedogenesis, most samples remained phytotoxic or genotoxic, with significant inhibition of seed germination, reduced mitotic activity, and persistent chromosomal damage.

A further contribution is the identification of Al, As, and V as likely contributors to genotoxic effects through correlation analysis supported by known toxicological mechanisms. The study also demonstrates that revegetation and early pedogenesis do not universally mitigate toxicity, challenging the assumption that natural attenuation necessarily reduces environmental risk at legacy coal ash disposal sites.

5.5. Paper V (Unpublished manuscript, Appendices V)

Name:

Coal ash fingerprints in surface waters: integrating geochemistry, isotopes, and radiological signatures in an understudied European coal region

Authors:

Marija Petrović, Gordon Williams, Robert Hill, Željka Fiket, Avner Vengosh

This study investigates the geochemical, isotopic, and radiological characteristics of coal combustion residues (CCR) from Southeast Europe and evaluates the applicability of isotope tracers for identifying coal-related contamination in surface waters surrounding active coal-fired power plants in Bosnia and Herzegovina. Using multi-element geochemical characterization, radionuclide activity measurements, standardized leaching experiments, and strontium and boron isotope analyses, the study assesses both source materials and 42 surface water samples collected from rivers, streams, and post-mining lakes in the Tuzla, Stanari, and Gacko coal basins.

The key novelty of this study lies in providing the first integrated isotopic and radiological characterization of CCR from Southeast Europe, a region where coal combustion remains environmentally relevant but detailed environmental fingerprinting data are scarce. The results demonstrate substantial differences in ash composition depending on parent coal type and mineralogy, including clear distinctions between Ca-rich and aluminosilicate-dominated CCR. The study further shows that environmentally relevant dissolved isotope signatures may differ from bulk ash composition due to selective dissolution of specific mineral phases.

A further major contribution is the application of isotope tracers to complex aquatic systems influenced by coal-related activities. Surface waters showed distinct but site-specific hydrochemical and isotopic signatures, demonstrating that coal-related contamination cannot be reliably identified using concentration data alone. The study establishes a framework for combining conventional hydrochemistry with isotope tracers for improved environmental source attribution and extends the dissertation from laboratory-based assessment of legacy CCR toward environmental forensic investigation of active coal-related contamination.

6. DISCUSSION

This dissertation investigated the long-term environmental evolution of coal combustion residues (CCR) through five interconnected research directions: (1) critical synthesis of existing knowledge and identification of major methodological and conceptual gaps in coal ash research, (2) physicochemical and pedogenetic transformation of weathered CCR, (3) changes in contaminant mobility during pedogenesis, (4) persistence of biological toxicity after decades of weathering, and (5) characterization and tracing of active CCR systems using geochemical, radiological, and isotopic approaches. Collectively, these studies demonstrate that CCR disposal sites are not chemically inert repositories of industrial waste, but dynamic technogenic systems continuously transformed by coupled mineralogical, geochemical, hydrological, and biological processes.

The Croatian CCR landfills investigated in this dissertation represent valuable natural analogues for studying long-term environmental evolution because they have undergone approximately 50 years of unmanaged weathering under contrasting climatic and geochemical conditions. Unlike some international studies focused on reclaimed or engineered sites (Kostić et al., 2018; Šourková et al., 2005; Vengosh et al., 2013; Weber et al., 2015), these deposits provide a rare opportunity to observe natural CCR transformation without anthropogenic soil amendments or active remediation. At the same time, investigations conducted at active thermal power plants in Bosnia and Herzegovina extend the dissertation from legacy waste systems toward characterization and environmental tracing of currently generated CCR. Together, these studies provide a multi-scale perspective on coal ash behaviour, spanning fresh ash generation, environmental fingerprinting, long-term weathering, and ecological consequences. Therefore, the central contribution of this dissertation is not only the characterization of two Croatian legacy CCR landfills and several Bosnian and Herzegovinian coal-related systems, but the integration of these observations into a broader conceptual model of CCR evolution.

The findings strongly support the view that CCR should not be regarded as static industrial waste materials, but rather as evolving anthropogenic substrates whose environmental behaviour changes substantially through time. However, the results also demonstrate that this transformation does not necessarily correspond to progressive environmental stabilization. Instead, weathering simultaneously promotes attenuation of some elements while amplifies others.

6.1. Long-term weathering drives transformation of CCR into Technosols

One of the clearest findings of this dissertation is that prolonged exposure to environmental conditions fundamentally transforms CCR through pedogenetic processes, resulting in the progressive development of Technosol-like systems. The *Catena* study demonstrated that both investigated Croatian landfills exhibited clear evidence of physicochemical and mineralogical evolution, including decreases in pH, formation of secondary minerals, accumulation of organic matter, increased structural differentiation, and establishment of pioneer vegetation communities.

These observations align with previous studies describing weathering of technogenic substrates and ash-derived soils. Uzarowicz et al. (2018b) reported similar stages of pedogenetic development in coal ash disposal sites in Poland, where carbonation, secondary mineral formation, and biological colonization progressively altered ash properties over several decades. Likewise, studies from Serbian ash deposits (Kostić et al., 2018) documented partial soil development and weathering-induced geochemical transformation in aged revegetated CCR systems. However, the Croatian sites provide valuable insight because they represent unmanaged deposits exposed to natural succession rather than engineered reclamation.

Despite similar ages, the two Croatian landfills exhibited different degrees of pedogenetic development. Plaški showed substantially more advanced transformation, reflected in higher cation exchange capacity, greater specific surface area, increased clay content, and more extensive vegetation colonization. In contrast, Štrmac remained comparatively less developed, in cemented unvegetated zones.

This divergence highlights the importance of site-specific environmental controls. Plaški is located in a humid temperate region characterized by greater annual precipitation, conditions that likely accelerated dissolution, mineral weathering, and biological succession (Filipčić, 2001; Šegota and Filipčić, 2003; Zaninović et al., 2008). Štrmac developed under Mediterranean climatic conditions (Filipčić, 2001; Šegota and Filipčić, 2003; Zaninović et al., 2008) and was strongly influenced by cementation resulting from lime-rich ash produced from combustion of Raša coal. Cementation significantly reduced permeability and root penetration, thereby limiting ecological succession and slowing pedogenesis.

This finding has broader implications because it demonstrates that time alone does not determine CCR evolution. Although the investigated sites were similar in age, their environmental trajectories diverged substantially due to differences in climate, hydrology, and

ash composition. Similar conclusions were drawn by Uzarowicz et al. (2018b), who emphasized that parent material composition and environmental conditions strongly influence Technosol evolution.

Mineralogical analyses further confirmed extensive weathering-induced transformation. Secondary mineral phases including calcite, gypsum, ettringite, and hydrotalcite became important controls on geochemical behaviour. These minerals reflect fundamental processes governing CCR weathering: carbonation of Ca-bearing phases, sulfate redistribution, and precipitation of new mineral phases under evolving chemical conditions.

Comparable mineralogical transformations, especially formation of ettringite, have been reported in alkaline CCR laboratory tests (Hassett et al., 2005; Izquierdo and Querol, 2012; Johnson et al., 1999; Wang et al., 2023). However, the present results demonstrate that these processes remain environmentally relevant even after five decades, indicating that mineralogical evolution continues over long timescales.

The use of solid-state ^{13}C and ^{29}Si NMR provided valuable mechanistic insight. Few CCR studies have applied these methods (Netzel, 1991; Wei, 2018), making this an important methodological contribution. The ^{13}C spectra demonstrated that unburned coal particles remained a major component of the organic carbon pool, while declining C:N ratios indicated progressive accumulation of biologically derived organic matter. The ^{29}Si data showed structural alteration of amorphous silicate phases, in bare ash, indicating ongoing depolymerization of the ash matrix.

Taken together, these findings strongly support the first hypothesis that long-term weathering substantially alters CCR physicochemical and mineralogical properties through pedogenetic transformation. More broadly, they demonstrate that CCR deposits can evolve into functioning soil-like systems while still retaining distinct technogenic characteristics.

6.2. Pedogenesis as a geochemical filter: implications for contaminant mobility

While pedogenesis clearly transformed the physical and mineralogical properties of CCR, the *Waste Management* paper demonstrated that it also fundamentally alters contaminant mobility. This represents one of the central scientific findings of the dissertation.

The environmental significance of coal ash is strongly linked to the behaviour of environmentally relevant trace elements, particularly oxyanion-forming contaminants such as arsenic, vanadium, molybdenum, selenium, uranium, and antimony (Izquierdo and Querol,

2012; Wang et al., 2022). Numerous studies have shown that these elements can remain mobile under alkaline conditions characteristic of fresh CCR (Ruhl et al., 2009; Yao et al., 2015; Harkness et al., 2016).

However, these studies focused on relatively fresh ash or short-term leaching experiments. Far less is known about how long-term weathering modifies these release mechanisms. The results presented here demonstrate that pedogenesis acts as a geochemical filter, fundamentally changing the dominant mechanisms controlling contaminant release. In less weathered bare ash, release of several contaminants followed availability-controlled leaching behaviour, consistent with dissolution of readily soluble phases. In contrast, more weathered and vegetated samples increasingly exhibited solubility-controlled behaviour, indicating stronger control by mineral equilibria and adsorption processes. This shift is important because it indicates that weathering does not simply reduce contaminant release by depleting available contaminant pools. Instead, pedogenesis restructures geochemical controls governing mobility.

The observed transition is consistent with findings from alkaline waste weathering systems where secondary mineral formation progressively alters contaminant speciation and release behaviour (Grünewald et al., 2007; Wang et al., 2022). Secondary minerals such as ettringite and hydrotalcite likely played especially important roles. These phases are known to incorporate or adsorb oxyanions including chromate, arsenate, molybdate, and selenate. However, their long-term stability depends strongly on pH and carbonate activity (Grünewald et al., 2007; Hassett et al., 2005; Johnson et al., 1999; Paredes et al., 2011; Uzarowicz et al., 2018b; Wang et al., 2022).

This introduces a critical environmental complexity: weathering may temporarily immobilize contaminants while simultaneously creating conditions for later remobilization.

The differing behaviours of Plaški and Štrmac reinforce this interpretation. Plaški exhibited greater evidence of advanced pedogenesis and altered leaching behaviour, while Štrmac retained stronger alkaline buffering associated with less transformed ash. This has major implications for environmental risk assessment. Many regulatory frameworks implicitly assume relatively stable waste behaviour (Sloot et al., 2009), yet the results clearly demonstrate otherwise.

6.3. Persistent toxicity despite decades of natural attenuation

Biological toxicity persisted despite approximately 50 years of natural weathering. This result contrasts with a simplistic expectation that natural attenuation and pedogenesis reduce ecological risk through progressive stabilization. Instead, the *ESPI* paper demonstrated that weathered CCR remained biologically active and capable of causing significant phytotoxic and genotoxic effects.

Both the seed germination assay and *Allium* cytogenetic test showed clear biological responses. Germination inhibition, root growth suppression, mitotic inhibition, and chromosomal aberrations remained evident in multiple eluates, including some derived from weathered or partially vegetated zones.

These findings align with international ecotoxicological evidence suggesting that CCR impacts may persist long after disposal. Lemly (2018) documented long-term ecological damage associated with coal ash-derived selenium contamination in aquatic systems, while Brandt et al. (2018) demonstrated persistent biological incorporation of CCR-derived strontium in fish populations.

What distinguishes the present study is its demonstration that such persistence also applies to terrestrial weathered CCR undergoing natural pedogenesis. One of the most important observations was that biological responses did not consistently correlate with elemental concentrations.

This directly supports one of the central arguments of the dissertation: concentration-based environmental assessment is insufficient. Samples with relatively moderate chemical concentrations still caused strong biological effects, whereas some chemically enriched samples produced weaker responses. This reflects the inherent complexity of CCR toxicity. Biological effects are influenced not only by total contaminant concentrations, but also by contaminant bioavailability, interactions between multiple toxicants, pH, salinity, dissolved ions, and physicochemical stress (Mathews et al., 2020; Stevenson et al., 2017; Vatansever et al., 2017).

The correlation between cytogenetic damage and Al, As, and V suggests likely contributors, but causality cannot be attributed to individual elements alone. This finding is consistent with broader ecotoxicological understanding of mixed industrial waste systems, where toxicity frequently reflects combined stressor interactions rather than single contaminants (Stevenson et al., 2017).

The results challenge regulatory assumptions that compliance with concentration thresholds implies environmental safety. Some biologically significant effects occurred despite concentrations below accepted regulatory limits.

6.4. Vegetation as a driver of geochemical and ecological transformation

Across all Croatian studies, vegetation emerged as one of the most important controls on CCR evolution. Its role extended far beyond functioning as a passive indicator of ecological succession. Instead, vegetation actively modified geochemical conditions, accelerated pedogenesis, influenced contaminant mobility, and shaped the broader ecological trajectory of the investigated landfills.

The establishment of vegetation on coal ash deposits has often been interpreted as evidence of stabilization or successful ecological recovery (Dick et al., 2006; Kostić et al., 2018; Wu, 2004). However, the findings presented here indicate that this interpretation requires greater nuance.

Vegetated zones consistently exhibited characteristics associated with more advanced pedogenesis, including lower pH, greater cation exchange capacity, increased specific surface area, higher organic matter content, and more pronounced secondary mineral formation. These changes strongly suggest that vegetation functions as an active geochemical engineer.

Root activity modifies mineral weathering through localized acidification, physical disruption of substrate structure, and stimulation of microbial processes (Antoniadis et al., 2017; Colombo et al., 2014). Organic matter inputs contribute additional sorption capacity and alter nutrient cycling, while vegetation also modifies hydrological pathways through interception, evapotranspiration, and preferential flow (Antoniadis et al., 2017; Colombo et al., 2014).

Comparable observations have been reported in reclamation studies of ash-derived substrates, where vegetation establishment enhanced soil development and physicochemical stabilization (Haynes, 2009; Kostić et al., 2018; Stefanowicz et al., 2015). However, many of those systems involved engineered amendments such as compost, topsoil addition, or active restoration measures. The Croatian sites are valuable because they demonstrate spontaneous vegetation-driven transformation under unmanaged conditions.

Nevertheless, vegetation did not eliminate environmental risk. Although vegetated zones generally exhibited reduced contaminant mobility compared with adjacent unvegetated areas, biological toxicity remained detectable in some samples, and incomplete stabilization persisted. This suggests that vegetation should not be interpreted as synonymous with remediation.

Instead, ecological recovery appears to operate as a threshold-dependent process. Early colonization may substantially improve physicochemical conditions and promote partial stabilization, yet these improvements do not necessarily correspond to full ecological safety. This distinction between apparent ecological recovery and functional environmental safety deserves greater emphasis in future CCR management strategies.

6.5. Active CCR systems in Bosnia and Herzegovina source composition and environmental transfer

While the Croatian studies focused on long-term weathering of historical disposal sites, the investigations at thermal power plants in Bosnia and Herzegovina extended the dissertation toward characterization of actively generated CCR and their transfer into surrounding aquatic systems. Together, these approaches provide a broader understanding of coal ash behaviour across its environmental lifecycle, linking source material composition, contaminant release, environmental transport, and long-term transformation.

The investigated thermal power plants (Tuzla, Stanari, and Gacko) exhibited substantial differences in coal type, ash composition, trace element enrichment, rare earth element distribution, isotopic composition, and radionuclide activity, confirming that CCR cannot be treated as compositionally uniform industrial materials. The results broadly distinguished aluminosilicate-dominated ashes from Ca-rich CCR, consistent with international observations that ash geochemistry is fundamentally controlled by coal geology and combustion conditions (Izquierdo and Querol, 2012). These compositional differences are environmentally important because they define both contaminant inventories and the mineral phases governing subsequent mobility. For example, the persistence of strong alkalinity, cementation, and specific contaminant behaviour observed in Štrmac can be linked to the mineralogical legacy of Ca-rich ash systems, whereas aluminosilicate-dominated residues are likely to follow different weathering trajectories characterized by alternative retention mechanisms.

The aquatic investigations further demonstrated that environmental transfer does not simply reproduce laboratory leachate compositions. Although standardized leaching experiments identified a broader suite of potentially mobile constituents, receiving waters reflected a more selective geochemical signal dominated by sulfate, boron, strontium, lithium, molybdenum, uranium, and rubidium. This indicates that environmental expression is shaped not only by intrinsic leaching potential, but also by selective dissolution, hydrological connectivity, dilution, attenuation, and ambient aqueous geochemistry.

Coal-related impacts also did not produce a single universal hydrochemical signature. Instead, each site displayed a distinct environmental expression. Gacko was characterized by sulfate-rich, Ca–Sr-dominated waters with elevated U and Mo, suggesting relatively direct transfer of coal-related dissolved constituents. Tuzla showed a more complex boron-rich signal reflecting overlapping influences from coal combustion, mining, urban wastewater, and industrial activity. In Stanari, conventional hydrochemical indicators were comparatively weak, whereas isotopic signatures provided clearer evidence of source influence, demonstrating the added value of environmental tracers in hydrologically complex systems.

Together, these findings strengthen one of the central conclusions of the dissertation: the environmental behaviour of CCR is controlled not only by long-term weathering, but also by parent coal composition, initial ash mineralogy, and site-specific transport pathways. Fresh CCR properties define the potential source signature, while weathering and environmental processes determine which components of that signature persist in surrounding ecosystems.

6.6. Isotope tracers and environmental forensics of CCR contamination

One of the most important broader contributions of this dissertation is the demonstration that isotope tracers substantially improve source attribution in complex coal-impacted environments where concentration data alone are insufficient. Conventional CCR assessment often relies on elevated concentrations of elements, however, elements may also derive from natural water-rock interaction, mining activity, industrial discharge, or urban wastewater (Vengosh et al., 2016). This creates uncertainty, particularly in coal-bearing regions such as Bosnia and Herzegovina, where geological and anthropogenic sources overlap.

The isotope study showed that strontium and boron isotopes provide a more diagnostic framework for distinguishing CCR-derived or coal-associated inputs. Strontium isotope ratios reflected parent coal geology and ash mineralogy, while boron isotopes provided complementary information on the dissolved, mobile fraction of CCR leachates. This is important because the environmentally relevant signature is not necessarily the bulk ash composition, but the isotopic composition of the fraction that actually dissolves and enters water.

A key finding was that dissolved Sr isotope signatures can differ substantially from bulk ash signatures. This was most evident for Gacko-cassette, where bulk ash showed the most radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ value, while the corresponding leachate was much less radiogenic. This likely reflects preferential dissolution of readily soluble Ca-bearing phases, such as gypsum,

anhydrite, or secondary carbonates, that host isotopically distinct Sr relative to the residual aluminosilicate matrix. Similar differences between bulk fly ash and water-soluble Sr isotope compositions were reported by Wang et al. (2020). This finding is critical for environmental tracing because aquatic systems record the dissolved leachable signature, not necessarily the whole-sample ash composition.

Application of these tracers to natural waters demonstrated their site-specific value. In Tuzla, downstream waters shifted toward more coal ash-like Sr isotope compositions and negative $\delta^{11}\text{B}$ values, supporting coal-associated influence despite complex mixed anthropogenic inputs. In Stanari, concentration-based evidence was comparatively weak, yet $^{87}\text{Sr}/^{86}\text{Sr}$ clearly distinguished impacted waters from background waters and overlapped with the Stanari ash leachate signature. In Gacko, isotopic shifts were modest but consistent with strong hydrochemical enrichment in sulfate, Sr, U, Li, and Mo.

The post-mining lakes further demonstrated that coal-related geochemical legacies persist beyond active discharge systems. Several Kreka basin lakes retained sulfate-Sr-rich signatures and less radiogenic Sr isotope values consistent with prolonged interaction with coal-bearing materials, mine spoil, and potentially ash-affected deposits. In contrast, Đurđevik basin lakes were more radiogenic but generally less mineralized, showing that isotopic composition does not directly correspond to contamination intensity but reflects basin-specific Sr sources and water-rock interaction.

Overall, the isotope results support the fourth hypothesis of this dissertation: isotope and radiological approaches improve CCR source attribution and environmental assessment. Their value lies not in replacing chemical data, but in resolving ambiguity where concentration patterns alone cannot distinguish between natural background, mining influence, industrial discharge, and CCR-derived contamination.

6.7. Spatial heterogeneity and implications for environmental monitoring

One of the most scientifically important findings emerging across the dissertation is the pronounced heterogeneity of CCR systems. Coal ash disposal sites are often treated as homogeneous waste bodies (European Council, 2003). The present results strongly challenge this assumption.

Significant differences in physicochemical properties, contaminant mobility, pedogenetic development, and biological toxicity were observed not only between Plaški and Štrmac, but

also within individual disposal sites. Bare ash, cemented zones, partially vegetated areas, and more developed Technosol-like sections frequently behaved as distinct geochemical environments despite close spatial proximity.

This heterogeneity has major practical implications. Standard monitoring strategies based on a limited number of bulk or composite samples may substantially underestimate environmental risk by masking localized hotspots. Similarly, remediation strategies based on average site properties may fail to address high-risk microenvironments. Comparable heterogeneity has been observed in other anthropogenic substrates, including mine tailings and industrial Technosols (Coussy et al., 2017; Uzarowicz et al., 2018b), yet it remains insufficiently incorporated into monitoring frameworks.

The present results suggest that sampling strategies should explicitly account for vegetation cover, hydrological variability, pedogenetic stage, mineralogical differentiation, and structural heterogeneity. Without such consideration, environmental assessment may produce misleadingly simplified interpretations. This is especially important because ecological succession itself creates heterogeneity, meaning that environmental complexity increases rather than decreases over time.

6.8. Temporal evolution, long-term stability, and uncertainty in CCR systems

A central theme emerging from this dissertation is the importance of time in controlling the environmental behaviour of coal combustion residues. The results clearly show that different transformation processes operate on distinct temporal scales. Some processes appear relatively rapid following disposal. Carbonation of highly reactive Ca-bearing phases, initial precipitation of secondary minerals, and reduction of extreme alkalinity likely occur relatively early due to immediate interaction with atmospheric CO₂ and infiltrating water. Similar early-stage transformations have been documented in alkaline ash systems by Rendek et al. (2007) and Cornelis et al. (2008).

By contrast, ecological succession, organic matter accumulation, microbial colonization, and development of structured Technosol horizons are substantially slower processes dependent on biological establishment and longer-term physicochemical stabilization. Persistent contaminant mobility, residual toxicity, incomplete pedogenesis, and continuing mineralogical transformation all indicate that weathering remains an active process. Environmental risk appears to evolve rather than disappear. This temporal perspective also reveals that different contaminants behave differently through time.

Highly soluble salts and readily reactive alkaline phases may decline relatively rapidly, while oxyanion-forming contaminants such as arsenic, vanadium, selenium, molybdenum, and uranium remain environmentally relevant over much longer timescales due to persistent pH sensitivity and mineral interactions.

This aligns with observations from U.S. coal ash studies, where environmentally significant impacts persisted long after disposal (Harkness et al., 2016; Ruhl et al., 2009).

An important uncertainty concerns future environmental trajectories. If substantial contaminant mobility and toxicity remain after 50 years, what should be expected after 100 or 200 years? Will continued weathering progressively stabilize these systems, or could future environmental changes promote remobilization?

Climate change introduces additional uncertainty into the long-term evolution of CCR systems. Shifts in precipitation intensity, drought frequency, temperature, and vegetation dynamics could alter infiltration rates, wetting-drying cycles, redox conditions, and mineral stability, thereby affecting contaminant release, transport, and retention (Calvin et al., 2023; OECD, 2012). Thus, CCR deposits should not be understood as fixed environmental legacies, but as evolving systems whose future trajectories remain uncertain.

6.9. Methodological contributions, novel approaches, limitations and uncertainties

A distinctive strength of this dissertation lies in its integrative methodology:

- Use of solid-state NMR (^{13}C , ^{29}Si) to characterize organic matter and silicate polymerization is rarely applied in CCR research and provides unique insight into early humification and glass alteration.
- Application of multiple leaching tests (EN 12457-2, TCLP-2, EPA 1313/1316) allowed a detailed pH- and L/S-dependent assessment of element behavior.
- The combination of field sampling, lab-based chemical analysis, and validated bioassays creates a holistic environmental risk profile that moves beyond concentration thresholds.

This methodological extent positions the work at the intersection of soil science, waste management, and ecotoxicology, and serves as a model for future assessments of legacy industrial waste sites.

However, although this dissertation provides substantial new insight into long-term CCR evolution, several limitations should be considered.

First, the Croatian investigations focused on two historical landfills, both located within specific climatic and geological settings. While many of the identified mechanisms are likely broadly relevant, rates and pathways of CCR evolution may differ significantly under other environmental conditions. For example, highly humid tropical climates, arid systems, or engineered reclamation sites may follow substantially different trajectories. Nevertheless, comparison with international studies suggests that the broader conceptual findings remain robust.

Second, laboratory leaching tests provide valuable mechanistic insight but inevitably simplify natural environmental complexity. Field systems are influenced by fluctuating hydrology, preferential flow, seasonal temperature variation, microbial processes, redox changes, biological uptake, and heterogeneous infiltration patterns. Consequently, standardized batch leaching protocols cannot fully replicate long-term in situ behaviour. However, the use of multiple complementary leaching methods in this dissertation significantly strengthens interpretation compared with reliance on a single protocol.

Third, interpretation of biological toxicity remains inherently complex. CCR are multicomponent systems containing trace metals, oxyanion-forming contaminants, salts, radionuclides, organic compounds, and mineral particles. Observed biological effects likely result from interacting stressors rather than single toxic agents. While correlation analyses identified likely contributors such as Al, As, and V, definitive mechanistic attribution remains difficult. This limitation is not unique to the present work, but reflects a broader challenge in environmental ecotoxicology.

Fourth, isotope-based environmental tracing, while highly powerful, is not universally straightforward. Overlap between isotopic signatures from geological background sources and anthropogenic contamination may reduce discriminatory power. This is precisely why multi-isotope approaches, such as combined $\delta^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ tracing, are increasingly recommended (Harkness et al., 2016; Ruhl et al., 2014).

Finally, uncertainty remains regarding centennial-scale evolution. Even 50 years represents only part of the environmental lifespan of historical CCR systems. Continued weathering, vegetation succession, hydrological shifts, and climate change may substantially alter long-term behaviour.

6.10. Policy implications and regulatory relevance

The findings of this dissertation have direct implications for environmental policy and management of legacy industrial waste sites. Perhaps the most important policy-relevant conclusion is that old CCR deposits remain environmentally active for decades after disposal. This directly challenges the assumption that aging alone reduces environmental significance.

A second major implication concerns the limitations of concentration-based regulatory frameworks. Current environmental regulation often relies heavily on threshold concentrations and chemical compliance criteria. The present findings demonstrate that such approaches may underestimate ecological risk. Biological effects occurred even when contaminant concentrations fell below conventional thresholds. This suggests that regulatory compliance does not necessarily equal ecological safety.

This is relevant to the EU Landfill Directive (1999/31/EC) (European Union, 1999), which emphasizes chemical leaching criteria and groundwater protection, but does not explicitly incorporate biological endpoints or evolving pedogenetic conditions.

Similarly, the EU Soil Strategy for 2030 (European Commission, 2021), which increasingly emphasizes soil health, pollution mitigation, and restoration of degraded soils, lacks clear guidance on legacy industrial waste sites. This exposes a regulatory ambiguity: materials that meet soil criteria for Technosols under the World Reference Base for Soil Resources (WRB) classification system (IUSS Working Group WRB, 2022) can simultaneously remain regulated as industrial waste, with limited guidance for transitional states.

Also, the REACH Regulation (EC 1907/2006) (European Commission, 2006), which governs chemical safety, does not account for naturally altered industrial residues that behave like reactive soils. Yet, as demonstrated here, these materials are dynamic systems that continue to release and immobilize contaminants under changing environmental conditions.

The dissertation therefore exposes regulatory classification challenges. The investigated Croatian sites increasingly exhibit soil-like structure, organic matter accumulation, mineral horizon differentiation, yet simultaneously retain contaminant mobility and biological toxicity. This raises an important question: At what point does industrial waste become soil? Current frameworks do not provide clear answers.

6.11. CCR-derived Technosols as Anthropocene landscapes

Beyond immediate environmental management, this dissertation raises broader conceptual questions regarding industrial waste, soil formation, and Anthropocene landscapes. Coal combustion residues represent direct geological consequences of fossil fuel combustion, one of the defining processes of industrial modernity. These materials are anthropogenic by origin yet progressively transformed by natural processes.

The Croatian sites demonstrate this duality clearly. Through weathering, vegetation colonization, and pedogenesis, industrial ash progressively becomes incorporated into ecological systems. Yet the same systems retain persistent chemical signatures of their industrial origin. This creates hybrid landscapes that are neither conventional waste deposits nor natural soils.

Such systems fit within broader emerging discussions of Anthropocene soils and technogenic geomaterials (Coussy et al., 2017; Legu  dois et al., 2016; Ruiz et al., 2020). CCR-derived Technosols may therefore be interpreted not merely as contaminated waste sites, but as characteristic Anthropocene ecosystems shaped by interactions between industrial history and ecological succession.

This interpretation has practical consequences. As coal combustion declines across Europe (Benalc  zar et al., 2017), legacy CCR sites will remain as long-lived environmental archives of fossil fuel dependence. Many such landscapes may undergo spontaneous revegetation and increasing ecological integration. However, the present findings demonstrate that visual greening does not necessarily indicate environmental safety. This is especially relevant for urban redevelopment, ecological restoration, and post-industrial land reuse.

From a land-use perspective, CCR landfills are increasingly being reconsidered as potential sites for urban redevelopment, green infrastructure, or ecological restoration. However, this dissertation highlights several critical cautions:

- While vegetation does improve soil structure and reduces leaching, the biological toxicity remains non-negligible. For example, *Allium* assays in the ESPI study showed chromosomal damage even in vegetated samples, meaning that phytotoxic legacy effects persist even in visually "green" areas.
- Restoration efforts must distinguish between aesthetically green and ecologically functional landscapes. Plant colonization alone is insufficient without evaluating underlying toxicity and chemical reactivity.

- In policy and practice, “green” does not always mean “safe”. Urban greening initiatives (e.g., tree planting, park development) on such sites should only proceed after comprehensive chemical–biological assessment, especially when public exposure is possible.

These studies underscore the need for science-informed remediation planning. Passive rewilding can contribute to stabilization, but targeted phytoremediation, soil capping, or ash amendment may still be necessary depending on site conditions and land-use goals.

6. 12. Challenges in classifying pedogenetically altered technogenic materials

One broader implication of this research concerns the classification of highly transformed technogenic substrates such as aged coal combustion residues (CCR). Although the World Reference Base for Soil Resources (WRB) recognizes Technosols as soils dominated by technogenic materials or artefacts (IUSS Working Group WRB, 2022), the present findings suggest that classification based primarily on material origin and morphology may not fully reflect the environmental behaviour of long-term weathered industrial residues.

The CCR-derived materials investigated in this dissertation showed clear evidence of pedogenic development, including vegetation establishment, organic matter accumulation, structural differentiation, and mineralogical transformation. At the same time, they retained features associated with their industrial origin, including residual contaminant mobility and measurable biological toxicity. These materials therefore occupy an intermediate state: they increasingly function as soils, yet continue to behave as environmentally reactive legacy industrial deposits.

This does not represent a limitation of soil taxonomy itself, which is intended for classification rather than environmental risk assessment. However, it does highlight a disconnect between taxonomic identity and functional environmental behaviour in some technogenic systems. The findings of this dissertation suggest that current Technosol classification may benefit from supplementary descriptors that better reflect environmentally relevant properties of highly reactive technogenic substrates. In particular, the present results highlight several characteristics that are environmentally significant but not explicitly conveyed through existing classification descriptors:

- Mineralogical reactivity (e.g., *ettringitic*, *glass-rich*, *calcic*), to reflect the presence of unstable or reactive mineral phases that control cementation, permeability, and contaminant mobility.
- Legacy contaminant loading (e.g., *metal-enriched*, *oxyanion-prone*), to denote persistent enrichment in environmentally relevant trace elements that remain geochemically mobile despite pedogenic transformation.
- Ecotoxicological legacy (e.g., *toxic residue-influenced*), to capture cases where measurable biological effects persist despite visible ecological succession or apparent soil development.

Such descriptors would not replace existing WRB classification criteria, but could provide a more functionally informative framework for interpreting technogenic soils with ongoing environmental relevance. This, in turn, supports more targeted management strategies, regulatory inclusion, and long-term monitoring protocols for technogenic landscapes.

6.13. Final synthesis

Taken together, the findings of this dissertation demonstrate that coal combustion residues are dynamic anthropogenic materials whose environmental behaviour evolves continuously through interactions between mineralogical transformation, contaminant redistribution, ecological succession, and climatic forcing.

The first hypothesis, that long-term weathering substantially alters CCR physicochemical and mineralogical properties through pedogenesis, was strongly supported.

The second hypothesis, that weathering reduces contaminant mobility and environmental risk, was only partially supported, as stabilization occurred alongside persistence of environmentally relevant contaminant release. The third hypothesis, that toxicity cannot be reliably predicted from concentration data alone, was strongly supported. The fourth hypothesis, that isotope and radiological approaches improve source attribution and environmental assessment, was likewise supported.

Most importantly, the dissertation demonstrates that CCR disposal sites should not be viewed as static repositories of industrial waste, but as evolving anthropogenic ecosystems whose environmental significance persists over decadal timescales.

Understanding such systems requires interdisciplinary integration across geochemistry, mineralogy, pedology, ecotoxicology, environmental forensics, and policy. This broader

perspective may become increasingly important as societies confront the long-term environmental legacies of fossil fuel combustion in the post-coal era.

7. CONCLUSION

The cumulative findings of this dissertation lead to several overarching conclusions:

1. CCR disposal sites undergo substantial transformation over time, evolving toward Technosol-like systems via natural pedogenesis. However, this process is uneven and heavily site-dependent.
2. Pedogenesis significantly alters contaminant mobility, shifting element release patterns from availability-controlled to solubility-limited processes. This complicates traditional leaching-based assessments used in environmental policy.
3. Despite chemical attenuation, biological toxicity remains pronounced, indicating persistent risks to both flora and potentially fauna. This confirms the inadequacy of chemical thresholds alone in evaluating environmental impact.
4. Vegetation is a crucial driver of system evolution, promoting physicochemical stabilization and reducing mobility, but it is not a panacea. Effective risk management must recognize its role while addressing site-specific limitations like cementation or shallow rooting.
5. Multi-tool, interdisciplinary approaches are essential to accurately assess the long-term behavior of CCR landfills. Regulatory frameworks should incorporate bioassays, mineralogical data, and leaching models to build more nuanced and site-relevant policies.
6. Finally, the classification of Technosols formed from CCRs remains challenging. The World Reference Base needs better alignment with anthropogenic substrates exhibiting cementation, glassy phases, and persistent elemental enrichment.

Future Research Directions

- Longitudinal studies to monitor continued pedogenic evolution beyond the 50-year mark.
- Broader geographic surveys to validate findings across different climates and coal types.
- Microbial and enzymatic studies to assess biogeochemical transformations during revegetation.
- Life cycle assessments (LCA) of remediated vs. unmanaged CCR sites to quantify ecosystem services and residual risk.

8. REFERENCES

- Able, C., Rellergert, D., Mazzoni, V., Grol, E., 2023. Assessment of combustion residual leachate volume, composition, and treatment costs. *J. Hazard. Mater.* 457, 131731. <https://doi.org/https://doi.org/10.1016/j.jhazmat.2023.131731>
- Akinyemi, S.A., Akinlua, A., Gitari, W.M., Petrik, L.F., 2011. Mineralogy and mobility patterns of chemical species in weathered coal fly ash. *Energy Sources, Part A Recover. Util. Environ. Eff.* 33, 768–784. <https://doi.org/10.1080/15567030903261881>
- Alvarenga, P., Palma, P., Gonçalves, A.P., Fernandes, R.M., de Varennes, A., Vallini, G., Duarte, E., Cunha-Queda, A.C., 2008. Evaluation of tests to assess the quality of mine-contaminated soils. *Environ. Geochem. Health* 30, 95–99. <https://doi.org/10.1007/s10653-008-9147-z>
- Antoniadis, V., Levizou, E., Shaheen, S.M., Ok, Y.S., Sebastian, A., Baum, C., Prasad, M.N.V., Wenzel, W.W., Rinklebe, J., 2017. Trace elements in the soil-plant interface: Phytoavailability, translocation, and phytoremediation—A review. *Earth-Science Rev.* 171, 621–645. <https://doi.org/10.1016/j.earscirev.2017.06.005>
- Bagwell, C.E., Rodríguez-Ramos, J.A., Hoyle, S., Phillips, S., Day-Lewis, F.D., Hensel, B., 2025. Examination of coal combustion management sites for microbiological and chemical signatures of groundwater impacts. *Front. Microbiol.* 16. <https://doi.org/10.3389/fmicb.2025.1593892>
- Bandarra, B.S., Gomes, L.A., Pereira, J.L., Gonçalves, F.J.M., Martins, R.C., Quina, M.J., 2020. Assessment of hazardous property HP 14 using ecotoxicological tests: a case study of weathered coal fly ash. *Environ. Sci. Pollut. Res.* 27, 20972–20983. <https://doi.org/10.1007/s11356-020-08515-8>
- Bartz, M.L.C., Dudas, R.T., Demetrio, W.C., Brown, G.G., 2024. Earthworms as soil health indicators in no-tillage agroecosystems. *Eur. J. Soil Biol.* 121, 103605. <https://doi.org/https://doi.org/10.1016/j.ejsobi.2024.103605>
- Bateman, K., Murayama, S., Hanamachi, Y., Wilson, J., Seta, T., Amano, Y., Kubota, M., Ohuchi, Y., Tachi, Y., 2022. Evolution of the Reaction and Alteration of Granite with Ordinary Portland Cement Leachates: Sequential Flow Experiments and Reactive Transport Modelling. *Minerals* 12. <https://doi.org/10.3390/min12070883>
- Benalcazar, P., Krawczyk, M., Kamiński, J., 2017. Forecasting global coal consumption: An artificial neural network approach. *Gospod. Surowcami Miner. / Miner. Resour. Manag.* 33, 29–44. <https://doi.org/10.1515/gospo-2017-0042>

- Boche, A.S., Dhoble, S.J., Gupte, S.S., Dudhe, C.M., Belekar, R.M., 2025. Fly ash-induced groundwater contamination and magnetic nanoparticles as an innovative adsorbent for remediation: A critical review. *Hybrid Adv.* 10, 100461.
<https://doi.org/10.1016/j.hybadv.2025.100461>
- BP, 2020. Statistical Review of World Energy 2020 [WWW Document]. URL <https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html> (accessed 12.4.23).
- Brandt, J.E., Bernhardt, E.S., Dwyer, G.S., Di Giulio, R.T., 2017. Selenium Ecotoxicology in Freshwater Lakes Receiving Coal Combustion Residual Effluents: A North Carolina Example. *Environ. Sci. Technol.* 51, 2418–2426. <https://doi.org/10.1021/acs.est.6b05353>
- Brandt, J.E., Lauer, N.E., Vengosh, A., Bernhardt, E.S., Di Giulio, R.T., 2018. Strontium Isotope Ratios in Fish Otoliths as Biogenic Tracers of Coal Combustion Residual Inputs to Freshwater Ecosystems. *Environ. Sci. Technol. Lett.* 5, 718–723.
<https://doi.org/10.1021/acs.estlett.8b00477>
- Bušatlić, I., Bušatlić, N., Merdić, N., Haračić, N., Mujezinović, L., 2025. Geopolymers based on fly ash with the addition of granulated blast furnace slag, in: XVI International Mineral Processing and Recycling Conference. Belgrade, pp. 598–604.
<https://doi.org/10.5937/imprc25598b>
- Calvin, K., Dasgupta, D., Krinner, G., Mukherji, A., Thorne, P.W., Trisos, C., Romero, J., Aldunce, P., Barrett, K., Blanco, G., Cheung, W.W.L., Connors, S., Denton, F., Diongue-Niang, A., Dodman, D., Garschagen, M., Geden, O., Hayward, B., Jones, C., Jotzo, F., Krug, T., Lasco, R., Lee, Y.-Y., Masson-Delmotte, V., Meinshausen, M., Mintenbeck, K., Mokssit, A., Otto, F.E.L., Pathak, M., Pirani, A., Poloczanska, E., Pörtner, H.-O., Revi, A., Roberts, D.C., Roy, J., Ruane, A.C., Skea, J., Shukla, P.R., Slade, R., Slangen, A., Sokona, Y., Sörensson, A.A., Tignor, M., van Vuuren, D., Wei, Y.-M., Winkler, H., Zhai, P., Zommers, Z., Hourcade, J.-C., Johnson, F.X., Pachauri, S., Simpson, N.P., Singh, C., Thomas, A., Totin, E., Alegría, A., Armour, K., Bednar-Friedl, B., Blok, K., Cissé, G., Dentener, F., Eriksen, S., Fischer, E., Garner, G., Guivarch, C., Haasnoot, M., Hansen, G., Hauser, M., Hawkins, E., Hermans, T., Kopp, R., Leprince-Ringuet, N., Lewis, J., Ley, D., Ludden, C., Niamir, L., Nicholls, Z., Some, S., Szopa, S., Trewin, B., van der Wijst, K.-I., Winter, G., Witting, M., Birt, A., Ha, M., 2023. IPCC, 2023: Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, H. Lee and J. Romero (eds.)]. IPCC, Geneva, Switzerland.

- <https://doi.org/10.59327/IPCC/AR6-9789291691647>
- Campbell, C.E., Pearson, B.N., Frost, C.D., 2008. Strontium isotopes as indicators of aquifer communication in an area of coal-bed natural gas production, Powder River Basin, Wyoming and Montana. *Rocky Mt. Geol.* 43, 171–197.
<https://doi.org/10.2113/gsrocky.43.2.171>
- Celik, M., Donbak, L., Unal, F., Yüzbaşıoğlu, D., Aksoy, H., Yilmaz, S., 2007. Cytogenetic damage in workers from a coal-fired power plant. *Mutat. Res. - Genet. Toxicol. Environ. Mutagen.* 627, 158–163. <https://doi.org/10.1016/j.mrgentox.2006.11.003>
- CEN, 2023. Compliance test for leaching of granular waste materials and sludges: EN 12457-2. Eur. Comm. Stand.
- Chakraborty, R., Mukherjee, A., 2009. Mutagenicity and genotoxicity of coal fly ash water leachate. *Ecotoxicol. Environ. Saf.* 72, 838–842.
<https://doi.org/10.1016/j.ecoenv.2008.09.023>
- Chakraborty, R., Mukherjee, A.K., Mukherjee, A., 2009. Evaluation of genotoxicity of coal fly ash in *Allium cepa* root cells by combining comet assay with the Allium test. *Environ. Monit. Assess.* 153, 351–357. <https://doi.org/10.1007/s10661-008-0361-z>
- Chandler, J., Taylor Eighmy, T., Hartlen, J., Hjelm, O., Kosson, D., Sawel, S., van der Sloot, H., Vehlouw, J., 1997. Chemical aspects of Leaching. *Stud. Environ. Sci.* 67, 507–578. <https://doi.org/10.12681/eadd/1834>
- Chen, Y., Fan, Y., Huang, Y., Liao, X., Xu, W., Zhang, T., Ash, F., 2024. A comprehensive review of toxicity of coal fly ash and its leachate in the ecosystem. *Ecotoxicol. Environ. Saf.* 269, 115905. <https://doi.org/10.1016/j.ecoenv.2023.115905>
- Choi, S.K., Lee, S., Song, Y.K., Moon, H.S., 2002. Leaching characteristics of selected Korean fly ashes and its implications for the groundwater composition near the ash disposal mound. *Fuel*. [https://doi.org/10.1016/S0016-2361\(02\)00006-6](https://doi.org/10.1016/S0016-2361(02)00006-6)
- Clarke, L., Sloss, L.L., 1992. Trace elements - emissions from coal combustion and gasification. IEA Coal Research., London.
- Colombo, C., Palumbo, G., He, J.Z., Pinton, R., Cesco, S., 2014. Review on iron availability in soil: Interaction of Fe minerals, plants, and microbes. *J. Soils Sediments* 14, 538–548. <https://doi.org/10.1007/s11368-013-0814-z>
- Coussy, S., Grangeon, S., Bataillard, P., Khodja, H., Maubec, N., Faure, P., Schwartz, C., Dagois, R., 2017. Evolution of iron minerals in a 100 years-old Technosol. Consequences on Zn mobility. *Geoderma* 290, 19–32.
<https://doi.org/10.1016/j.geoderma.2016.12.009>

- Crnić, A.P., Damijanić, D., Bilandžić, N., Sedak, M., Medunić, G., 2022. Enhanced levels of hazardous trace elements (Cd, Cu, Pb, Se, Zn) in bird tissues in the context of environmental pollution by Raša coal. *Rud. Geol. Naft. Zb.* 37, 19–30.
<https://doi.org/10.17794/rgn.2022.1.3>
- DAE Pumps, 2021. Overcoming Coal Ash Pumping Challenges [WWW Document]. URL <https://www.daepumps.com/resources/overcoming-coal-ash-pumping-challenges/> (accessed 7.1.25).
- Daniell, A., van Deventer, P.W., 2018. An overview of pedogenesis in Technosols in South Africa. *South African J. Plant Soil* 35, 281–291.
<https://doi.org/10.1080/02571862.2018.1470265>
- Davidson, G.R., Bassett, R.L., 1993. Application of Boron Isotopes for Identifying Contaminants such as Fly Ash Leachate in Groundwater. *Environ. Sci. Technol.* 27, 172–176. <https://doi.org/10.1021/es00038a020>
- Dick, D.P., Knicker, H., Ávila, L.G., Inda, A. V., Giasson, E., Bissani, C.A., 2006. Organic matter in constructed soils from a coal mining area in southern Brazil. *Org. Geochem.* 37, 1537–1545. <https://doi.org/10.1016/j.orggeochem.2006.06.017>
- Dijkstra, J.J., Van Der Sloot, H.A., Comans, R.N.J., 2006. The leaching of major and trace elements from MSWI bottom ash as a function of pH and time. *Appl. Geochemistry* 21, 335–351. <https://doi.org/10.1016/j.apgeochem.2005.11.003>
- Dwivedi, S., Saquib, Q., Al-Khedhairi, A.A., Ali, A.Y.S., Musarrat, J., 2012. Characterization of coal fly ash nanoparticles and induced oxidative DNA damage in human peripheral blood mononuclear cells. *Sci. Total Environ.* 437, 331–338.
<https://doi.org/10.1016/j.scitotenv.2012.08.004>
- Earthjustice, 2021. CCR Rule Compliance [WWW Document]. URL <https://docs.google.com/spreadsheets/d/1SF6KTLrFSkPglJaKQyN6ZKoYp6k6ZHqGVOdCAGi7rng/edit#gid=0> (accessed 4.20.21).
- European Commission, 2006. Regulation (EC) 1907/2006 of the European Parliament and of the Council of 18 December 2006 - REACH. *Off. J. Eur. Union* 396–849.
- European Commission, 2021. EU Soil Strategy for 2030. Reaping the benefits of healthy soils for people, food, nature and climate. COM 2.
- European Council, 2003. Criteria and procedures for the acceptance of waste at landfills. *Off. J. Eur. Communities* 11, 27–48.
- European Union, 1999. Council Directive 1999/31/EC on the landfill. *Off. J. Eur. Communities* L182/1-19. <https://doi.org/10.1039/ap9842100196>

- FAO, 2014. World reference base for soil resources 2014. International soil classification system for naming soils and creating legends for soil maps, World Soil Resources Reports No. 106.
- Fiket, Ž., Medunić, G., Vidaković-Cifrek, Ž., Jezidžić, P., Cvjetko, P., 2020. Effect of coal mining activities and related industry on composition, cytotoxicity and genotoxicity of surrounding soils. *Environ. Sci. Pollut. Res.* 27, 6613–6627.
<https://doi.org/10.1007/s11356-019-07396-w>
- Fiket, Z., Mikac, N., Kniewald, G., 2016. Mass Fractions of Forty-Six Major and Trace Elements , Including Rare Earth Elements , in Sediment and Soil Reference Materials Used in Environmental Studies. *Geostand. Geoanalytical Res.* 41, 123–135.
<https://doi.org/10.1111/ggr.12129>
- Filipčić, A., 2001. Boundary separation of Köppen's climatic types Cf and Cs in Croatia. *Acta Geogr. Croat.* 35, 7–18. <https://doi.org/10.1111/ggr.12129> (In Croatian)
- Finkelman, R.B., Dai, S., French, D., 2019. The importance of minerals in coal as the hosts of chemical elements: A review. *Int. J. Coal Geol.* 212, 103251.
<https://doi.org/10.1016/j.coal.2019.103251>
- Fiskesjö, G., 1993. The Allium Test - a potential standard for the assessment of environmental toxicity., in: Gorsuch, J.W., Dwyer, F.J., Ingersoll, C.G., La Point, T.W. (Eds.), *Environmental Toxicology and Risk Assessment: 2nd Volume*, American Society for Testing and Materials. STP 1216, Philadelphia, pp. 331–345.
- Fiskesjö, G., 1985. The Allium test as a standard in environmental monitoring. *Hereditas* 102, 99–112. <https://doi.org/10.1111/j.1601-5223.1985.tb00471.x>
- Fleming, L.N., Abinteh, H.N., Inyang, H.I., 1996. Leachant pH effects on the leachability of metals from fly ash. *Soil Sediment Contam.* 5, 53–59.
<https://doi.org/10.1080/15320389609383512>
- Gamage, N., Liyanage, K., Fragomeni, S., Setunge, S., 2013. Overview of different types of fly ash and their use as a building and construction material. *Int. Conf. Struct. Eng. Constr. Manag.*
- Garcia, E., Wen, Y., Liu, P., Tang, Y., 2026. Speciation and Partitioning: A Survey Study of Rare Earth Elements (REEs) in Coal Fly Ash. *Environ. Sci. Process. Impacts* 28.
<https://doi.org/10.1039/D5EM00857C>
- Garrabrants, A., Kosson, D., DeLapp, R., Kariher, P., Seignette, P., van der Sloot, H., Stefanski, L., Baldwin, M., 2012. Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Method 1314 and Method 1315,

Epa/600/R-12/624.

- Grünewald, G., Kaiser, K., Jahn, R., 2007. Alteration of secondary minerals along a time series in young alkaline soils derived from carbonatic wastes of soda production 71, 487–496. <https://doi.org/10.1016/j.catena.2007.03.022>
- Gupta, N., Yadav, K.K., Kumar, V., Kumar, S., Chadd, R.P., Kumar, A., 2019. Trace elements in soil-vegetables interface: Translocation, bioaccumulation, toxicity and amelioration - A review. *Sci. Total Environ.* 651, 2927–2942. <https://doi.org/10.1016/j.scitotenv.2018.10.047>
- Haefner, R.J., 2001. Sulfur-isotope mixing model to trace leachate from pressurized fluidized bed combustion byproducts in an abandoned-coal-mine setting. *Fuel* 80, 829–836. [https://doi.org/10.1016/S0016-2361\(00\)00161-7](https://doi.org/10.1016/S0016-2361(00)00161-7)
- Hagemeyer, A.N., Sears, C.G., Zierold, K.M., 2019. Respiratory health in adults residing near a coal-burning power plant with coal ash storage facilities: A cross-sectional epidemiological study. *Int. J. Environ. Res. Public Health* 16. <https://doi.org/10.3390/ijerph16193642>
- Harkness, J.S., Darrah, T.H., Moore, M.T., Whyte, C.J., Mathewson, P.D., Cook, T., Vengosh, A., 2017. Naturally Occurring versus Anthropogenic Sources of Elevated Molybdenum in Groundwater: Evidence for Geogenic Contamination from Southeast Wisconsin, United States. *Environ. Sci. Technol.* 51, 12190–12199. <https://doi.org/10.1021/acs.est.7b03716>
- Harkness, J.S., Ruhl, L.S., Millot, R., Kloppman, W., Hower, J.C., Hsu-Kim, H., Vengosh, A., 2015. Lithium Isotope Fingerprints in Coal and Coal Combustion Residuals from the United States. *Procedia Earth Planet. Sci.* 13, 134–137. <https://doi.org/10.1016/j.proeps.2015.07.032>
- Harkness, J.S., Sulkin, B., Vengosh, A., 2016. Evidence for Coal Ash Ponds Leaking in the Southeastern United States. *Environ. Sci. Technol.* 50, 6583–6592. <https://doi.org/10.1021/acs.est.6b01727>
- Harris, D., Heidrich, C., Feuerborn, J., 2019. Global aspects on Coal Combustion Products. *VGB Power Tech* 10, 25–33.
- Hassett, D.J., Pflughoeft-Hassett, D.F., Heebink, L. V., 2005. Leaching of CCBs: Observations from over 25 years of research. *Fuel* 84, 1378–1383. <https://doi.org/10.1016/j.fuel.2004.10.016>
- Hayes, S.M., White, S.A., Thompson, T.L., Maier, R.M., Chorover, J., 2009. Changes in lead and zinc lability during weathering-induced acidification of desert mine tailings:

- Coupling chemical and micro-scale analyses. *Appl. Geochemistry* 24, 2234–2245.
<https://doi.org/10.1016/j.apgeochem.2009.09.010>
- Haynes, R.J., 2009. Reclamation and revegetation of fly ash disposal sites – Challenges and research needs. *J. Environ. Manage.* 90, 43–53.
<https://doi.org/10.1016/j.jenvman.2008.07.003>
- Hemmings, R.T., Berry, E.E., 1987. On the Glass in Coal Fly Ashes: Recent Advances. *MRS Proc.* 113. <https://doi.org/10.1557/proc-113-3>
- Hernández, F., Oldenkamp, R.E., Webster, S., Beasley, J.C., Farina, L.L., Wisely, S.M., 2017. Raccoons (*Procyon lotor*) as Sentinels of Trace Element Contamination and Physiological Effects of Exposure to Coal Fly Ash. *Arch. Environ. Contam. Toxicol.* 72, 235–246. <https://doi.org/10.1007/s00244-016-0340-2>
- Hopkins, W.A., Mendonça, M.T., Rowe, C.L., Congdon, J.D., 1998. Elevated trace element concentrations in southern toads, *Bufo terrestris*, exposed to coal combustion waste. *Arch. Environ. Contam. Toxicol.* 35, 325–329. <https://doi.org/10.1007/s002449900383>
- Hower, J.C., Henke, K.R., Dai, S., Ward, C.R., French, D., Liu, S., Graham, U.M., 2017. Generation and nature of coal fly ash and bottom ash, Coal Combustion Products (CCPs): Characteristics, Utilization and Beneficiation. Elsevier Ltd.
<https://doi.org/10.1016/B978-0-08-100945-1.00002-2>
- Hughey, M.C., Walke, J.B., Becker, M.H., Umile, T.P., Burzynski, E.A., Minbiole, K.P.C., Iannetta, A.A., Santiago, C.N., Hopkins, W.A., Belden, L.K., 2016. Short-term exposure to coal combustion waste has little impact on the skin microbiome of adult spring peepers (*Pseudacris crucifer*). *Appl. Environ. Microbiol.* 82, 3493–3502.
<https://doi.org/10.1128/AEM.00045-16>
- Hurst, R.W., Davis, T.E., Elseewi, A.A., 1991. Strontium isotopes as tracers of coal combustion residue in the environment. *Eng. Geol.* 30, 59–77.
[https://doi.org/10.1016/0013-7952\(91\)90035-J](https://doi.org/10.1016/0013-7952(91)90035-J)
- International Energy Agency, 2020. Global Energy Review 2020 [WWW Document]. URL <https://www.iea.org/reports/global-energy-review-2020> (accessed 8.29.20).
- IUSS Working Group WRB, 2022. World Reference Base for Soil Resources. International soil classification system for naming soils and creating legends for soil maps., 4th ed. International Union of Soil Sciences (IUSS), Vienna, Austria.
- Ivanić, M., Durn, G., Škapin, S.D., Sondi, I., 2020. Size-related mineralogical and surface physicochemical properties of the mineral particles from the recent sediments of the Eastern Adriatic Sea. *Chemosphere* 249, 126531.

- <https://doi.org/10.1016/j.chemosphere.2020.126531>
- Izquierdo, M., Querol, X., 2012. Leaching behaviour of elements from coal combustion fly ash: An overview. *Int. J. Coal Geol.* 94, 54–66.
<https://doi.org/10.1016/j.coal.2011.10.006>
- Jakovljević, I., Mešić, I., Pehcec, G., 2022. Soil pollution of the Labin city area with polycyclic aromatic hydrocarbons derived from Raša coal mining and associated industries. *Rud. Geol. Naft. Zb.* 37, 139–150. <https://doi.org/10.17794/rgn.2022.1.12>
- Jana, A., Ghosh, M., Sinha, S., Jothiramajayam, M., Nag, A., Mukherjee, A., 2017. Hazard identification of coal fly ash leachate using a battery of cyto-genotoxic and biochemical tests in *Allium cepa*. *Arch. Agron. Soil Sci.* 63, 1443–1453.
<https://doi.org/10.1080/03650340.2017.1280730>
- Johnson, C.A., Kaeppli, M., Brandenberger, S., Ulrich, A., Baumann, W., 1999. Hydrological and geochemical factors affecting leachate composition in municipal solid waste incinerator bottom ash. *J. Contam. Hydrol.* 40, 239–259.
[https://doi.org/10.1016/s0169-7722\(99\)00052-2](https://doi.org/10.1016/s0169-7722(99)00052-2)
- Johnson, R.C., Stewart, A.R., Limburg, K.E., Huang, R., Cocherell, D., Feyrer, F., 2020. Lifetime Chronicles of Selenium Exposure Linked to Deformities in an Imperiled Migratory Fish. *Environ. Sci. Technol.* 54, 2892–2901.
<https://doi.org/10.1021/acs.est.9b06419>
- Jones, K.B., Ruppert, L.F., Swanson, S.M., 2012. Leaching of elements from bottom ash, economizer fly ash, and fly ash from two coal-fired power plants. *Int. J. Coal Geol.* 94, 337–348. <https://doi.org/10.1016/j.coal.2011.10.007>
- Kalaitzoglou, M., Terzi, E., Samara, C., 2004. Patterns and sources of particle-phase aliphatic and polycyclic aromatic hydrocarbons in urban and rural sites of western Greece. *Atmos. Environ.* 38, 2545–2560. <https://doi.org/10.1016/j.atmosenv.2004.01.042>
- Karavuş, M., Aker, A., Cebeci, D., Taşdemir, M., Bayram, N., Çali, Ş., 2002. Respiratory Complaints and Spirometric Parameters of the Villagers Living around the Seyitomer Coal-Fired Thermal Power Plant in Kütahya, Turkey. *Ecotoxicol. Environ. Saf.* 52, 214–220. <https://doi.org/10.1006/eesa.2002.2158>
- Kaya, M., Çavuşoğlu, K., Yalçın, E., Acar, A., 2023. DNA fragmentation and multifaceted toxicity induced by high-dose vanadium exposure determined by the bioindicator *Allium* test. *Sci. Rep.* 13, 1–11. <https://doi.org/10.1038/s41598-023-35783-4>
- Kim, Y., Kim, K., Jeong, G.Y., 2017. Study of detailed geochemistry of hazardous elements in weathered coal ashes. *Fuel* 193, 343–350. <https://doi.org/10.1016/j.fuel.2016.12.080>

- Konstantinov, A., Novoselov, A., Konstantinova, E., Loiko, S., Kurasova, A., Minkina, T., 2020. Composition and properties of soils developed within the ash disposal areas originated from peat combustion (Tyumen, Russia). *Soil Sci. Annu.* 71, 3–14.
<https://doi.org/10.37501/soilsa/121487>
- Kooch, Y., Heydari, M., Parsapour, M.K., Valkó, O., 2025. Earthworm: a keystone species of soil quality, health and functions. *Acta Oecologica* 128, 104106.
<https://doi.org/https://doi.org/10.1016/j.actao.2025.104106>
- Košnář, Z., Mercl, F., Perná, I., Tlustoš, P., 2016. Investigation of polycyclic aromatic hydrocarbon content in fly ash and bottom ash of biomass incineration plants in relation to the operating temperature and unburned carbon content. *Sci. Total Environ.* 563–564, 53–61. <https://doi.org/10.1016/j.scitotenv.2016.04.059>
- Kosson, D.S., Garrabrants, A.C., DeLapp, R., van der Sloot, H.A., 2014. pH-dependent leaching of constituents of potential concern from concrete materials containing coal combustion fly ash. *Chemosphere* 103, 140–147.
<https://doi.org/10.1016/j.chemosphere.2013.11.049>
- Kosson, D.S., Garrabrants, A.C., Thorneloe, S.A., Fagnant, D., Helms, G., Connolly, K., Rodgers, M., 2019. Leaching Environmental Assessment Framework (LEAF) How-To Guide [WWW Document]. U.S. EPA. URL <https://www.epa.gov/hw-sw846/how-guide-leaching-environmental-assessment-framework>
- Kosson, D.S., Van Der Sloot, H.A., Sanchez, F., Garrabrants, A.C., 2002. An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials. *Environ. Eng. Sci.* 19, 159–204. <https://doi.org/10.1089/109287502760079188>
- Kostić, O., Jarić, S., Gajić, G., Pavlović, D., Pavlović, M., Mitrović, M., Pavlović, P., 2018. Pedological properties and ecological implications of substrates derived 3 and 11 years after the revegetation of lignite fly ash disposal sites in Serbia. *Catena* 163, 78–88.
<https://doi.org/10.1016/j.catena.2017.12.010>
- Kostova, I., Vassileva, C., Dai, S., Hower, J.C., Apostolova, D., 2013. Influence of surface area properties on mercury capture behaviour of coal fly ashes from some Bulgarian power plants. *Int. J. Coal Geol.* 116–117, 227–235.
<https://doi.org/10.1016/j.coal.2013.03.008>
- Kruger, R.A., 2017. Introduction to the utilization of coal combustion products, *Coal Combustion Products (CCPs): Characteristics, Utilization and Beneficiation*. Elsevier Ltd. <https://doi.org/10.1016/B978-0-08-100945-1.00004-6>
- Lauer, N.E., Hower, J.C., Hsu-Kim, H., Taggart, R.K., Vengosh, A., 2015. Naturally

- Occurring Radioactive Materials in Coals and Coal Combustion Residuals in the United States. *Environ. Sci. Technol.* 49, 11227–11233. <https://doi.org/10.1021/acs.est.5b01978>
- Leguédois, S., Séré, G., Auclerc, A., Cortet, J., Huot, H., Ouvrard, S., Watteau, F., Schwartz, C., Morel, J.L., 2016. Modelling pedogenesis of Technosols. *Geoderma* 262, 199–212. <https://doi.org/10.1016/j.geoderma.2015.08.008>
- Lemly, A.D., 2018. Selenium poisoning of fish by coal ash wastewater in Herrington Lake, Kentucky. *Ecotoxicol. Environ. Saf.* 150, 49–53. <https://doi.org/10.1016/j.ecoenv.2017.12.013>
- León-Mejía, G., Silva, L.F.O., Civeira, M.S., Oliveira, M.L.S., Machado, M., Villela, I.V., Hartmann, A., Premoli, S., Corrêa, D.S., Da Silva, J., Henriques, J.A.P., 2016. Cytotoxicity and genotoxicity induced by coal and coal fly ash particles samples in V79 cells. *Environ. Sci. Pollut. Res.* 23, 24019–24031. <https://doi.org/10.1007/s11356-016-7623-z>
- Li, J., Zhuang, X., Querol, X., Font, O., Moreno, N., 2018. A review on the applications of coal combustion products in China. *Int. Geol. Rev.* 60, 671–716. <https://doi.org/10.1080/00206814.2017.1309997>
- Liu, G., Cai, Y., Hernandez, D., Schrlau, J., Allen, M., 2016. Mobility and speciation of arsenic in the coal fly ashes collected from the Savannah River Site (SRS). *Chemosphere* 151, 138–144. <https://doi.org/10.1016/j.chemosphere.2016.02.071>
- Liu, J., Zhao, J., Wang, Y., Zhao, Y., Wu, K., 2024. Speciation distribution and leaching behavior of heavy metals in coal gasification fine ash: Influence of particle size, carbon content and mineral composition. *Sci. Total Environ.* 947, 174498. <https://doi.org/https://doi.org/10.1016/j.scitotenv.2024.174498>
- Liu, Y., Zeng, F., Sun, B., Jia, P., Graham, I.T., 2019. Structural Characterizations of Aluminosilicates in Two Types of Fly Ash Samples from Shanxi Province, North China. *Minerals* 9, 358. <https://doi.org/10.3390/min9060358>
- Lohner, T.W., Reash, R.J., Willet, V.E., Rose, L.A., 2001. Assessment of tolerant sunfish populations (*Lepomis* sp.) inhabiting selenium-laden coal ash effluents: 1. Hematological and population level assessment. *Ecotoxicol. Environ. Saf.* 50, 203–216. <https://doi.org/10.1006/eesa.2001.2097>
- Luo, Y., Liang, J., Zeng, G., Chen, M., Mo, D., Li, G., Zhang, D., 2018. Seed germination test for toxicity evaluation of compost: Its roles, problems and prospects. *Waste Manag.* 71, 109–114. <https://doi.org/10.1016/j.wasman.2017.09.023>
- Madan, S., Hussain, A., 2014. Groundwater contamination due to fly ash disposal: A Review.

- Int. J. Adv. Res. Biol. Sci. 1, 143–147.
- Mahajan, V.E., Yadav, R.R., Dakshinkar, N.P., Dhoot, V.M., Bhojane, G.R., Naik, M.K., Shrivastava, P., Naoghare, P.K., Krishnamurthi, K., 2012. Influence of mercury from fly ash on cattle reared nearby thermal power plant. *Environ. Monit. Assess.* 184, 7365–7372. <https://doi.org/10.1007/s10661-011-2505-9>
- Markad, V.L., Adav, S.S., Ghole, V.S., Sze, S.K., Kodam, K.M., 2016. Proteomics study revealed altered proteome of *Dichogaster curgensis* upon exposure to fly ash. *Chemosphere* 160, 104–113. <https://doi.org/https://doi.org/10.1016/j.chemosphere.2016.06.075>
- Markad, V.L., Kodam, K.M., Ghole, V.S., 2012. Effect of fly ash on biochemical responses and DNA damage in earthworm, *Dichogaster curgensis*. *J. Hazard. Mater.* 215–216, 191–198. <https://doi.org/10.1016/j.jhazmat.2012.02.053>
- Marques, J.E., Martins, V., Santos, P., Ribeiro, J., Mansilha, C., Melo, A., Rocha, F., Flores, D., 2021. Changes induced by self-burning in technosols from a coal mine waste pile: A hydropedological approach. *Geosci.* 11. <https://doi.org/10.3390/geosciences11050195>
- Mathews, T.J., Stevenson, L.M., Pickhardt, P.C., Murphy, C.A., Nisbet, R.M., Antczak, P., Garcia-Reyero, N., Gergs, A., 2020. The Effect of Dietary Exposure to Coal Ash Contaminants within Food Ration on Growth and Reproduction in *Daphnia magna*. *Environ. Toxicol. Chem.* 39, 1998–2007. <https://doi.org/10.1002/etc.4819>
- Matzenbacher, C.A., Garcia, A.L.H., dos Santos, M.S., Nicolau, C.C., Premoli, S., Corrêa, D.S., de Souza, C.T., Niekraszewicz, L., Dias, J.F., Delgado, T.V., Kalkreuth, W., Grivicich, I., da Silva, J., 2017. DNA damage induced by coal dust, fly and bottom ash from coal combustion evaluated using the micronucleus test and comet assay in vitro. *J. Hazard. Mater.* 324, 781–788. <https://doi.org/10.1016/j.jhazmat.2016.11.062>
- McNally D, Crowley-Parmentier J, Whitman B, 2012. Trace Metal Leaching and Bioavailability of Coal-Generated Fly Ash. *Int. Res. J. Environ. Sci. J. Environ. Sci* 1, 76–80.
- Medunić, G., Ahel, M., Mihalić, I.B., Srček, V.G., Kopjar, N., Fiket, Ž., Bituh, T., Mikac, I., 2016a. Toxic airborne S, PAH, and trace element legacy of the superhigh-organic-sulphur Raša coal combustion: Cytotoxicity and genotoxicity assessment of soil and ash. *Sci. Total Environ.* 566–567, 306–319. <https://doi.org/10.1016/j.scitotenv.2016.05.096>
- Medunić, G., Kuharić, Ž., Krivohlavek, A., Đuroković, M., Dropučić, K., Rađenović, A., Oberiter, B.L., Krizmanić, A., Bajramović, M., 2018. Selenium, sulphur, trace metal, and BTEX levels in soil, water, and lettuce from the croatian raša bay contaminated by

- superhigh-organic-sulphur coal. Geosci. 8. <https://doi.org/10.3390/geosciences8110408>
- Medunić, G., Rađenović, A., Bajramović, M., Švec, M., Tomac, M., 2016b. Once grand, now forgotten: What do we know about the superhigh-organic-sulphur Raša coal? Rud. Geol. Naft. Zb. 31, 27–45. <https://doi.org/10.17794/rgn.2016.3.3>
- Mehra, A., Farago, M.E., Banerjee, D.K., 1998. Impact of fly ash from coal-fired power stations in Delhi, with particular reference to metal contamination. Environ. Monit. Assess. <https://doi.org/10.1023/A:1005860015123>
- Mendez, M.O., Maier, R.M., 2008. Phytostabilization of mine tailings in arid and semiarid environments--an emerging remediation technology. Environ. Health Perspect. 116, 278–283. <https://doi.org/10.1289/ehp.10608>
- Meyer, C.B., Schlekot, T.H., Walls, S.J., Iannuzzi, J., Souza, M.J., 2015. Evaluating risks to wildlife from coal fly ash incorporating recent advances in metals and metalloids risk assessment. Integr. Environ. Assess. Manag. 11, 67–79. <https://doi.org/10.1002/ieam.1576>
- Miljević, N., Golobočanin, D., 2007. Potential use of environmental isotopes in pollutant migration studies. Arh. Hig. Rada Toksikol. 58, 251–262. <https://doi.org/10.2478/v10004-007-0015-5>
- Mizwar, A., Trihadiningrum, Y., 2015. PAH Contamination in Soils Adjacent to a Coal-Transporting Facility in Tapin District, South Kalimantan, Indonesia. Arch. Environ. Contam. Toxicol. 69, 62–68. <https://doi.org/10.1007/s00244-015-0141-z>
- Mtisi, M., Gwenzi, W., 2019. Evaluation of the phytotoxicity of coal ash on lettuce (*Lactuca sativa* L.) germination, growth and metal uptake. Ecotoxicol. Environ. Saf. 170, 750–762. <https://doi.org/10.1016/j.ecoenv.2018.12.047>
- Netzel, D.A., 1991. Multinuclear NMR Approach Coal Fly Ash Characterization. DOE/MC/11076-3200. <https://www.osti.gov/servlets/purl/6687192> (2.5.2023.).
- Neupane, G., Donahoe, R.J., 2013. Leachability of elements in alkaline and acidic coal fly ash samples during batch and column leaching tests. Fuel 104, 758–770. <https://doi.org/10.1016/j.fuel.2012.06.013>
- Nezirović, S., 2019. Exploitation and use of non-metal mineral resources of the Tuzla Canton. J. Geogr. 14, 83–96. <https://doi.org/10.18690/rg.14.1.3663>
- Nikova, I., Tsoleva, V., 2017. Mobility of trace elements in virgin soils from the Bobov dol valley, Bulgaria. Int. Res. J. Eng. Technol. 743–751.
- NRDC, E. and, 2025. Toxic Coal Ash in New York: Addressing Coal Plants' Hazardous Legacy [WWW Document]. Earthjustice. URL <https://earthjustice.org/feature/coal-ash->

- states/new-york?utm_source=chatgpt.com
- OECD, 2012. OECD Environmental Outlook to 2050 [WWW Document]. OECD Publ. URL http://www.oecd-ilibrary.org/environment/oecd-environmental-outlook-to-2050_9789264122246-en (accessed 8.10.20).
- Oreščanin, V., Kollar, R., Buben, K., Mikelic, I.L., Kollar, K., Kollar, M., Medunic, G., 2012. Chemical and radiological characterization of fly and bottom ash landfill of the former sulfate pulp factory Plaški and its surroundings. *J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng.* 47, 1592–1606. <https://doi.org/10.1080/10934529.2012.680780>
- Pacwa-Płociniczak, M., Płociniczak, T., Yu, D., Kurola, J.M., Sinkkonen, A., Piotrowska-Seget, Z., Romantschuk, M., 2018. Effect of *Silene vulgaris* and Heavy Metal Pollution on Soil Microbial Diversity in Long-Term Contaminated Soil. *Water. Air. Soil Pollut.* 229. <https://doi.org/10.1007/s11270-017-3655-3>
- Paredes, S.P., Valenzuela, M.A., Fetter, G., Flores, S.O., 2011. TiO₂/MgAl layered double hydroxides mechanical mixtures as efficient photocatalysts in phenol degradation. *J. Phys. Chem. Solids* 72, 914–919. <https://doi.org/10.1016/j.jpcs.2011.03.017>
- Peters, K.E., Walters, C.C., Moldowan, J.M. (Eds.), 2004. Organic chemistry, in: *The Biomarker Guide: Volume 1: Biomarkers and Isotopes in the Environment and Human History*. Cambridge University Press, Cambridge, pp. 18–44. <https://doi.org/DOI:10.1017/CBO9780511524868.004>
- Petrović, M., Fiket, Ž., 2022. Environmental damage caused by coal combustion residue disposal: A critical review of risk assessment methodologies. *Chemosphere* 299, 134410. <https://doi.org/10.1016/j.chemosphere.2022.134410>
- Petrović, M., Ivanić, M., Vdović, N., Dolenec, M., Čermelj, B., Šket, P., Medunić, G., Fiket, 2023. Physicochemical and mineral characteristics of soil materials developed naturally on two ~ 50 years old coal combustion residue disposal sites in Croatia. *Catena* 231. <https://doi.org/10.1016/j.catena.2023.107338>
- Plant, J.A., Bone, J., Voulvoulis, N., Kinniburgh, D.G., Smedley, P.L., Fordyce, F.M., Klinck, B., 2013. Arsenic and Selenium, 2nd ed, *Treatise on Geochemistry: Second Edition*. Elsevier Ltd. <https://doi.org/10.1016/B978-0-08-095975-7.00902-5>
- Puig, R., Àvila, A., Soler, A., 2008. Sulphur isotopes as tracers of the influence of a coal-fired power plant on a Scots pine forest in Catalonia (NE Spain). *Atmos. Environ.* 42, 733–745. <https://doi.org/10.1016/j.atmosenv.2007.09.059>
- Querol, X., Juan, R., Lopez-Soler, A., Fernandez-Turiel, J.L., Ruiz, C.R., 1996. Mobility of

- trace elements from coal and combustion wastes. *Fuel* 75, 821–838.
[https://doi.org/10.1016/0016-2361\(96\)00027-0](https://doi.org/10.1016/0016-2361(96)00027-0)
- Radić, S., Medunić, G., Kuharić, Ž., Roje, V., Maldini, K., Vujčić, V., Krivohlavek, A., 2018. The effect of hazardous pollutants from coal combustion activity: Phytotoxicity assessment of aqueous soil extracts. *Chemosphere* 199, 191–200.
<https://doi.org/10.1016/j.chemosphere.2018.02.008>
- Rahmawati, N.U.S., Rahmawati Sutopo, N., Nuraini, Y., Handayanto, E., 2020. Phytotoxicity of coal fly ash on plant growth and heavy metal uptake by plant in an acid soil. *J. Degrad. Min. Lands Manag.* 7, 2502–2458.
<https://doi.org/10.15243/jdmlm.2020.073.2233>
- Ribeiro, J., Silva, T.F., Mendonça Filho, J.G., Flores, D., 2014. Fly ash from coal combustion - An environmental source of organic compounds. *Appl. Geochemistry* 44, 103–110.
<https://doi.org/10.1016/j.apgeochem.2013.06.014>
- Rogers, S.W., Ong, S.K., Kjartanson, B.H., Golchin, J., Stenback, G.A., 2002. Natural Attenuation of Polycyclic Aromatic Hydrocarbon- Contaminated Sites : Review 141–155.
- Romero, F.M., Armienta, M.A., González-Hernández, G., 2007. Solid-phase control on the mobility of potentially toxic elements in an abandoned lead/zinc mine tailings impoundment, Taxco, Mexico. *Appl. Geochemistry* 22, 109–127.
<https://doi.org/10.1016/j.apgeochem.2006.07.017>
- Rowe, C.L., Hopkins, W.A., Congdon, J.D., 2002. Ecotoxicological Implications of Aquatic Disposal of Coal Combustion Residues in the United States: a Review. *Environ. Monit. Assess.* 80, 207–276. [https://doi.org/https://doi.org/10.1023/A:1021127120575](https://doi.org/10.1023/A:1021127120575)
- Rowe, C.L., Kinney, O.M., Fiori, A.P., Congdon, J.D., 1996. Oral deformities in tadpoles (*Rana catesbeiana*) associated with coal ash deposition: Effects on grazing ability and growth. *Freshw. Biol.* 36, 723–730. <https://doi.org/10.1046/j.1365-2427.1996.00123.x>
- Rowe, C.L., Kinney, O.M., Nagle, R.D., Congdon, J.D., 1998. Elevated maintenance costs in an anuran (*Rana catesbeiana*) exposed to a mixture of trace elements during the embryonic and early larval periods. *Physiol. Zool.* 71, 27–35.
<https://doi.org/10.1086/515885>
- Ruhl, L., Vengosh, A., Dwyer, G.S., Hsu-Kim, H., Deonaraine, A., Bergin, M., Kravchenko, J., 2009. Survey of the potential environmental and health impacts in the immediate aftermath of the coal ash spill in Kingston, Tennessee. *Environ. Sci. Technol.*
<https://doi.org/10.1021/es900714p>

- Ruhl, L.S., Dwyer, G.S., Hsu-Kim, H., Hower, J.C., Vengosh, A., 2014. Boron and strontium isotopic characterization of coal combustion residuals: Validation of new environmental tracers. *Environ. Sci. Technol.* 48, 14790–14798. <https://doi.org/10.1021/es503746v>
- Ruiz, F., Cherubin, M.R., Ferreira, T.O., 2020. Soil quality assessment of constructed Technosols: Towards the validation of a promising strategy for land reclamation, waste management and the recovery of soil functions. *J. Environ. Manage.* 276. <https://doi.org/10.1016/j.jenvman.2020.111344>
- Ruwei, W., Jiamei, Z., Jingjing, L., Liu, G., 2013. Levels and patterns of polycyclic aromatic hydrocarbons in coal-fired power plant bottom ash and Fly ash from Huainan, China. *Arch. Environ. Contam. Toxicol.* 65, 193–202. <https://doi.org/10.1007/s00244-013-9902-8>
- Saeedi, M., Li, L.Y., Grace, J.R., 2018. Desorption and mobility mechanisms of co-existing polycyclic aromatic hydrocarbons and heavy metals in clays and clay minerals. *J. Environ. Manage.* 214, 204–214. <https://doi.org/https://doi.org/10.1016/j.jenvman.2018.02.065>
- Sambandam, B., Devasena, T., Hairul Islam, V.I., Prakhya, B.M., 2015. Characterization of coal fly ash nanoparticles and their induced in vitro cellular toxicity and oxidative DNA damage in different cell lines. *Indian J. Exp. Biol.* 53, 585–593.
- Savić, D., Nisic, D., Malic, N., Dragosavljevic, Z., Medenica, D., 2018. Research on power plant ash impact on the quality of soil in Kostolac and Gacko coal basins. *Minerals* 8, 1–16. <https://doi.org/10.3390/min8020054>
- Schwartz, G.E., Hower, J.C., Phillips, A.L., Rivera, N., Vengosh, A., Hsu-Kim, H., 2018. Ranking Coal Ash Materials for Their Potential to Leach Arsenic and Selenium: Relative Importance of Ash Chemistry and Site Biogeochemistry. *Environ. Eng. Sci.* 35, 728–738. <https://doi.org/10.1089/ees.2017.0347>
- Sears, C.G., Zierold, K.M., 2017. Health of Children Living Near Coal Ash. *Glob. Pediatr. Heal.* 4. <https://doi.org/10.1177/2333794X17720330>
- Šegota, T., Filipčić, A., 2003. Köppen's classification of climates and the problem of corresponding Croatian terminology. *Geoadria* 8, 17–37.
- Séré, G., Schwartz, C., Ouvrard, S., Renat, J.C., Watteau, F., Villemin, G., Morel, J.L., 2010. Early pedogenic evolution of constructed Technosols. *J. Soils Sediments* 10, 1246–1254. <https://doi.org/10.1007/s11368-010-0206-6>
- Shah, P., Strezov, V., Prince, K., Nelson, P.F., 2008. Speciation of As, Cr, Se and Hg under coal fired power station conditions. *Fuel* 87, 1859–1869.

- <https://doi.org/10.1016/j.fuel.2007.12.001>
- Shakeel, A., Khan, A.A., Alharby, H.F., Bamagoos, A.A., Tombuloglu, H., Hakeem, K.R., 2021. Evaluation of coal fly ash for modulating the plant growth, yield, and antioxidant properties of daucus carota (L.): A sustainable approach to coal waste recycling. *Sustain.* 13. <https://doi.org/10.3390/su13095116>
- Singh, P.K., Tripathi, P., Dwivedi, S., Awasthi, S., Shri, M., Chakrabarty, D., Tripathi, R.D., 2016. Fly-ash augmented soil enhances heavy metal accumulation and phytotoxicity in rice (*Oryza sativa* L.); A concern for fly-ash amendments in agriculture sector. *Plant Growth Regul.* 78, 21–30. <https://doi.org/10.1007/s10725-015-0070-x>
- Singh, S.N., Kulshreshtha, K., Ahmad, K.J., 1997. Impact of fly ash soil amendment on seed germination, seedling growth and metal composition of *Vicia faba* L. *Ecol. Eng.* 9, 203–208. [https://doi.org/10.1016/S0925-8574\(97\)10004-0](https://doi.org/10.1016/S0925-8574(97)10004-0)
- Sloot, H.A. Van Der, Meeussen, J.C.L., Garrabrants, A.C., Kosson, D.S., 2009. Review of the physical and chemical aspects of leaching assessment. *Energy Res. Cent. Netherlands.*
- Smith, J.W., Batts, B.D., 1974. The distribution and isotopic composition of sulfur in coal. *Geochim. Cosmochim. Acta* 38, 121–133. [https://doi.org/10.1016/0016-7037\(74\)90198-7](https://doi.org/10.1016/0016-7037(74)90198-7)
- Šourková, M., Frouz, J., Šantrůčková, H., 2005. Accumulation of carbon, nitrogen and phosphorus during soil formation on alder spoil heaps after brown-coal mining, near Sokolov (Czech Republic). *Geoderma* 124, 203–214. <https://doi.org/https://doi.org/10.1016/j.geoderma.2004.05.001>
- Stefanowicz, A.M., Kapusta, P., Błońska, A., Kompała-Baba, A., Woźniak, G., 2015. Effects of *Calamagrostis epigejos*, *Chamaenerion palustre* and *Tussilago farfara* on nutrient availability and microbial activity in the surface layer of spoil heaps after hard coal mining. *Ecol. Eng.* 83, 328–337. <https://doi.org/10.1016/j.ecoleng.2015.06.034>
- Stevenson, L.M., Krattenmaker, K.E., Johnson, E., Bowers, A.J., Adeleye, A.S., McCauley, E., Nisbet, R.M., 2017. Standardized toxicity testing may underestimate ecotoxicity: Environmentally relevant food rations increase the toxicity of silver nanoparticles to *Daphnia*. *Environ. Toxicol. Chem.* 36, 3008–3018. <https://doi.org/10.1002/etc.3869>
- Tang, Y., Pan, J., Li, B., Zhao, S., Zhang, L., 2021. Residual and ecological risk assessment of heavy metals in fly ash from co-combustion of excess sludge and coal. *Sci. Rep.* 11, 1–11. <https://doi.org/10.1038/s41598-021-81812-5>
- Tarnawczyk, M., Uzarowicz, Ł., Pędziwiatr, A., Kwasowski, W., 2025. Micromorphological, submicromorphological and chemical indicators of pedogenesis in Spolic Technosols

- developed at historical mining and metallurgical sites in the Tatra Mountains, southern Poland. *Soil Sci. Annu.* 76. <https://doi.org/10.37501/soilsa/211370>
- Thavamani, P., Megharaj, M., Naidu, R., 2012. Multivariate analysis of mixed contaminants (PAHs and heavy metals) at manufactured gas plant site soils. *Environ. Monit. Assess.* 184, 3875–3885. <https://doi.org/10.1007/s10661-011-2230-4>
- Thomas, R., 2001. A Beginner's Guide to Spectroscopy. *Spectroscopy* 10, 38–48.
- Thorneloe, S.A., Kosson, D., Helms, G., Garrabrants, A.C., 2009. Improved Leaching Test Methods for Environmental Assessment of Coal Ash and Recycled Materials Used in Construction, in: *Proceedings Sardinia 2009, Twelfth International Waste Management and Landfill Symposium*. CISA Publisher, Cagliari, Italy.
- Turhan, S., Parmaksiz, A., Köse, A., Yüksel, A., Arikan, I.H., Yücel, B., 2010. Radiological characteristics of pulverized fly ashes produced in Turkish coal-burning thermal power plants. *Fuel* 89, 3892–3900. <https://doi.org/10.1016/j.fuel.2010.06.045>
- U.S. Environmental Protection Agency, 2007. Human and Ecological Risk Assessment of Coal Combustion Wastes. *Fed. Regist.* 409.
- Ugolini, F., Baronti, S., Lanini, G.M., Maienza, A., Ungaro, F., Calzolari, C., 2020. Assessing the influence of topsoil and technosol characteristics on plant growth for the green regeneration of urban built sites. *J. Environ. Manage.* 273, 111168. <https://doi.org/10.1016/j.jenvman.2020.111168>
- USEPA, 2017. Validated Test Method 1316: Liquid-Solid Partitioning as a Function of Liquid-to-Solid Ratio in Solid Materials Using a Parallel Batch Procedure. [WWW Document]. URL https://www.epa.gov/sites/default/files/2017-10/documents/method_1316_-_final_8-3-17.pdf (accessed 10.1.22).
- USEPA, 2015. SW-846 Test Method 1311: Toxicity Characteristic Leaching Procedure. [WWW Document]. URL <https://www.epa.gov/sites/default/files/2015-12/documents/1313.pdf> (accessed 10.1.22).
- Uzarowicz, Ł., Kwasowski, W., Spiewak, O., Switoniak, M., 2018a. Indicators of pedogenesis of Technosols developed in an ash settling pond at the Bełchatów thermal power station (central Poland). *Soil Sci. Annu.* 69, 49–59. <https://doi.org/10.2478/ssa-2018-0006>
- Uzarowicz, Ł., Skiba, M., Leue, M., Zagórski, Z., Gąsiński, A., Trzciński, J., 2018b. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part II. Mineral transformations and soil evolution. *Catena* 162, 255–269. <https://doi.org/10.1016/j.catena.2017.11.005>
- Uzarowicz, L., Zagorski, Z., 2015. Mineralogy and chemical composition of technogenic soils

- (Technosols) developed from fly ash and bottom ash from. *Soil Sci. Annu.* 66, 82–91.
<https://doi.org/10.1515/ssa-2015-0023>
- Uzarowicz, Ł., Zagórski, Z., Mendak, E., Bartmiński, P., Szara, E., Kondras, M., Oktaba, L., Turek, A., Rogoziński, R., 2017. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part I. Properties, classification, and indicators of early pedogenesis. *Catena* 157, 75–89.
<https://doi.org/10.1016/j.catena.2017.05.010>
- Vallejo Vallejo, L.A., Torres Agredo, J., Agudelo-Morales, C.E., 2024. Evaluation of particulate matter in coal bottom ash and its possible ecotoxic effects: a preliminary study. *Ing. y Compet.* 26, 1–14. <https://doi.org/10.25100/iyv.v26i1.13113>
- Van Dyk, J.C., Benson, S.A., Laumb, M.L., Waanders, B., 2009. Coal and coal ash characteristics to understand mineral transformations and slag formation. *Fuel*.
<https://doi.org/10.1016/j.fuel.2008.11.034>
- Vassilev, S. V, Vassileva, C.G., 1996. Occurrence , abundance and origin of minerals in coals and coal ashes 48, 85–106.
- Vatansever, R., Ozyigit, I.I., Filiz, E., 2017. Essential and Beneficial Trace Elements in Plants, and Their Transport in Roots: a Review. *Appl. Biochem. Biotechnol.* 181, 464–482. <https://doi.org/10.1007/s12010-016-2224-3>
- Vejahati, F., Xu, Z., Gupta, R., 2010. Trace elements in coal: Associations with coal and minerals and their behavior during coal utilization - A review. *Fuel* 89, 904–911.
<https://doi.org/10.1016/j.fuel.2009.06.013>
- Vengosh, A., Cowan, E.A., Coyte, R.M., Kondash, A.J., Wang, Z., Brandt, J.E., Dwyer, G.S., 2019. Evidence for unmonitored coal ash spills in Sutton Lake, North Carolina: Implications for contamination of lake ecosystems. *Sci. Total Environ.* 686, 1090–1103.
<https://doi.org/10.1016/j.scitotenv.2019.05.188>
- Vengosh, A., Coyte, R., Karr, J., Harkness, J.S., Kondash, A.J., Ruhl, L.S., Merola, R.B., Dwyer, G.S., 2016. Origin of Hexavalent Chromium in Drinking Water Wells from the Piedmont Aquifers of North Carolina. *Environ. Sci. Technol. Lett.* 3, 409–414.
<https://doi.org/10.1021/acs.estlett.6b00342>
- Vengosh, A., Heumann, K.G., Juraske, S., Kasher, R., 1994. Boron Isotope Application for Tracing Sources of Contamination in Groundwater. *Environ. Sci. Technol.* 28, 1968–1974. <https://doi.org/10.1021/es00060a030>
- Vengosh, A., Lindberg, T.T., Merola, B.R., Ruhl, L., Warner, N.R., White, A., Dwyer, G.S., Di Giulio, R.T., 2013. Isotopic imprints of mountaintop mining contaminants. *Environ.*

- Sci. Technol. 47, 10041–10048. <https://doi.org/10.1021/es4012959>
- Verma, C., Madan, S., Hussain, A., 2016. Heavy metal contamination of groundwater due to fly ash disposal of coal-fired thermal power plant, Parichha, Jhansi, India. *Cogent Eng.* <https://doi.org/10.1080/23311916.2016.1179243>
- Verma, S.K., Masto, R.E., Gautam, S., Choudhury, D.P., Ram, L.C., Maiti, S.K., Maity, S., 2015. Investigations on PAHs and trace elements in coal and its combustion residues from a power plant. *Fuel* 162, 138–147. <https://doi.org/10.1016/j.fuel.2015.09.005>
- Voltaggio, M., Spadoni, M., Sacchi, E., Sanam, R., Pujari, P.R., Labhasetwar, P.K., 2015. Assessment of groundwater pollution from ash ponds using stable and unstable isotopes around the Koradi and Khaperkheda thermal power plants (Maharashtra, India). *Sci. Total Environ.* <https://doi.org/10.1016/j.scitotenv.2015.02.083>
- Wang, S., Huang, W., Ao, W., 2025. The Distribution of Rare Earth Elements in Coal Fly Ash Determined by LA-ICP-MS and Implications for Its Economic Significance. *Sustain.* 17. <https://doi.org/10.3390/su17010275>
- Wang, X., Garrabrants, A.C., van der Sloot, H.A., Chen, Z., Brown, K.G., Hensel, B., Kosson, D.S., 2023. Leaching and geochemical evaluation of oxyanion partitioning within an active coal ash management unit. *Chem. Eng. J.* 454, 140406. <https://doi.org/https://doi.org/10.1016/j.cej.2022.140406>
- Wang, X., Hu, W., Zhang, S., Kang, N., Wang, H., Dong, Y., Bian, H., Meng, Y., 2021. Occupational Dust Hazards and Risk Assessment of Coal-Fired Thermal Power Plants of Different Capacities — China, 2017–2019. *China CDC Wkly.* 3, 901–905. <https://doi.org/10.46234/ccdcw2021.221>
- Wang, X., van der Sloot, H.A., Brown, K.G., Garrabrants, A.C., Chen, Z., Hensel, B., Kosson, D.S., 2022. Application and uncertainty of a geochemical speciation model for predicting oxyanion leaching from coal fly ash under different controlling mechanisms. *J. Hazard. Mater.* 438. <https://doi.org/10.1016/j.jhazmat.2022.129518>
- Wang, Z., Coyte, R.M., Cowan, E.A., Stapleton, H.M., Dwyer, G.S., Vengosh, A., 2021. Evaluation and Integration of Geochemical Indicators for Detecting Trace Levels of Coal Fly Ash in Soils. *Environ. Sci. Technol.* 55, 10387–10397. <https://doi.org/10.1021/acs.est.1c01215>
- Wang, Z., Coyte, R.M., Dwyer, G.S., Ruhl, L.S., Hsu-Kim, H., Hower, J.C., Vengosh, A., 2020. Distinction of strontium isotope ratios between water-soluble and bulk coal fly ash from the United States. *Int. J. Coal Geol.* 222, 103464. <https://doi.org/10.1016/j.coal.2020.103464>

- Wang, Z., Dwyer, G.S., Coleman, D.S., Vengosh, A., 2019. Lead Isotopes as a New Tracer for Detecting Coal Fly Ash in the Environment. *Environ. Sci. Technol. Lett.* 6, 714–719. <https://doi.org/10.1021/acs.estlett.9b00512>
- Watteau, F., Huot, H., Séré, G., Begin, J.C., Rees, F., Schwartz, C., Morel, J.L., 2018. Micropedology to reveal pedogenetic processes in technosols. *Spanish J. Soil Sci.* 8, 148–163. <https://doi.org/10.3232/SJSS.2018.V8.N2.02>
- Watteau, F., Morel, J.L., Liu, C., Tang, Y., Huot, H., 2025. Technosol Micromorphology Reveals the Early Pedogenesis of Abandoned Rare Earth Element Mining Sites Undergoing Reclamation in South China. *Minerals* 15, 1–26. <https://doi.org/10.3390/min15050514>
- Weber, J., Straczyńska, S., Kocowicz, A., Gilewska, M., Bogacz, A., Gwizdz, M., Debicka, M., 2015. Properties of soil materials derived from fly ash 11 years after revegetation of post-mining excavation. *Catena* 133, 250–254. <https://doi.org/10.1016/j.catena.2015.05.016>
- Wei, Q., 2018. Study on Structure Evolution Characteristics of High-Organic-Sulfur Coals from Typical Chinese Areas. <https://doi.org/10.3390/min8020049>
- Wong, M.H., Wong, J.W.C., 1989. Germination and seedling growth of vegetable crops in fly ash-amended soils. *Agric. Ecosyst. Environ.* 26, 23–35. [https://doi.org/10.1016/0167-8809\(89\)90035-2](https://doi.org/10.1016/0167-8809(89)90035-2)
- World Coal Association, 2020. Coal and electricity [WWW Document].
- Wu, L., 2004. Review of 15 years of research on ecotoxicology and remediation of land contaminated by agricultural drainage sediment rich in selenium. *Ecotoxicol. Environ. Saf.* 57, 257–269. [https://doi.org/10.1016/S0147-6513\(03\)00064-2](https://doi.org/10.1016/S0147-6513(03)00064-2)
- Wu, X., Cobbina, S.J., Mao, G., Xu, H., Zhang, Z., Yang, L., 2016. A review of toxicity and mechanisms of individual and mixtures of heavy metals in the environment. *Environ. Sci. Pollut. Res.* 23, 8244–8259. <https://doi.org/10.1007/s11356-016-6333-x>
- Xu, H., Liu, C., Mi, X., Wang, Z., Han, J., Zeng, G., Liu, P., Guan, Q., Ji, H., Huang, S., 2021. Extraction of lithium from coal fly ash by low-temperature ammonium fluoride activation-assisted leaching. *Sep. Purif. Technol.* 279, 119757. <https://doi.org/10.1016/J.SEPPUR.2021.119757>
- Xu, S., Zhang, Y., Guo, J., Wu, A., Xiang, X., Sun, H., 2025. Experimental and modeled analysis of contaminant mobility in coal fly ash landfills under continuous rainfall regimes. *Sci. Rep.* 15, 1–21. <https://doi.org/10.1038/s41598-025-86591-x>
- Zaninović, K., Gajić-Čapka, M., Perčec Tadić, M., Al, E., 2008. Climate atlas of Croatia /

- Klimatski atlas Hrvatske 1961-1990., 1971-2000. Državni hidrometeorološki zavod, Zagreb, Croatia.
- Zhang, C.H., Sears, L., Myers, J. V, Brock, G.N., Sears, C.G., Zierold, K.M., 2022. Proximity to coal-fired power plants and neurobehavioral symptoms in children. *J. Expo. Sci. Environ. Epidemiol.* 32, 124–134. <https://doi.org/10.1038/s41370-021-00369-7>
- Zhang, S., Dai, S., Finkelman, R.B., Graham, I.T., French, D., Hower, J.C., Li, X., 2019. Leaching characteristics of alkaline coal combustion by-products: A case study from a coal-fired power plant, Hebei Province, China. *Fuel* 255, 115710. <https://doi.org/10.1016/j.fuel.2019.115710>
- Zhang, X., 2014. Management of coal combustion wastes [WWW Document]. IEA Clean Coal Cent. URL [https://usea.org/sites/default/files/012014_Management of coal combustion wastes_ccc231.pdf](https://usea.org/sites/default/files/012014_Management%20of%20coal%20combustion%20wastes_ccc231.pdf) (accessed 3.4.26).
- Zhang, Z., Cai, W., Hu, Y., Yang, K., Zheng, Y., Fang, C., Ma, C., Tan, Y., 2022. Ecological Risk Assessment and Influencing Factors of Heavy-Metal Leaching From Coal-Based Solid Waste Fly Ash. *Front. Chem.* 10, 1–12. <https://doi.org/10.3389/fchem.2022.932133>
- Zhang, Z., Ma, L., Ngo, I., Yu, K., Zhai, J., Guo, Z., Zhao, Z., Peng, C., Yang, R., 2026. Mitigating heavy metals leachability from CO₂ carbonated coal-based solid waste backfill in high-salinity environments via biochar-clay-nanomaterial synergistic modification. *RSC Adv.* 16, 21201–21219. <https://doi.org/10.1039/d5ra09892k>
- Zikeli, S., Jahn, R., Kastler, M., 2002. Initial soil development in lignite ash landfills and settling ponds in Saxony-Anhalt, Germany. *J. Plant Nutr. Soil Sci.* 165, 530–536. [https://doi.org/10.1002/1522-2624\(200208\)165:4<530::AID-JPLN530>3.0.CO;2-J](https://doi.org/10.1002/1522-2624(200208)165:4<530::AID-JPLN530>3.0.CO;2-J)
- Zikeli, S., Kastler, M., Jahn, R., 2004. Cation exchange properties of soils derived from lignite ashes. *J. Plant Nutr. Soil Sci.* 167, 439–448. <https://doi.org/10.1002/jpln.200421361>

9. CURRICULUM VITAE

Marija Petrović was born on January 18, 1996, in Zagreb. After graduating from I. Gymnasium, she enrolled in Environmental Sciences at the Faculty of Science, University of Zagreb, first completing her undergraduate degree (2014–2017) with a thesis *The microclimate of speleological objects*, and later her master's degree (2017–2019, magna cum laude) with a thesis *Leaching potential of selenium and metals from unregulated waste of slag, ash, and Raša coal*. During her studies, she spent time abroad as a CEEPUS exchange student at Mendel

University in Brno (2018) and an Erasmus exchange student at Lancaster University in the UK (2019).

Since 2020, she has worked as a Research Assistant at the Ruđer Bošković Institute (Zagreb, Croatia), investigating the long-term environmental impacts of coal ash disposal, with a particular focus on transformation of coal ash during weathering. During her PhD studies, she expanded this research through several international collaborations. As a Visiting Researcher at the University of Ljubljana (Slovenia), under the supervision of Prof. Matej Dolenc, she conducted mineralogical characterization of coal ash using X-ray diffraction (XRD). In 2023, she was awarded a Fulbright Scholarship as a Visiting PhD Student at Duke University's Nicholas School of the Environment (USA) under the supervision of Prof. Avner Vengosh, where she worked on isotope-based tracing of coal ash leachates in surface waters of Bosnia and Herzegovina. Earlier that year, she was a CEEPUS Visiting Researcher at Montanuniversität Leoben (Austria) in the group of Prof. Reinhard Sachsenhofer, where she focused on biomarker analysis of coal and coal ash. She also participated in a short research stay at Lancaster University (UK) through a British Embassy-funded Impact Fund project.

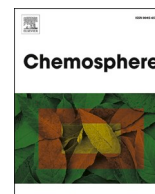
Her achievements include the Award for Outstanding Academic Achievement (Faculty of Science, 2019), the Ruđer Bošković Annual Award (2025) and Best Poster Award (Inspire Adriatic, 2025). She has also contributed to the scientific community through organizational roles, including the Science Committee of STEM Games (2021) and the co-chair of the Organizing Committee of the PhD Student Symposium (2022, 2023, 2025).

She has authored and co-authored 11 scientific papers, including 7 as first author. To date, she has presented her work at 17 international and national conferences.

9.1. List of published articles

1. Petrović, M.; Vidaković-Cifrek, Ž.; Medunić, G.; Fiket, Ž. Toxicity assessment of coal ash after 50 years of weathering: integration of multielement analysis and biological endpoints. *Environmental Science: Processes & Impacts*. 2026, in press.
<https://doi.org/10.1039/d5em01010a>
2. Petrović, M.; Ninčević Grassino, A.; Lapić, J.; Djaković, S.; Furdek Turk, M.; Medunić, G.; Fiket, Ž. Changes in the mobility of oxyanions from coal combustion residues after 50 years of natural weathering. *Waste Management*. 2026, 216, 115450.
<https://doi.org/10.1016/j.wasman.2026.115450>
3. Williams, G.; Petrović, M.; Hill, R.; Hall, G.; Vengosh, A. The water quality impacts of legacy hard-rock lithium mining and processing. *Environmental Science & Technology*. 2025, 59(49), 26492–26505. <https://doi.org/10.1021/acs.est.5c13682>
4. Verma, D.; Singh Patel, K.; Pandey, P. K.; Wakhle, B.; Sharma, S.; Petrović, M.; Fiket, Ž.; Yurdakul, S.; Varol, S.; Martín-Ramos, P. Environmental and health implications of land pollution in Ambagarh Chowki, India. *Journal of Hazardous, Toxic, and Radioactive Waste*. 2025, 29(4), 05025002.
<https://doi.org/10.1061/JHTRBP.HZENG-1531>
5. Fiket, Ž.; Dutour Sikirić, M.; Gal, D.; Petrović, M.; Strasser, V.; Kovač, V.; Frka, S.; Vdović, N.; Saikia, B. Stability of nanodiamonds and carbon dots in aqueous environments: insights into aggregation behavior and additive influence. *Environmental Science: Nano*. 2025, 12, 3904–3920.
<https://doi.org/10.1039/d5en00264h>
6. Petrović, M.; Medunić, G.; Fiket, Ž. Essential role of multi-element data in interpreting elevated element concentrations in areas impacted by both natural and anthropogenic influences. *PeerJ*. 2023, 11, e15904.
<https://doi.org/10.7717/peerj.15904>
7. Petrović, M.; Ivanić, M.; Vdović, N.; Dolenec, M.; Čermelj, B.; Šket, P.; Medunić, G.; Fiket, Ž. Physicochemical and mineral characteristics of soil materials developed naturally on two ~50-year-old coal combustion residue disposal sites in Croatia. *Catena*. 2023, 231, 107338. <https://doi.org/10.1016/j.catena.2023.107338>
8. Petrović, M.; Fiket, Ž. Environmental damage caused by coal combustion residue disposal: a critical review of risk assessment methodologies. *Chemosphere*. 2022, 299, 134410. <https://doi.org/10.1016/j.chemosphere.2022.134410>

9. Petrović, M.; Medunić, G.; Fiket, Ž.; Chakravarty, S. Mobility of metals and metalloids from SHOS coal ash and slag deposit: mineralogical and geochemical constraints. *Environmental Science and Pollution Research*. 2022, 29, 46916–46928. <https://doi.org/10.1007/s11356-022-19074-5>
10. Fiket, Ž.; Petrović, M.; Medunić, G.; Ivošević, T.; Fiket, T.; Xu, L. Z.; Wang, Y.; Ding, S. Evaluation of the potential release tendency of metals and metalloids from estuarine sediments: a case study of Raša Bay. *Molecules*. 2021, 26(21), 6656. <https://doi.org/10.3390/molecules26216656>
11. Petrović, M.; Selenium: widespread yet scarce, essential yet toxic. *ChemTexts*. 2021, 7(2), 11. <https://doi.org/10.1007/s40828-021-00137-y>



Environmental damage caused by coal combustion residue disposal: A critical review of risk assessment methodologies

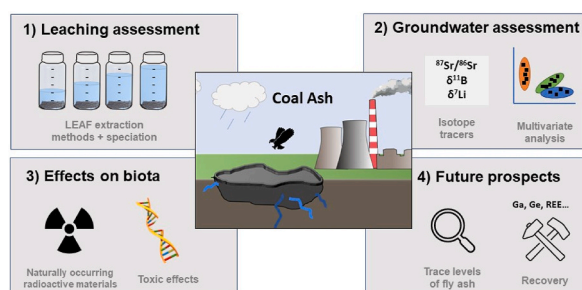
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HIGHLIGHTS

- LEAF methods in combination with other analyzes allow a comprehensive risk assessment of coal ash.
- Climate changes may further promote leaching from old coal ash disposal sites.
- Isotope tracers are a powerful tool for characterizing and tracing coal ash leachate.
- Synergistic effects of multiple contaminants should be considered when assessing toxicity.
- Residents living near coal ash are at higher risk for cardiovascular and physiological disease.

GRAPHICAL ABSTRACT



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ABSTRACT

Coal combustion generates almost 40% of world's electricity. However, it also produces 1.1 billion tons of coal combustion residues (CCR) annually, half of which end up in landfills. Although current regulations require proper lining and monitoring programs, the ubiquitous old, abandoned landfills are often not lined nor included in these programs. In addition, the total number of coal ash disposal sites and their status in the world is unknown. Therefore, this article reviews the environmental damage caused by CCR and three commonly used risk assessment methodologies: leaching assessment, groundwater assessment, and toxicity testing.

Leaching methods are usually the first step in coal ash risk assessment, however, a large number of methods with different parameters make a comparison of data difficult. Groundwater pollution is commonly detected near coal ash disposal sites, but other anthropogenic activities may also exist nearby. Therefore, multivariate statistical methods and isotope tracers should be used to differentiate between different sources of pollution. So far, both stable ($\delta^{18}\text{O}$, δD , $\delta^{11}\text{B}$, $\delta^{34}\text{S}$, $\delta^7\text{Li}$) and radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{207}\text{Pb}$) isotopes have been successfully used as coal ash pollution tracers. Coal ash also negatively affects biota, reduces the diversity of organisms, affects children's health, and increases the risk for developing various diseases. Toxicity studies are great for early screening of coal ash safety; however, they provide no insights into mechanisms causing the adverse effects.

Future directions are also proposed, such as the development of new 'low-level' detection methods for coal ash pollution and sustainable and selective method for recovery of critical elements.

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1. Introduction

Coal has been one of the dominant energy sources over the last two centuries and currently provides ~38% of the world's electricity (World Coal Association, 2020) (Fig. 1). Although several authors have predicted that coal consumption will increase in the future (Benalcázar et al., 2017; BP, 2020), the annual growth rate of production and consumption will most likely decrease in all countries due to environmental initiatives and the current pandemic (International Energy Agency, 2020).

Despite the possible decline in coal consumption, the legacy of coal combustion will remain in the environment for decades in the form of disposed coal combustion residues (CCR) and persistent pollutants released into the atmosphere prior to various regulations. Coal combustion residuals is the general term for four non-combustible parts of coal that remain after combustion - fly ash, bottom ash, boiler slag, and flue gas desulfurization byproducts. It is estimated that about 1.1 billion tons of CCRs are generated annually (Harris et al., 2019), with half of the CCRs being reused in the manufacture of cement, concrete, road construction, as mine fill material, and in agriculture (Fig. 1) (Kruger, 2017; Li et al., 2018; Ukwattage et al., 2013).

Although some sources imply that all fly ash is already used, only some countries (Netherlands, France, Italy) utilize 100% of fly ash, while some countries use less than 60% (India, China, UK) (Ghazali et al., 2019; Kruger, 2017; Surabhi, 2017). Nevertheless, CCRs also consist of other types of waste, so a significant amount of waste is still disposed of. It is estimated that 40–50% of all CCRs is disposed of

annually either in ash ponds (wet storage) or landfills (dry storage) (Harkness et al., 2016; Li et al., 2018; Ruhl et al., 2012).

CCRs are generally enriched with trace elements and organic pollutants compared to the original coal. Therefore, current regulations require proper lining and leachate collection, which in theory should ensure the environmental safety of the landfill (Zhang, 2014). However, a recent study of groundwater contamination in the U.S. found that 91% of the 265 coal-fired plants with multiple regulated landfills surveyed have unsafe levels of one or more ash constituents in downgradient wells. In addition, a large number of landfills were constructed before the regulations went into effect, leaving waste in unlined landfills for decades (Fig. 2) (Russ and Bernhardt, 2019).

Pollution of air, soil and water with heavy metals and organic compounds from CCRs has been widely documented and may persist for decades after disposal (Brandt et al., 2017, 2018; Lemly, 2018a; Madan and Hussain, 2014; Medunić et al., 2018; Pacwa-Płociniczak et al., 2018; Verma et al., 2016). On all continents, a large number of lawsuits against poor coal ash disposal practices show that people are affected by the negligence of coal companies. The existence of law firms specializing in coal ash lawsuits further confirms this point (e.g. <https://www.simmonsfirm.com/complex-litigation/environmental-litigation/coal-ash-lawsuits/>). Nevertheless, the total number of coal ash disposal sites and their status (lined, open) in the world is unknown.

In addition to leaching, several structural failures of existing ponds have occurred in the past, spilling coal ash over villages, rivers, and agricultural lands. Since 1955, there have been approximately 40 coal ash accidents in the United States (Sierra Club, 2018; U.S. EPA, 2015).

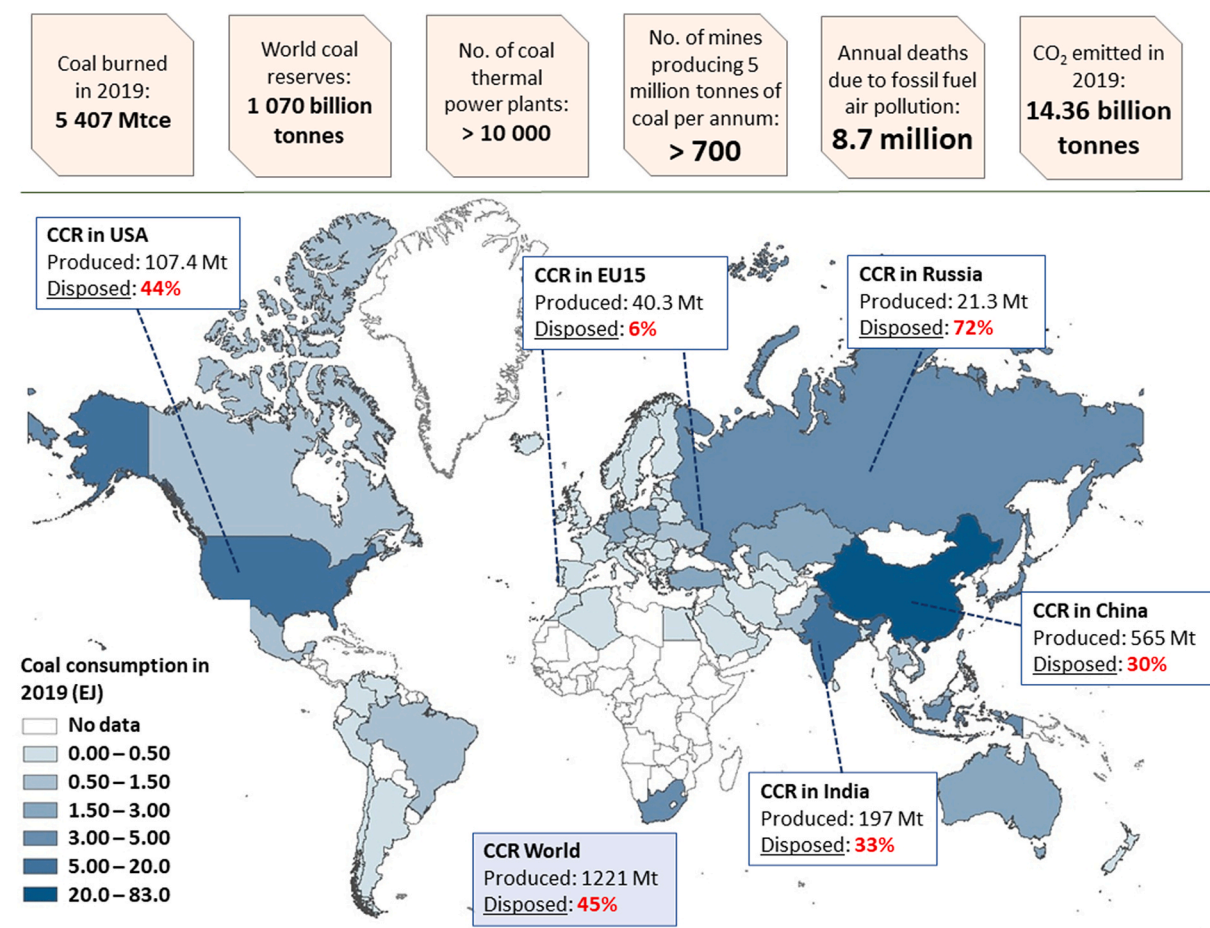


Fig. 1. Coal consumption by country and generated CCRs. The highest consumers and CCR producers are China, India and the USA. Europe has the highest CCR utilization rate (94%) (BP, 2020). References for trends in the world (yellow boxes) are: coal burned (International Energy Agency, 2020), coal reserves (BP, 2020), number of power plant and number of mines (Global Monitor Energy et al., 2021), annual deaths (Vohra et al., 2021), CO₂ emissions (Friedlingstein et al., 2020). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

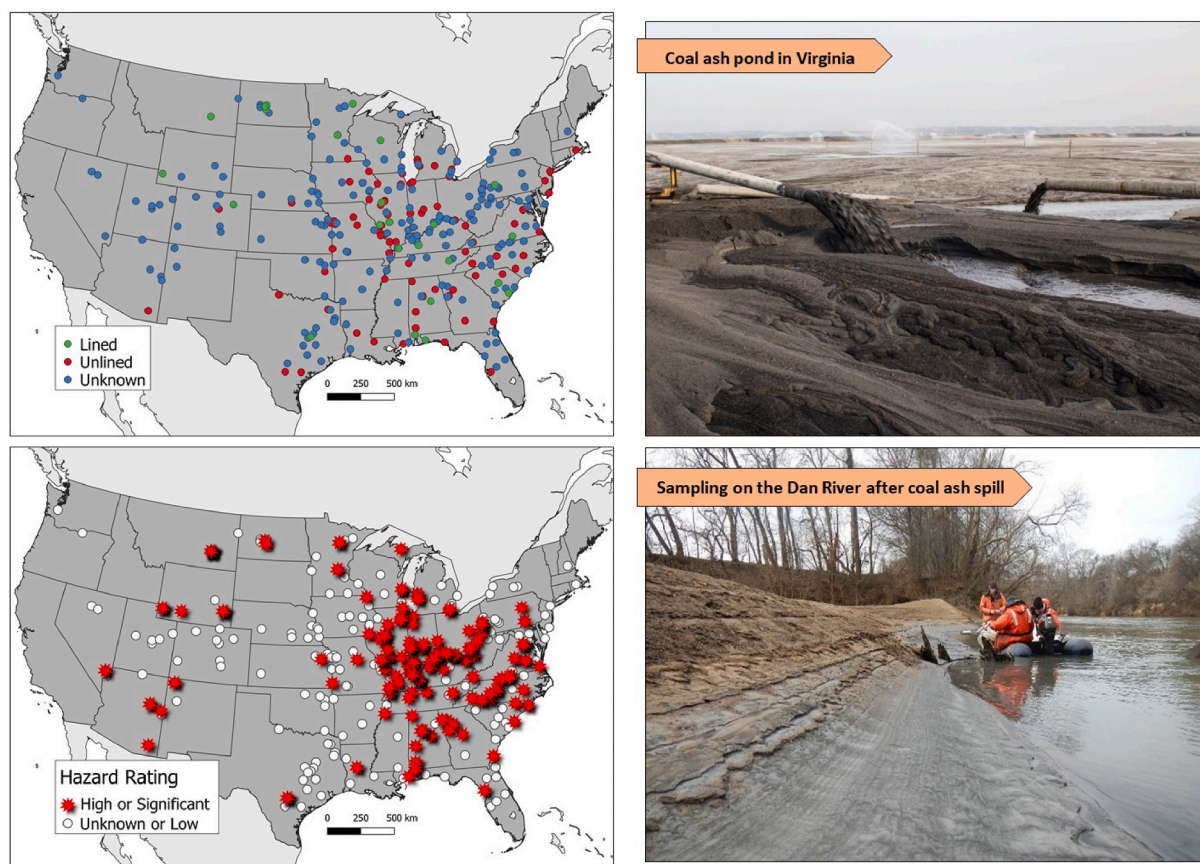


Fig. 2. a) Lining status of coal ash ponds in the USA – approximately 450 unlined ash ponds; b) Hazard rating of coal ash ponds. Describes the potential for loss of life or damage if there is a dam failure at a coal ash impoundment. There are 6 ratings, and the high and significant ratings are described as follows: 1. **high:** Failure or mis-operation of these dams will probably cause loss of human life. 2. **significant:** Failure or mis-operation of these dams would cause economic loss, environmental damage, and disruption of lifeline facilities. Data for the maps is publicly available, however the spreadsheet generated by Earthjustice was used (Earthjustice, 2021). c) Filling the coal ash pond in Virginia © Nenad Živković, Shutterstock; d) Sampling on Dan river after coal ash pond spill. © US Fish & Wildlife Service, public domain.

The largest ash accident in the United States occurred in Kingston, where approximately 4.1 million cubic metres of coal ash spilled into nearby rivers (Ramsey et al., 2019; Stanley et al., 2013). Although the site was immediately remediated and is now considered safe, several news media reported that more than 200 workers who remediated the site had adverse health effects or died from various types of cancer. Although there is currently no precise evidence that coal ash is responsible for the poor health of workers, it is worth noting that the company responsible for the cleanup is currently being sued by workers with health problems (Bruggers, 2018; Powers, 2020).

However, a pond failure does not have to be as massive as Kingston accident to be equally devastating. For example, a sinkhole in a coal ash pond at Plant Bowen in Georgia released over 280 tonnes of ash into a tributary of the Euharlee creek. The spill deposited 20 cm of ash over 172 m² of streambed and killed most of the aquatic life in that area (Lemly, 2015).

In addition to pond failures in the US, about 76 coal ash pond accidents in India were reported in the media between 2010 and June 2020, resulting in the deaths of local residents and flooding of villages and agricultural land (Healthy Energy Initiative, 2020). These accidents include barges filled with fly ash overturning in rivers and spilling the ash directly into waterways. In 2020, at least 5 capsized accidents occurred involving fly ash being transported from India to Bangladesh (Healthy Energy Initiative, 2020).

Coal ash spills have also occurred in other parts of the world, such as Brazil (Civeira et al., 2016) and Slovakia (Jurković et al., 2011). It is estimated that about 3000 people have died worldwide due to the failure

of coal ash ponds and tailings piles (Santamarina et al., 2019). The total number of ash pond failures worldwide is currently unknown, as the media usually “only” reports major incidents in which local residents lost their lives (Healthy Energy Initiative, 2020).

As several of the accidents have occurred in recent years, the reliability of existing ash ponds and potential future accidents raises numerous concerns. Inspection of the structural stability of ash ponds by EPA further confirms these concerns, with only 3 of 38 inspected ponds in Illinois rated “satisfactory” (Sierra Club, 2018).

Both ash pond failures and long-term leaching from regulated landfills and forgotten landfills highlight the need to review the environmental impacts of coal ash and the methodology used to assess environmental impacts. Most often, only one approach (e.g., geochemical or biological) is used for assessment, while new research demonstrates the need for an interdisciplinary approach to properly assess the environmental impacts of coal ash (Fiket et al., 2020).

Therefore, the sections are divided as follows:

- i) **mobility studies**, in which factors affecting the mobility of elements and extraction methods are described.
- ii) **groundwater contamination**, where persistent contamination and source identification methods are described.
- iii) **effects on biota**, where past exposures of organisms to coal ash and toxicity tests of coal ash are described.

The aim of the paper is to inform readers about the global problem of coal ash landfills, the commonly used methods and their limitations, and

the need for an interdisciplinary approach to ash landfill assessment.

2. The mobility of elements from CCR

Leaching of elements is one of the main mechanisms of contaminant transport from wastes to the environment. Therefore, the first step in coal ash risk assessment is to measure the leaching potential of elements (Kadir et al., 2016). This can be measured by extraction methods that extract the available fraction of elements.

Several factors influence the leaching of elements - both intrinsic properties of the waste (mineralogy, organic matter content, types of element occurrence, particle size, permeability, porosity, etc.) and external conditions (leachate pH, climatic and hydrological conditions) (Jones et al., 2012a; Kosson et al., 2019a; Sloot et al., 2009).

2.1. pH – the main factor affecting leaching

The pH is considered to be the most important parameter affecting leaching as it controls the solubility of elements and the sorption/desorption of elements on the surface of oxides, clays, minerals, and organic matter (Chandler et al., 1997a, 1997b; Sloot et al., 2009). Typically, ashes can be categorised on the basis of their pH (Izquierdo and Querol, 2012): (i) **strongly alkaline ashes** (pH 11–13), where carbonates are the dominant minerals in the waste; (ii) **slightly alkaline ashes** (pH 8–9) where dissolution of anhydrite and gypsum dominates the leaching; (iii) **acidic ashes**, which have an abundance of pyrite and lack of the above minerals.

The same element will have different mobility in highly alkaline wastes compared to acidic ashes due to the difference in pH. When ashes are tested over the pH range, elements can be categorised into four groups (Fig. 3) (Kosson et al., 2014, 2019a): (i) **highly soluble species**, which are soluble over the entire pH range due to association with soluble salts (sulphates and chlorides); (ii) **cationic species**, which have a maximum concentration in the acidic pH range. Most elements show this behaviour because the acidic leachate increases the intensity of attack on metal-bearing minerals (Fleming et al., 1996); (iii) **oxy-anionic species**, which show a maximum concentration in the slightly alkaline pH range (e.g. As, Cr, Mo, Se ...), while their concentration decreases in the acidic and strongly alkaline waste; (iv) **amphoteric species**, which show a maximum concentration in the acidic pH range, decreasing in the neutral range and increasing again in the strongly alkaline range (e.g. Ba).

In addition to these four typical behaviours, elements may also exhibit “atypical” behaviours, usually due to their association with other minerals or other factors. Examples of “atypical” behaviours and a detailed overview of element mobility can be found elsewhere (Izquierdo and Querol, 2012).

2.2. Impact of liquid to solid ratio (L/S) on leaching

In addition to pH and mineralogy, the liquid-solid ratio (L/S) has been shown to be an important parameter in correctly describing the leaching behavior of elements (Cao et al., 2018). In practice, the liquid-solid ratio depends on the rate of rainfall and the volume of waste

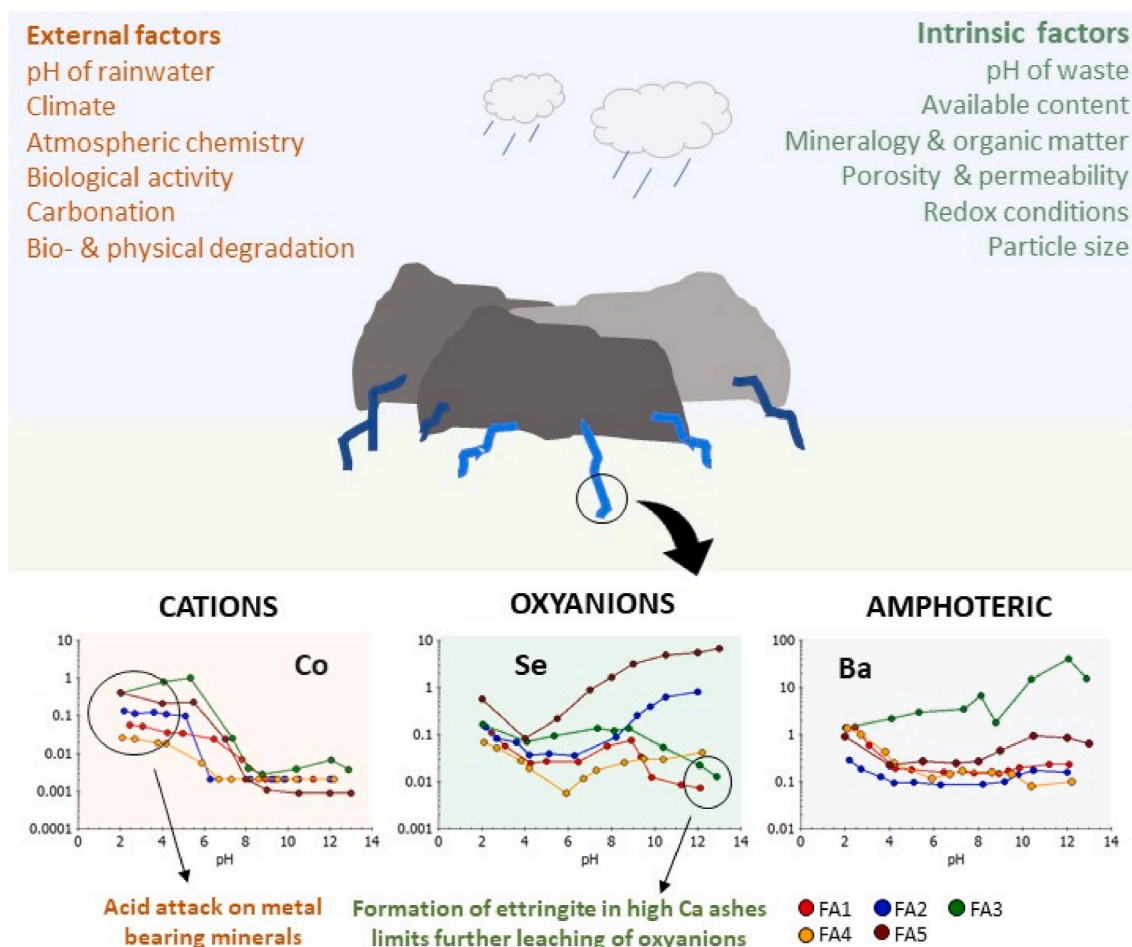


Fig. 3. External and intrinsic factors affecting the leaching of elements, and the most common mobility patterns of elements in different pH. Data for fly ashes were extracted from LeachXS Lite database (Kosson et al., 2009; Garrabrants et al., 2012; 2014).

in the landfill (Chandler et al., 1997b; Sloot et al., 2009). When rain infiltrates the waste, a local equilibrium is reached between the solid phase and the contacting leachate. Typically, leaching of elements has one of two outcomes (Kosson et al., 2002, 2019a): (i) **leaching with limited available content** - the available portion of the element has been released and transfer of the element from the solid to the liquid stops. (ii) **solubility-limited leaching** - the available fraction of the element has been partially released and the remainder of the available fraction remains in the solid. Leaching stops because the water phase is saturated.

Typically, highly soluble species (e.g., salts) are controlled by the available fraction. Because of their solubility, they are highly mobile at the beginning of leaching. However, as leaching progresses and water transports the soluble species, the concentration of these elements decreases due to depletion of the elements in the solid (Kosson et al., 2002, 2019a; Thorneloe et al., 2009). Elements controlled by solubility will typically leach at a relatively constant rate over extended periods of time as long as pH or other factors do not change and affect their solubility. Changes in L/S can change the outcome of leaching. For example, changes in precipitation rate can change solubility-limited leaching to content-limited leaching due to increased water volume.

However, not every element will reflect these behaviors in L/S because coal ash is a complex material. The release of elements may also be controlled by retention in the matrix due to minerals or complexing agents that could increase their solubility (Agnieszka et al., 2014; Querol et al., 1996; Vejehati et al., 2010). Nevertheless, testing the behavior of elements in different L/S is useful because it can predict the time required for the elements to be depleted in the solid.

2.3. Aging of waste and environmental conditions

The disposal of coal ash means a perpetual solution for coal ash, as the ash sits in landfills for centuries. Over time, severe chemical, physical, and biological reactions can occur within the material, including soil formation (Konstantinov et al., 2020; Uzarowicz et al., 2017, 2018). These reactions alter the primary properties of the ash and affect the leaching behavior of the elements (Chandler et al., 1997a; Kosson et al., 2019a; Sloot et al., 2009). Therefore, aged waste have different compositions and properties than at the time of disposal. For example, physical degradation by erosion may alter the permeability of the material and cause higher leaching due to greater infiltration of water (Gschwend et al., 1990). Depletion of primary constituents (Ca, SO₄, OH⁻, etc.) due to leaching can change the L/S and pH of the waste, which in turn changes the behavior of the elements. The formation of secondary precipitates alters the mineralogy of the waste and immobilizes leached constituents (Coussy et al., 2017; Johnson et al., 1999; Uzarowicz and Zagorski, 2015).

When waste is deposited in a landfill that has been continuously covered with soil, biodegradation can generate organic acids and alter the redox potential. Changes in redox potential can alter the mobility of polyvalent elements, as their mobility changes when the oxidation state is altered (Romero et al., 2007; Schwartz et al., 2018). Revegetation also affects the leaching of elements from coal ash landfills and usually reduces the mobility of elements (Chu, 2008; Kostić et al., 2018).

In addition, changes in climatic conditions (e.g. precipitation rate, precipitation pH) can further affect the pH and L/S of the waste (Hayes et al., 2009, 2014; Johnson et al., 1999).

3. Leaching methods for the evaluation of coal ash

More than 100 extraction methods have been developed for measuring the leaching potential of elements. Selecting a method and comparing data is challenging due to the large number of methods, all of which differ in physicochemical parameters (pH and type of leaching solution, liquid-solid ratio, contact time, particle size, etc.) (Kosson et al., 2014; Neupane and Donahoe, 2013).

Since the leaching methods are the first step in the risk assessment of coal ash, an incorrect assessment could lead to the utilization of hazardous waste or the disposal of waste suitable for utilization (Tiwareti et al., 2015). Considering that the Toxicity Characteristic Leaching Procedure (TCLP) was a required test method for CCRs in the United States for decades, it is possible that misclassification of waste occurred (Tiwareti et al., 2015). This is because TCLP was developed for a specific purpose - for joint disposal of industrial and municipal wastes. Therefore, it uses acetic acid as a leaching solution (Hassett et al., 2005). Since ashes can be alkaline, TCLP can mask the leaching of oxyanions (As, Mo, Se, U, V), which are most mobile under slightly alkaline conditions and immobile in the acidic range (da Silva et al., 2018; Jones et al., 2012b; Tiwareti et al., 2015; Zhao et al., 2020).

3.1. LEAF – Leaching Environmental Assessment Framework

Currently, the most comprehensive characterization of coal combustion wastes can be made according to the US EPA's Leaching Environmental Assessment Framework (LEAF) (da Silva et al., 2018; Zhang et al., 2019; Zhao et al., 2020). LEAF was developed for the purpose of leaching characterization of CCRs over a wide pH and L/S range.

LEAF combines four dynamic (serial batch and column) methods (Methods 1313, 1314, 1315, 1316) that focus on different aspects of leaching - changes in pH and changes in L/S, as well as equilibrium and mass transfer-based leaching (Kosson et al., 2019a).

To enable comparison of data, methods were developed in accordance with European Union. In addition, a large database of leaching results and the LeachXStm Lite data management program were developed and published online (Kosson et al., 2019b).

3.2. Additional measurements

Most leaching methods observe the pattern of elements under different pH values and, more recently, under different liquid/solid ratios. However, to properly assess the long-term scenario of the disposed waste, other factors should be considered, both intrinsic properties of the waste and external conditions (Chandler et al., 1997c; Kosson et al., 2019a; Sloot et al., 2009). The analysis of so many factors is often too complex but should be performed when an unusual leaching behaviour is observed.

Sometimes only additional analysis of the main mineral phases from the coal ash by XRD and XRF or geochemical modelling helps to identify the main factor controlling leaching. Speciation analysis by geochemical modelling, sequential extraction methods or XANES spectroscopy could further reveal the physical (particulate, colloidal, dissolved) and chemical form (organic and inorganic complexes, free metal ions with different oxidation states) of the elements in the solid (Coussy et al., 2017; Liu et al., 2016; Minkina et al., 2019; Shah et al., 2008). This is important because speciation alters the mobility, toxicity, and bioavailability of elements (Baun and Christensen, 2004; Fu et al., 2018).

Typically, less than 10% of total metal concentrations are present as free metal ions in the leachate and are more likely to be bound to the colloids or complexes (Chandler et al., 1997b). Therefore, the characterization of organic, colloidal, and particulate materials should not be neglected (Baun and Christensen, 2004). Research on the physical speciation of elements in coal ash leachate is sparse, so many of the factors controlling colloidal behaviour and contaminant transport are still unclear (Baun and Christensen, 2004; Gschwend et al., 1990; Hennebert et al., 2013; Uddh Söderberg et al., 2019; Zhai et al., 2019).

However, the use of LEAF methods in combination with mineralogical and metal speciation analyses could provide the necessary comprehensive risk assessment of coal ash and more detailed insight into the factors controlling element leaching.

4. Groundwater pollution caused by coal ash

For many years, groundwater received almost no attention in water-focused policy (Kath and Dyer, 2017). A report prepared by the OECD and the Netherlands Environmental Assessment Agency (OECD, 2012) in 2012 identified groundwater pollution as the environmental problem not well managed and likely to increase by 2050. As the second largest source of groundwater pollution is industrial activities (waste disposal, mining, industrial effluents) and global water demand is expected to increase by about 55% by 2050 (OECD, 2012), global groundwater pollution from coal ash should be accurately identified.

4.1. Coal Ash Rule

In 2015, EPA issued “Coal Ash Rule”, the first federal regulation on coal ash disposal. The regulation required groundwater monitoring for coal ash landfills and that companies make the data available to the public. In 2018, 91% of the 265 coal-fired plants with multiple regulated landfills surveyed had unsafe levels of one or more coal ash constituents in groundwater below ash landfills. Arsenic and lithium were present at unsafe levels in more than 50% of groundwater wells. One site had more than 3.5 mg/L of arsenic, increasing cancer risk in 1 in 6 people (Russ and Bernhardt, 2019; U.S. EPA, 2012).

The biggest oversight of Coal Ash Rule is that hundreds of older ash landfills that were closed prior to Coal Ash Rule were not included in the groundwater monitoring programme. Considering that contamination has been found in groundwater near the ash pond closed 13 years ago (Harkness et al., 2016), groundwater contamination is likely even more widespread than covered by Coal Ash Rule. Therefore, assessment of all old ash pond sites needs to be done urgently.

Coal Ash Rule is an important provision to increase transparency between thermal power plants and residents affected by ash ponds. In other countries, there is a lack of transparency in data, which makes it difficult to track global coal ash pollution. Recently, most studies on groundwater pollution are conducted in India (Baba and Kaya, 2004; Pandey et al., 2020; Prasad and Mondal, 2008; Spadoni et al., 2014; Verma et al., 2016). However, coal ash pollution of groundwater has been found all over the world - e.g., Bangladesh (Us-Sakib et al., 2018), USA (Harkness et al., 2016; Simsiman et al., 1987), Europe (Crisan and Bakos, 2008), Brazil (Binotto et al., 2000). These studies are only a fraction of the groundwater pollution found, but clearly show the global problem of coal ash.

4.2. Methods used for groundwater quality assessment

A common method of assessing groundwater quality is to measure various physiochemical parameters, which are then compared to WHO or national standards to determine water quality. Due to the high mobility of soluble salts, high concentrations of major ions and increased hardness are often measured in groundwater affected by coal ash. Determination of high concentration of various elements including Mn, Cr, Pb, B, Fe, Zn is also of great importance as the contaminants may remain in the aquifer for decades.

However, there are several shortcomings in this method. Water quality standards have been made for individual metals (Jadhav et al., 2007), although the mixture of heavy metals can cause toxic effects even when present at small doses (Wu et al., 2016). In addition, physiochemical analysis often results in a large data set that can be difficult to interpret (Tanvir Rahman et al., 2020; Wagh et al., 2018). To overcome this last shortcoming, water quality indices (WQIs) are commonly calculated.

Furthermore, physiochemical analysis does not provide information about the relationship between the measured variables, nor about the source of the metals and ions. The source of the contaminants is important, especially in areas where related industries are nearby or elevated levels could be due to geogenic origin. Therefore, various

multivariate statistical methods and isotopic traces should be used.

4.3. Water quality indices (HPI, HEI, cd)

WQIs combine several parameters in a single unitless value, which allows universal comparability, easier interpretation and consider the effects of all influencing parameters. There are many different indices commonly used for determining the heavy metal presence in the water. Among them are Heavy Metal Pollution Index (HPI) (Prasad and Bose, 2001), Heavy Metal Evaluation Index (HEI) (Edet and Offiong, 2002), Degree of Contamination (Dc) (Backman et al., 1998), Water Quality index (WQI) (Debels et al., 2005), Hazard Index (HI); and all indices have the same goal – determine the quality of water considering the heavy metals and their limiting values.

Almost all indices were used to assess the groundwater quality impacted by coal ash (Ahmad et al., 2020; Prasad and Sangita, 2008) and found high pollution (Fig. 4a).

However, the major shortcoming of water quality indices is the poor correlation between the indices (Chaturvedi et al., 2019; Tanvir Rahman et al., 2020) or theoretically good correlation that results in different classification (Fig. 4b) (Bhuiyan et al., 2010).

5. Isotope tracers of coal ash pollution

Isotope tracers have proven to be an excellent tool for determining the origin of elements in groundwater. Both stable ($\delta^{18}\text{O}$, δD , $\delta^{11}\text{B}$, $\delta^{34}\text{S}$, $\delta^7\text{Li}$) and radiogenic ($^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{207}\text{Pb}$) isotopes have been identified as potentially good indicators of CCR leachate because they are abundant in coal ash, leach readily, and do not fractionate during coal deposition, combustion, CCR formation, and mobilization (Ruhl et al., 2014; Voltaggio et al., 2015).

The use of isotopic tracers is important to distinguish the effects of coal ash from those of related industries (e.g., gas and oil effluents) that could cause similar elevated element concentrations (Harkness et al., 2015).

5.1. Stable isotopes

Boron isotopes are one of the most commonly used tracers of coal ash pollution. Most studies found that boron isotope ratios in coal ash and leachate have a wide range of negative values (Davidson and Bassett, 1993; Ruhl et al., 2014; Williams and Hervig, 2004), while in natural waters the $\delta^{11}\text{B}$ values are positive ($\delta^{11}\text{B} = 0\text{--}40\text{‰}$) (Vengosh et al., 1994). Therefore, if the water body is polluted by leachate, it would exhibit intermediate ratios between original ash and unpolluted water, and a mass balance equation could reveal the degree of leachate infiltration (Davidson and Bassett, 1993). Accordingly, 5% of the dissolved constituents in the downstream French Broad River (Ashville, NC) originated from the CCR discharge (Ruhl et al., 2014).

Similar results were found for $\delta^7\text{Li}$ in coal and CCR from three watersheds in the USA (Harkness et al., 2015). The ratios of coal and CCRs were similar to those of leachate from coal ash basins ($\delta^7\text{Li} = -6.2$ to $+8.7\text{‰}$) and were in a much narrower range than $\delta^7\text{Li}$ in river and groundwater (from $+1\text{‰}$ to $+44\text{‰}$ and from $+6\text{‰}$ to $+29\text{‰}$) (Penniston-Dorland et al., 2017), respectively) confirming the possible use of $\delta^7\text{Li}$ as a tracer for coal ash pollution (Fig. 5).

Sulphur isotopes, whose ratios mostly reflect the mineral phases to which the sulphur has been bound, are also a potential tool for tracking pollution. Strongly positive $\delta^{34}\text{S}$ values ($+6.1\text{‰}$ to $+12.9\text{‰}$) are typical of organically bound sulphur in low-sulphur (<1 wt%) coals, while negative $\delta^{34}\text{S}$ values (-2.7‰ to -3.2‰) reflect pyritic sulphur (FeS_2) (Miljević and Golobočanin, 2007; Smith and Batts, 1974). Negative $\delta^{34}\text{S}$ values in pyrite are due a faster response of ^{32}S during bacterial sulphate reduction than of ^{34}S , resulting in an enrichment of ^{32}S in pyrite (Chmielewski and Licki, 2006). Therefore, sulphate in groundwater derived from pyrite reflects the same values, allowing detection and

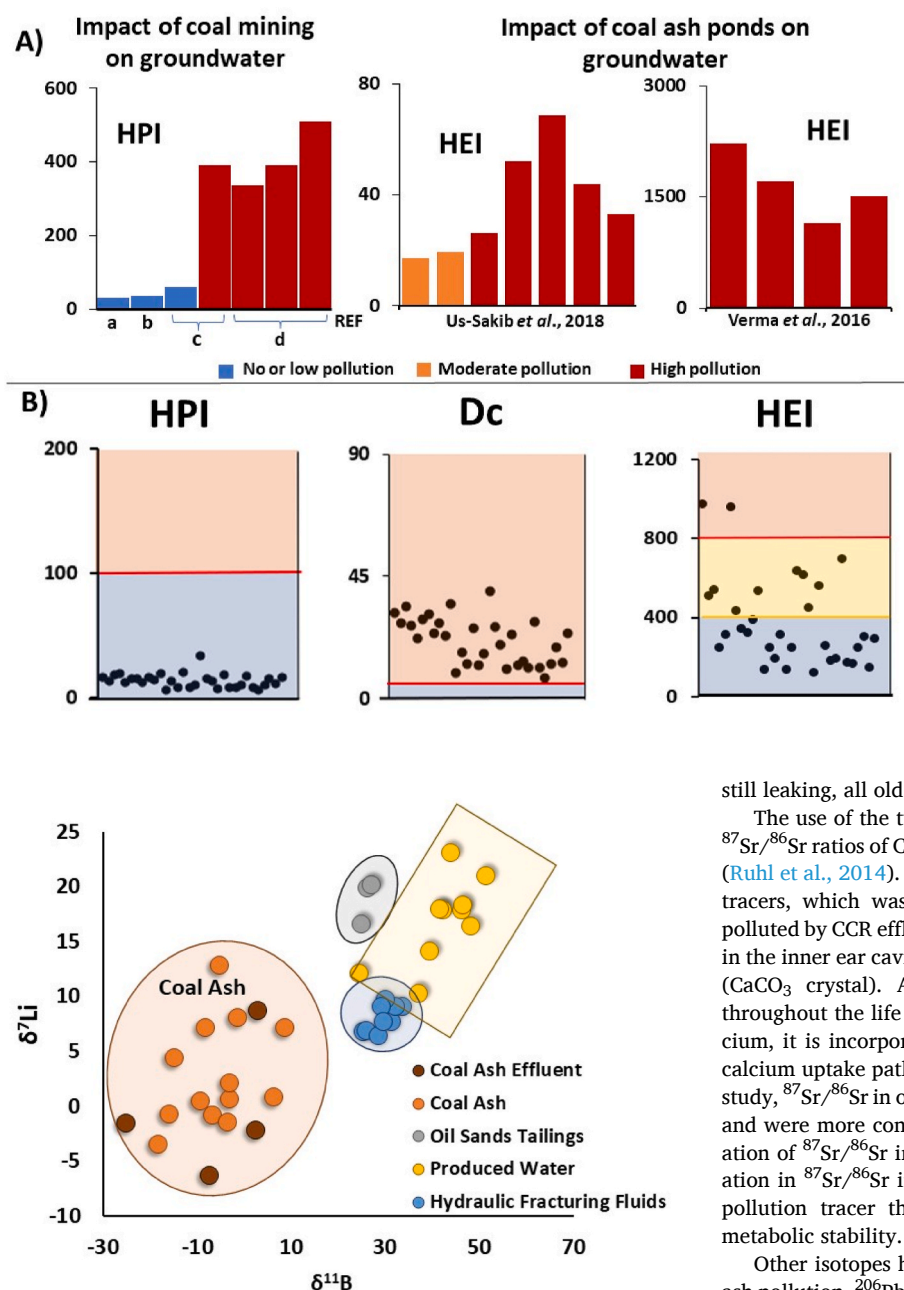


Fig. 5. Lithium and boron isotopes from different industries. The image was adapted from Harkness et al. (2015). Boron values for coal ash are from Ruhl et al. (2014), while isotopes for hydraulic fracturing fluids and all others are from Warner et al. (2014).

quantification of ash leachate input (Haefner, 2001).

5.2. Radiogenic isotopes

Strontium is one of the most commonly used isotopes in coal ash pollution studies (Campbell et al., 2008; Chandler et al., 1997c; Harkness et al., 2016; Hurst et al., 1991; Vengosh et al., 2019; Voltaggio et al., 2015) and has also been used to distinguish the origin of elevated Cr(VI) (Vengosh et al., 2016) and Mo (Harkness et al., 2017) in groundwater near coal ash ponds. Recently, two-isotope system ($\delta^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) was used to identify leaching of 22 coal ash ponds in groundwater and surface water (Harkness et al., 2016). Of the 165 groundwater wells analysed, 65 were contaminated by coal ash. It should be noted that one site analysed was an ash pond that closed 13 years ago. Since this site is

Fig. 4. a) Impact of coal mining and coal ash ponds on groundwater as expressed by two commonly used water quality indices – Heavy metal pollution index (HPI) (Sahoo and Khaoash, 2020; Prasad and Sangita, 2008; Bhuiyan et al., 2010; Ahamad et al., 2020) and heavy metal evaluation index (HEI) (Us-Sakib et al., 2018; Verma et al., 2016). b) Shortcoming of water quality indices. The same datasets result in three different classifications – low pollution by HPI and high pollution by Dc. HEI was developed to overcome mentioned shortcoming (Edet and Offiong, 2002).

still leaking, all old ash pond sites need to be evaluated urgently.

The use of the two-isotope system has proven valuable because the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of CCRs could have the same ratios as background water (Ruhl et al., 2014). In addition, Sr isotopes can also be used as biogenic tracers, which was highlighted by a study of fish otoliths in lakes polluted by CCR effluents (Brandt et al., 2018, Fig. 6). Otoliths are found in the inner ear cavity of teleosts and are mainly composed of aragonite (CaCO_3 crystal). Aragonite grows concentrically and continuously throughout the life of the animal. Since Sr is chemically similar to calcium, it is incorporated into the mineral fractions of fish otoliths via calcium uptake pathways (Loewen et al., 2016). In the aforementioned study, $^{87}\text{Sr}/^{86}\text{Sr}$ in otoliths and polluted sediment pore water overlapped and were more constant than $^{87}\text{Sr}/^{86}\text{Sr}$ in surface water (Fig. 6). Variation of $^{87}\text{Sr}/^{86}\text{Sr}$ in surface water is most likely due to temporal variation in $^{87}\text{Sr}/^{86}\text{Sr}$ inputs. This implies that otoliths may be a stronger pollution tracer than surface water due to their geochemical and metabolic stability.

Other isotopes have also been used as geochemical tracers for coal ash pollution. $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios in coal fly ash and in sediments from Sutton Lake in North Carolina overlapped and confirmed pollution by ash leaching. The study found that the Pb isotopes of three fly ashes in the U.S. ranged from 1.2173 to 1.2271, which is distinct enough from other anthropogenic sources (leaded gasoline and paint) (Wang et al., 2019).

Isotopes remain one of the most powerful tools for identifying pollution sources, especially when a multi-isotope approach is used.

6. Effects of coal ash on biota

Since the last century, adverse effects of coal ash have been reported in both terrestrial and aquatic ecosystems. Exposure to CCR caused numerous histopathological, behavioral, and physiological effects in many organisms (Rowe et al., 2002). Many species come into direct contact with coal ash by inhabiting the area around landfills. Some animals, such as deer, eat the ash due to nutrient deficiency, which can be prevented by fencing around landfills (Sample and Suter, 2002). However, fencing cannot prevent small animals or birds from nesting near such sites (Bryan et al., 2012). In addition, aquatic insects may lay

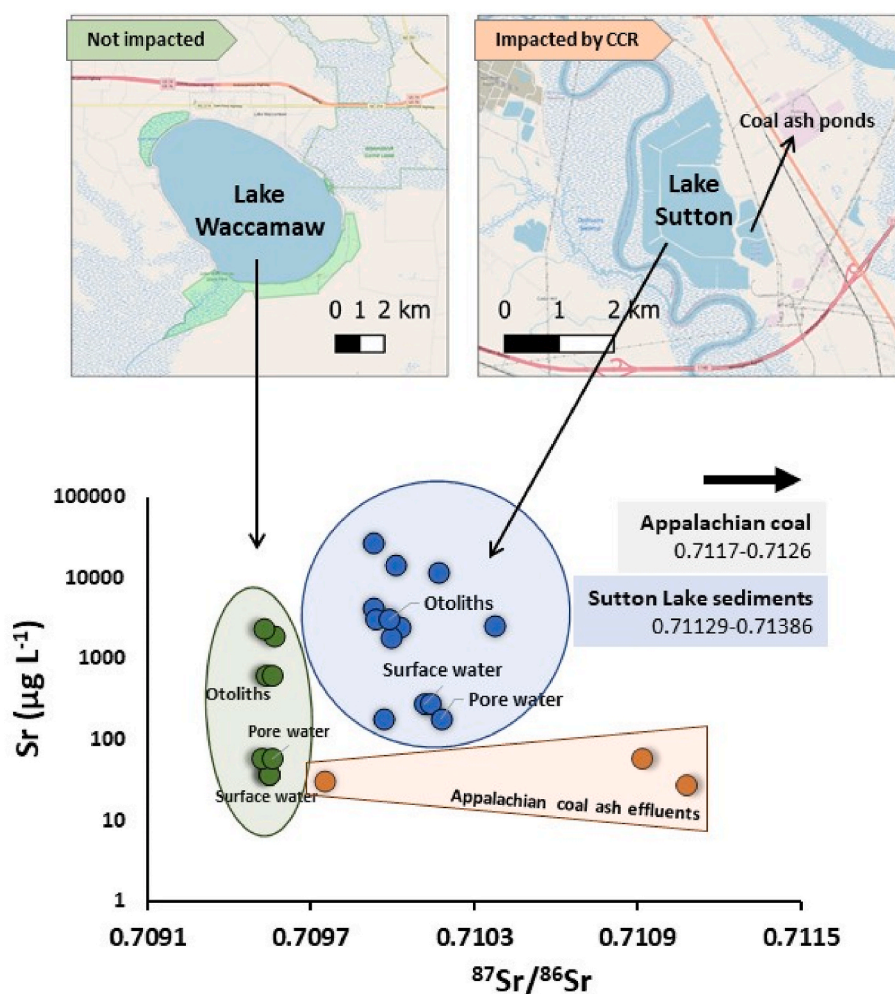


Fig. 6. Strontium isotopes and strontium concentrations in two lakes in North Carolina. Lake Waccamaw is not contaminated by CCR, but Lake Sutton is. CCR near Sutton Lake was produced by burning Appalachian coal. Sr isotope ratios in fish otoliths, surface (Brandt et al., 2018) and pore water, and sediment leachate (Vengosh et al., 2019) from Sutton Lake are all higher than in the reference lake (green) and are intermediate between the reference lake and effluents from Appalachian coal combustion (Ruhl et al., 2014). Values for Appalachian coal are from Vengosh et al. (2013) and for Sutton Lake sediment are from Vengosh et al. (2019). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

their eggs in ash ponds and ascend from the site to the uncontaminated area (Lemly, 2010). All this can lead to bioaccumulation and biomagnification, especially of Se and Hg, which are common bioaccumulation pollutants (Cervantes-Ramírez et al., 2018).

Amphibians are particularly vulnerable due to their permeable skin, especially if they live in coal ash ponds. Adverse effects of coal ash have been observed in many toads living near coal ash deposits (Hopkins et al., 1998). Coal ash caused oral deformities that subsequently resulted in a decreased ability to graze periphyton (Rowe et al., 1996). In addition, coal ash impaired metabolic rate (Rowe et al., 1998), swimming speed, and the ability of toads to escape predators (Raimondo et al., 1998).

Adverse effects have also been observed in other animals. For example, deformities of the spine and skull were observed in fish in Lake Herrington that were contaminated with coal ash (Lemly, 2018b). Mercury poisoning has been observed in cattle grazing within a 5 km radius of a coal-fired power plant (Mahajan et al., 2012). Coal ash pollution may also affect natural selection on rotifer morphology (Xue et al., 2017). Rotifers, like many other zooplankton species, are known for their phenotypic plasticity as an adaptive response to environmental change (Garza-Mouriño et al., 2005; Sanoamuang, 1993). Therefore, rotifers in lakes polluted by coal ash effluent may have smaller bodies, as they require less energy to survive (Cattaneo et al., 1998), and lay larger eggs, which would ensure neonate survival (Xue et al., 2017).

Pollution also reduces the diversity and density of organisms and increases the dominance of more resistant organisms (Sun et al., 2007). Therefore, an altered spatial distribution of plants and animals can often

be observed near ash dumps.

Humans can also be affected by leached constituents. According to EPA, a person living within one mile of an unlined coal ash pond has a 1 in 50 chance of developing cancer if they drink water contaminated with coal ash. The risk and rates of heart, lung, and liver disease, as well as poor child health, are also increased among residents living near coal ash ponds (Kravchenko and Lyerly, 2018; Sears and Zierold, 2017; U.S. EPA, 2014).

It is clear that coal ash can have negative impacts on biota and human health. To truly illustrate the ecological damage caused by CCRs, the monetary cost of ecological damage from coal ash deposition was calculated to be \$2.31 billion for 22 sites in the United States (Lemly, 2010). All 22 sites caused lethal and sublethal effects at all trophic levels of organisms and impacted overall populations. In addition to the total costs, the fact that 12 of the 22 sites were legally permitted to release pollutants through effluent is disturbing. Other sites caused ecological damage due to structural deficiencies and unauthorized discharge of ash pond effluent.

6.1. Toxicity testing

Toxicological studies can be conducted to better understand and predict the potential harm of coal ash on organisms. Toxic effects of coal ash have been studied over the last century. The objectives of toxicity studies have been either to determine the toxic capacity of coal ash as a pollutant or to ensure the safety of fly ash used as a soil amendment. In general, mutagenic properties of fly ash have been observed in the

toxicological studies conducted to date when tested on various plants and animals and when not mixed with stabilizers (El-Mogazi et al., 1988). The extent of the toxic effects depended on the ash composition, which differs significantly even among ashes from the same power plant. This reconfirms the complexity of coal ash and makes it difficult to detect the specific pathway of coal ash toxicity. Most likely, toxicity is the result of several factors - heavy metals, organic pollutants and radioactive elements.

6.2. Phytotoxicity

Coal ash toxicity has been observed on various plants (e.g. lettuce (Banks and Schultz, 2005), rice (Singh et al., 2016), beans (Aitken and Bell, 1985) and on standard species used for toxicity testing (Artico et al., 2018; Chakraborty et al., 2009; Fiket et al., 2020; Jana et al., 2017), *Lemna minor* (Radić et al., 2018). Usually, one of the following criteria is assessed: seed germination, radicle extension, mitotic changes and DNA damage.

Seed germination usually decreases in the presence of coal ash, which was observed in *Vicia faba* L. seeds (Singh et al., 1997) and *Brassica parachinensis* and *Brassica chinensis* seeds (Wong and Wong, 1989). However, some seeds are not affected until they germinate (Singh et al., 1997; Wong and Wong, 1989). This reduced sensitivity is due to the protection of embryonic tissues by the seed coats (Mtisi and Gwenzi, 2019). To overcome this shortcoming, radicle elongation could be evaluated along with seed germination to better characterise coal ash toxicity (Luo et al., 2018).

Cytotoxicity is most commonly indicated by root growth inhibition, mitotic and chromosomal abnormalities (chromosome stickiness, hanging chromosomes, chromosome breaks), and low mitotic index (the ratio of the number of dividing cells to the total number of cells observed). Genotoxicity is most commonly assessed by detecting DNA damage by comet assay and measuring lipid peroxidation, which reflects oxidative stress in plant cells (Çelik et al., 2008). Both cyto- and genotoxic effects caused by coal ash have been observed in numerous organisms exposed to coal ash and associated polluted sites (Table 1) (Artico et al., 2020; Chakraborty and Mukherjee, 2009; Jana et al., 2017; Mtisi and Gwenzi, 2019; Patel et al., 2016; Radić et al., 2018; Singh et al., 2016).

6.3. Other toxicity studies

Although phytotoxicity tests are more commonly used in evaluating the toxicity of coal ash, tests have also been conducted on invertebrate species, particularly earthworms. Earthworms are generally considered indicators of soil health as they are responsible for nutrient cycling, plant growth and water movement (Shi et al., 2017). Fly ash induced oxidative stress, destabilization of lysosomal membranes and DNA damage in earthworms even at low concentrations of fly ash leachate (Manerikar et al., 2008; Markad et al., 2012).

In addition to phytotoxicity and toxicity to invertebrates, cells of various organisms (Medunić et al., 2016; Sambandam et al., 2015), including human cells, were also used. Both cyto- and genotoxicity of coal ash was observed in VT9 cells (Chinese hamster lung fibroblasts) (León-Mejía et al., 2016; Matzenbacher et al., 2017) and human peripheral blood mononuclear cells (Table 1) (Dwivedi et al., 2012).

6.4. Factors affecting toxicity of coal ash

All the above studies have shown that coal ash has adverse effects on various organisms at all stages of growth. Toxicity tests are useful before coal ash is recycled or disposed of. However, no specific pathways of contaminant effects can be derived from these analyzes. The main obstacle is that observed effects may be caused by multiple factors that are difficult to identify, such as soil properties, resource availability, and mixture of elements (Gupta et al., 2019).

Soil properties alter the mobility of the elements and thus the available concentration of the elements discussed in the first part of this article. This is particularly important for ash that is covered with soil or ash that is affected by pedogenesis. Physiochemical properties, such as cation exchange capacity, clay content, and exchangeable Ca and Mg cations, may have a greater influence on the uptake of metals by earthworms than pH (Bustos et al., 2015; Delgadillo et al., 2017). In addition, physiochemical properties may play a greater role in toxicity than the metals present in the contaminated soil. For example, earthworms may be more sensitive to high electrical conductivity caused by salinity than to elevated Cu (Bustos et al., 2015). Therefore, physiochemical parameters should be measured in toxicity studies.

In addition, aging of the waste alters the intrinsic properties of the ash and thus its toxicity. Current Technosols, soils developed on man-made surfaces, including coal ash, could be useful for predicting the long-term toxicity potential of coal ash. An old landfill in Croatia caused genotoxic and cytotoxic effects in *Allium ascalonicum* roots 40 years after its disposal (Fiket et al., 2020). Several resistant plants are also likely to be established on Technosols. Therefore, root exudates could alter the microchemistry of the landfill and its toxic potential. Interestingly, one study showed that root extracts from plants growing abundantly and spontaneously in the environment of a thermal power plant caused cytotoxicity, genotoxicity, and mutagenicity in *Allium cepa*, a common bioassay species (Artico et al., 2020).

Most standards, including remediation standards, have been established for single elements without considering possible interactions between elements (Jadhav et al., 2007). However, a mixture of elements at low doses could cause more harm than elevated levels of one element (Cui et al., 2005; Jadhav et al., 2007; Mortazavi et al., 2016; Wu et al., 2016). This could be due to a synergistic interaction of elements, but also to other factors, such as food shortages. Food scarcity is common in polluted environments and affects the growth, reproduction and sensitivity of the organism to pollutants (Stevenson et al., 2017). However, most standard toxicity tests recommend food ratios hundreds of times higher than those found in landfills, potentially underestimating the toxic potential of coal ash (Mathews et al., 2020). In addition, different species have different sensitivities to contaminants based on their epidermal surfaces (Lanno et al., 2019; Van Gestel et al., 2012) or trophic level (Cervantes-Ramírez et al., 2018; Chakraborty et al., 2009; Stevenson et al., 2017), underscoring the importance of using multi-species toxicity tests.

It is evident that many different factors affect toxicity, from pollutants and physiochemical properties of ash to food scarcity usually present in polluted environments. Identifying the exact cause of toxicity from such complex material is often difficult, as it is likely that a mixture of factors caused it. Besides that, many toxicity studies seriously lack geochemical analysis. For example, several studies in Table 1 did not compare the concentrations of measured contaminants in ash to controls or background values, and only relatively analysed the concentrations – ordering the elements from highest to lowest concentrations (e.g. Cu > Zn > Co). However, such analysis is useless, as each element has its own background concentration, and some elements are potentially toxic at relatively low concentrations (e.g. Se at > 0.5 mg kg⁻¹), while such concentration of Zn is considered deficient.

6.5. Exposure to naturally occurring radioactive materials (NORM)

One of the potential health problems associated with coal ash disposal is the inhalation of CCR particles originating from coals with high uranium content (Galhardi et al., 2017). Most coals have uranium concentration of 3 ppm, but some coals are enriched in U with concentrations reaching several hundred ppm (Lauer et al., 2015, 2017). CCRs generated from these coals are even more enriched in U, and consequently in naturally occurring radioactive materials (NORM) - ²³⁸U and ²³²Th and their decay products, as well as ⁴K (Coles et al., 2002). Due to the ionizing radiation emitted by NORM, long-term

Table 1

Selected papers on the toxicity of coal ash, with details of the type of test used, the contaminants measured, and the adverse effects observed. Most studies used different organisms. Although that complicates the comparison of the data, it highlights that coal ash negatively impacts different species.

Reference	Type of test	Organism used	Material used	Measured contaminants in material	Elevated contaminants in material	Effects observed
Chakraborty et al. (2009)	Cytotoxicity (<i>Allium</i> test) Genotoxicity (comet assay)	<i>Allium cepa</i> L. (onion)	fly ash	Zn, Pb, Cu, Ni, Co, Mn, Cr	did not compare it to control/background	dose-dependent inhibition of root growth and mitotic indices, binucleated cells and DNA strand breaks
Chakraborty et al. (2009)	Mutagenicity assay (The Ames Salmonella) Genotoxicity (alkaline comet assay)	<i>Salmonella typhimurium</i> human blood cells <i>Nicotiana</i> sp	fly ash leachate (pH = 7.5)	Na, Si, K, Ca, Mg, Fe, Mn, Zn, Cd, Ni, Cu, Pb, Al, As, Fe, SO ₄	Na, Si, K, Ca, Mg, Fe, Mn, Zn, SO ₄	dose-dependent increases in DNA damage in whole blood cells, lymphocytes, and <i>Nicotiana</i> plants
Markad et al. (2012)	The neutral red retention assay Genotoxicity (comet assay)	<i>Dichogaster curgensis</i> (earthworm)	fly ash (pH = 8.02)	PAHs, PCBs, Si, Ca, P, Na, Mg, Fe, Al, Mn, Pb, As, Zn, Ni, Cd, Cr, Cu	did not compare it to standards, however Cd, Pb, As, and Cr bioaccumulated	dose and time dependent increase in antioxidant enzymes and lysosomal membrane destabilization DNA damage and DNA-protein crosslinks in coelomocytes mitochondrial membrane damage, DNA and chromosomal breakage
Dwivedi et al. (2012)	Genotoxicity (comet, cytokinesis blocked micronucleus, and alkaline unwinding assays)	human peripheral blood mononuclear cells	fly ash nanoparticles	Cr, Cu, Fe, Ni	did not compare it to control/background	
Sambandam et al., 2015	Cytotoxicity assay	Chang liver, HS294T & LL29 cell lines	coal fly ash nanoparticles	Al, C, Ca, Fe, Mg, Mo, Na, S, Si, Ar, Ba, Cd, Cr, K, Mn, Nd, Pb, Rh, Se, Sr, Ti, V, Zn	did not compare it to control/background	dose-dependent inhibition of cellular metabolism, induced ROS, decrease in the total intracellular glutathione, and DNA laddering
Singh et al. (2016)	Cytotoxicity assay	<i>Oryza sativa</i> L. (rice)	Fly-ash augmented soil (50% of FA) (pH = 8.0)	Mn, Co, Ni, Cu, Zn, Se, Cr, As, Cd, Hg and Pb	higher than in garden soil, Cd, Cr, Pb, As bioaccumulated	decrease in the root, shoot and panicle length, increased lipid peroxidation and activities of antioxidant enzymes
León-Mejía et al., 2016	Cytotoxicity assay Genotoxicity (alkaline and modified comet assay)	lung fibroblast cell line (V79)	coal and fly ash	PAHs, As, Co, Cr, Fe, Hg, Mn, Ni, Pb, V, Zn	did not compare it to control/background	cytotoxic effects (apoptosis and necrosis) and chromosomal instability (nucleoplasmic bridges, nuclear buds, and micronucleus formation), primary DNA lesions DNA and oxidative damage
Matzenbacher et al. (2017)	Mutagenicity assay (The Ames Salmonella) Genotoxicity (alkaline comet assay)	lung fibroblast cell line (V79)	coal dust, fly and bottom ash	PAHs, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn	did not compare it to control/background	
Jana et al. (2017)	Cytotoxicity (<i>Allium</i> test) Genotoxicity (comet assay)	<i>Allium cepa</i> L. (onion)	fly ash leachate (pH = 8.5)	Co, Cr, Cu, Mn, Cd, Ni, Pb, Zn	did not compare it to control/background	dose-dependent increase in frequency of chromosome aberrations and binucleate cells dose-dependent increase in DNA damage and antioxidant enzymes
Artico et al. (2018)	Cytotoxicity (<i>Allium</i> test)	<i>Allium cepa</i> L. (onion)	contaminated surface water near TPP	/	/	inhibition of mitotic indices and occurrence of abnormal seedlings
Radić et al. (2018)	Cytotoxicity (<i>Lemna</i> bioassay)	<i>Lemna minor</i> L.	soils around TPP	PAHs, Fe, Pb, Cd, Zn, Cu, Ni, Al, Co, Cr, As, Mn, Sr, Ba	naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene and fluoranthene, Fe, Pb, Cd, Zn, Cu, Ni, Al, Co, Sr, Ba	growth inhibition, impaired antioxidant levels
Mtisi & Gwenzi (2019)	Phytotoxicity (germination, radicle elongation, and pot bioassay)	<i>Lactuca sativa</i> L. (lettuce)	fly ash augmented soil (pH = 11.1)	Cu, Ni, Mn, Pb, Zn, Fe	All below US EPA limit for (bio)solids for land application	no effect on germination, hormetic effects on radicle elongation, dose-dependent reduced lettuce growth and edible biomass yield
Fiket et al. (2020)	Cytotoxicity (<i>Allium</i> test) Genotoxicity (comet assay)	<i>Allium ascalonicum</i> L. (shallot)	Leachate from coal mine contaminated soil and old coal ash deposit	Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sc, Se, Sr, Ti, Tl, V, Zn	Ba, Co, Cr, Cu, Mo, Ni, Pb, Se, V, Zn	mitotic spindle failure, chromosome stickiness, increased level of lipid peroxidation, DNA damage
Artico et al. (2020)	Cytotoxicity (<i>Allium</i> test)	<i>Allium cepa</i> L. (onion)	extracts from <i>Eragrostis plana</i> growing near TPP	/	/	abnormal seedlings, reduced cell division, chromosomal alterations, micronucleus formation

exposure to radiation from these CCR increases the risk of developing cancer (Gilbert, 2009).

At the forefront of NORM radiation are workers at coal-fired power plants (CTPP), so studies of worker exposure to radiation are important (Turhan et al., 2010). Besides radionuclide content (in Bq kg⁻¹), several different indices are often calculated to assess the possible exposure risk, such as the annual effective dose, the radium equivalent activity, the external hazardous index, and the gamma index. These indices are then compared to typical values provided by U.N. Scientific Committee on the Effects of Atomic Radiation (UNSCEAR, 2000) or to control soils.

Some studies found these indices and radionuclide content in coal ash ponds and near-by soils to be lower or equal to typical values by UNSCEAR or local soils (Orešćanin et al., 2012; Tso and Leung, 1996; Turhan et al., 2010), while some found higher values (Habib et al., 2019; Orešćanin et al., 2006; Parial et al., 2016), pointing to the difference in coal burned and possible radiation hazard. Most of studies that found lower values of calculated indices considered ash generated from low U coal or did not know what type of coal was burned (Orešćanin et al., 2012).

Recent systematic studies on NORM content in U-rich Chinese and U. S. coals and associated coal ashes highlighted the scarcity of data from coals and coal ash landfills originated from U-rich coals (Lauer et al., 2015, 2017). Some Chinese coal ash analysed in the study contained radiation 43 times higher than the maximum safe limit set for residential building materials by the UNSCEAR (Lauer et al., 2017). Considering that these ashes could not be used in residential building materials, it can also be speculated that particles originating from such landfills are also not safe for residents or workers, which remains to be investigated.

It was also proposed that ²²⁶Ra and ²²⁸Ra activities could be estimated from U and Th content and ash yield of parent coals (Lauer et al., 2015, 2017), which could speed up radiological assessment of old landfills. However, type of coal used in some historic CCR landfills is unknown or it contains CCRs from different coals (Orešćanin et al., 2006), which limits the prediction and relies solely on measurements.

7. Future directions

7.1. Global reports and the development of new detection methods

Although it is evident that coal ash is a global pollutant, there is still a lack of data on coal ash generation, coal ash accidents and groundwater pollution in different countries. That is highlighted by [Supplementary Table S1](#), where such data for 6 out of the 8 largest coal-consuming countries is mostly missing. Although it is possible that such accidents have not occurred in these countries, we assume that they are simply not reported or are not available in English. This point is supported by recent initiatives in India and the US, which summarized coal ash accidents and groundwater pollution in these countries, respectively. Prior to these reports, these incidents would not be widely known and coal ash impact would be underestimated (Healthy Energy Initiative, 2020; Russ and Bernhardt, 2019; Sierra Club, 2018). Therefore, compiling such data for other countries is needed.

Besides global reports, 'low-level' detection methods for coal fly ash in the environment have yet to be developed. Recently, a combination of trace elements, Ra nuclides and Pb stable isotopes with physical observation has been proposed to detect trace levels of coal fly ash in soils (present at < 10%) (Wang et al., 2021). This highlights the need for the use and the development of new detection tools to properly assess coal ash pollution.

7.2. Recovery of critical elements from CCR

One of the promising approaches to reduce the environmental impact of industry's historic waste is the recovery of critical materials. Critical materials are economically important but carry a high supply risk. In 2020, the EU has labeled 30 raw materials as critical, including

REEs, Platinum Group Metals, phosphorus and various metals (Sb, Be, Bi, Co, Ga, Ge, Hf, In, Mg, Nb, Sc, Ta, W, V, Li, Ti, Sr) (European Commission, 2020).

Recovery of many critical metals from coal ash is feasible, as coal ash can have critical metal concentrations comparable to the respectful ores (Stoy et al., 2021). For example, ores with a germanium content of 0.001% (i.e. 10 g/t) are exploitable, and the Ge content in coal ash can reach 1% (Zhang and Xu, 2016).

The recovery of Ga, Ge, Sc, U, W, V, Li, and REE from coal ash has been explored in recent years (Huang et al., 2020; Masoum et al., 2021; Smith et al., 2019; Stoy et al., 2021; Xu et al., 2021; Yellishetty et al., 2017; Zhang et al., 2021; Zhao et al., 2019). Recovery of gallium (Ga) and germanium (Ge) is perhaps the most promising, since both Ga and Ge have already been successfully extracted from Chinese coals on an industrial scale (Zhao et al., 2019), and several pilot plants have been built to extract both Ge and Ga from CCR (Arroyo et al., 2009, 2015; Ding et al., 2017).

In addition to Ge and Ga, recovery of rare earth elements (REE) is also promising due to their high content in coal ash. The most recent estimate for the total annual value of REEs from U.S. coal fly ash are \$4.3 billion, based on 2013 prices (Taggart et al., 2016). However, the estimate excluded U.S. historical ash, so the value is likely higher. However, technologies for the extraction and recovery of REEs from coal ash are not yet well developed (Smith et al., 2019).

7.2.1. The search for a method

The key obstacle in recovering critical metals from CCR is the development of both sustainable and selective methods to extract the selected element. To date, various methods have been used to recover Ga, Ge and REE, most of which are hydrometallurgical (Kamran Haghighi et al., 2018). Although high in recovery, many hydrometallurgical methods produce large amounts of waste liquid and residues (Binnemans et al., 2015; Zhang and Xu, 2016). Therefore, various other methods have been proposed. For example, vacuum metallurgical method for Ge recovery (Zhang and Xu, 2016) and recyclable ionic liquid for REE recovery (Stoy et al., 2021).

Most methods have primarily addressed coal fly ash, but bottom ash could also be a promising source of critical elements (Valentim et al., 2019), as could wastewater (Smith et al., 2019). In addition, most research has been on unweathered fly ash and there is scarcity of data for weathered coal fly ash. Recently, weathered coal fly ash showed slightly higher REE leaching efficiency than unweathered coal fly ash, which is a noteworthy finding considering that currently millions of tons off landfilled ash serve no purpose (Stoy et al., 2021).

Nonetheless, the search for a cost-effective and highly efficient, as well as environmentally friendly, method for extracting metals remains a frontline in this research field.

8. Conclusions

The burning of coal has left enormous pollution in the form of ash dumps that continue to impact people and the environment decades after disposal. Numerous lawsuits, groundwater contamination, deformities in aquatic organisms, and behavioral disorders in children highlight the negative impacts of coal ash, while the total number, condition, and structural safety of landfills are still unknown. All of this particularly emphasizes the need to pay attention to closed landfills, as they may not be included in monitoring programs, as seen in 'Coal Ash Rule'.

A number of existing methodologies for assessing the impacts of such landfills, as well as different approaches, show that efforts are underway to manage the consequences of coal ash disposal. However, further research is needed to achieve sustainable management of these landfills, including standardization of methods, application of multiparametric approaches and advanced statistical techniques, as well as the development of detection methods for trace levels of coal ash in the

environment.

Existing standards for disposal and remediation may also need to be re-evaluated, as many different factors influence the leaching and toxicity of coal ash. Only the combination of toxicological and other geochemical analyzes will ensure an adequate understanding of the toxic potential of coal ash in the coming decades.

Since recovery of elements is a one possible way of utilizing the historic waste, developing both selective and environmentally friendly method for extraction of critical elements is out of the most importance.

Credit author statement

Marija Petrović; : Conceptualization, Investigation, Validation, Visualisation, Writing – original draft. **Željka Fiket**: Supervision, Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2022.134410>.

References

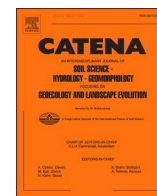
- Agnieszka, B., Tomasz, C., Jerzy, W., 2014. Chemical properties and toxicity of soils contaminated by mining activity. *Ecotoxicology* 23, 1234–1244. <https://doi.org/10.1007/s10646-014-1266-y>.
- Ahamad, A., Raju, N.J., Madhav, S., Khan, A.H., 2020. Trace elements contamination in groundwater and associated human health risk in the industrial region of southern Sonbhadra, Uttar Pradesh, India. *Environ. Geochem. Health* 7. <https://doi.org/10.1007/s10653-020-00582-7>.
- Aitken, R.L., Bell, L.C., 1985. Plant uptake and phytotoxicity of boron in Australian fly ashes. *Plant Soil* 84, 245–257. <https://doi.org/10.1007/BF02143187>.
- Arroyo, F., Fernández-Pereira, C., Bermejo, P., 2015. Demonstration plant equipment design and scale-up from pilot plant of a leaching and solvent extraction process. *Minerals* 5, 298–313. <https://doi.org/10.3390/min5020298>.
- Arroyo, F., Fernández-Pereira, C., Olivares, J., Coca, P., 2009. Hydrometallurgical recovery of germanium from coal gasification fly ash: pilot plant scale evaluation. *Ind. Eng. Chem. Res.* 48, 3573–3579. <https://doi.org/10.1021/ie800730h>.
- Artico, L.L., Kömmling, G., Clarindo, W.R., Menezes, A.P.S., 2020. Cytotoxic, genotoxic, mutagenic, and phytotoxic effects of the extracts from *eragrostis plana* nees, 1841 (poaceae), grown in a coal-contaminated region. *Water Air Soil Pollut.* 231, 1–9. <https://doi.org/10.1007/s11270-020-4457-6>.
- Artico, L.L., Kömmling, G., Migita, N.A., Menezes, A.P.S., 2018. Toxicological effects of surface water exposed to coal contamination on the test system *Allium cepa*. *Water Air Soil Pollut.* 229. <https://doi.org/10.1007/s11270-018-3904-0>.
- Baba, A., Kaya, A., 2004. Leaching characteristics of solid wastes from thermal power plants of western Turkey and comparison of toxicity methodologies. *J. Environ. Manag.* 73, 199–207. <https://doi.org/10.1016/j.jenvman.2004.06.005>.
- Backman, B., Bodiš, D., Lahermo, P., Rapant, S., Tarvainen, T., 1998. Application of a groundwater contamination index in Finland and Slovakia. *Environ. Geol.* 36, 55–64. <https://doi.org/10.1007/s002540050320>.
- Banks, M.K., Schultz, K.E., 2005. Comparison of plants for germination toxicity tests in petroleum-contaminated soils. *Water Air Soil Pollut.* 167, 211–219. <https://doi.org/10.1007/s11270-005-8553-4>.
- Baun, D.L., Christensen, T.H., 2004. Speciation of heavy metals in landfill leachate: a review. *Waste Manag. Res.* 22, 3–23. <https://doi.org/10.1177/0734242X04042146>.
- Benalcázar, P., Krawczyk, M., Kamiński, J., 2017. Forecasting global coal consumption: an artificial neural network approach. *Gospod. Surowcami Miner./Miner. Resour. Manag.* 33, 29–44. <https://doi.org/10.1515/gospo-2017-0042>.
- Bhuiyan, M.A.H., Islam, M.A., Dampare, S.B., Parvez, L., Suzuki, S., 2010. Evaluation of hazardous metal pollution in irrigation and drinking water systems in the vicinity of a coal mine area of northwestern Bangladesh. *J. Hazard Mater.* 179, 1065–1077. <https://doi.org/10.1016/j.jhazmat.2010.03.114>.
- Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Pontikes, Y., 2015. Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review. *J. Clean. Prod.* 99, 17–38. <https://doi.org/10.1016/j.jclepro.2015.02.089>.
- Binotto, R.B., Teixeira, E.C., Sanchez, J.C.D., Migliavacca, D., Nanni, A.S., 2000. Environmental assessment: contamination of phreatic aquifer in areas impacted by waste from coal processing activities. *Fuel* 79, 1547–1560. [https://doi.org/10.1016/S0016-2361\(99\)00291-4](https://doi.org/10.1016/S0016-2361(99)00291-4).
- BP, 2020. Statistical Review of World Energy 2020 [WWW Document]. URL, 12.4.20. <https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html>.
- Brandt, J.E., Bernhardt, E.S., Dwyer, G.S., Di Giulio, R.T., 2017. Selenium ecotoxicology in freshwater lakes receiving coal combustion residual effluents: a North Carolina example. *Environ. Sci. Technol.* 51, 2418–2426. <https://doi.org/10.1021/acs.est.6b05353>.
- Brandt, J.E., Lauer, N.E., Vengosh, A., Bernhardt, E.S., Di Giulio, R.T., 2018. Strontium isotope ratios in fish otoliths as biogenic tracers of coal combustion residual inputs to freshwater ecosystems. *Environ. Sci. Technol. Lett.* 5, 718–723. <https://doi.org/10.1021/acs.estlett.8b00477>.
- Bruggers, J., 2018. A Coal Ash Spill Made These Workers Sick. Now, They're Fighting for Compensation [WWW Document]. *Insid. Clim. News*. URL, 5.2.20. <https://insideclimatenews.org/>.
- Bryan, A.L., Hopkins, W.A., Parikh, J.H., Jackson, B.P., Unrine, J.M., 2012. Coal fly ash basins as an attractive nuisance to birds: parental provisioning exposes nestlings to harmful trace elements. *Environ. Pollut.* 161, 170–177. <https://doi.org/10.1016/j.envpol.2011.10.021>.
- Bustos, V., Mondaca, P., Verdejo, J., Sauvé, S., Gaete, H., Celis-Diez, J.L., Neaman, A., 2015. Thresholds of arsenic toxicity to *Eisenia fetida* in field-collected agricultural soils exposed to copper mining activities in Chile. *Ecotoxicol. Environ. Saf.* 122, 448–454. <https://doi.org/10.1016/j.ecoenv.2015.09.009>.
- Campbell, C.E., Pearson, B.N., Frost, C.D., 2008. Strontium isotopes as indicators of aquifer communication in an area of coal-bed natural gas production, Powder River Basin, Wyoming and Montana. *Rocky Mt. Geol.* 43, 171–197. <https://doi.org/10.2113/gsrocky.43.2.171>.
- Cao, S., Zhou, C., Pan, J., Liu, C., Tang, M., Ji, W., Hu, T., Zhang, N., 2018. Study on influence factors of leaching of rare earth elements from coal fly ash. *Energy Fuel* 32, 8000–8005. <https://doi.org/10.1021/acs.energyfuels.8b01316>.
- Cattaneo, A., Ascoli, A., Comoli, P., Manca, M., 1998. Organisms' response in a chronically polluted lake supports hypothesized link between stress and size. *Limnol. Oceanogr.* 43, 1938–1943.
- Çelik, A., Ünyayar, S., Çekiç, F.Ö., Güzel, A., 2008. Micronucleus frequency and lipid peroxidation in *Allium sativum* root tip cells treated with gibberellic acid and cadmium. *Cell Biol. Toxicol.* 24, 159–164. <https://doi.org/10.1007/s10565-007-9025-y>.
- Cervantes-Ramírez, L.T., Ramírez-López, M., Mussali-Galante, P., Ortiz-Hernández, M.L., Sánchez-Salinas, E., Tovar-Sánchez, E., 2018. Heavy metal biomagnification and genotoxic damage in two trophic levels exposed to mine tailings: a network theory approach. *Rev. Chil. Hist. Nat.* 91, 1–13. <https://doi.org/10.1186/s40693-018-0076-7>.
- Chakraborty, R., Mukherjee, A., 2009. Mutagenicity and genotoxicity of coal fly ash water leachate. *Ecotoxicol. Environ. Saf.* 72, 838–842. <https://doi.org/10.1016/j.ecoenv.2008.09.023>.
- Chakraborty, R., Mukherjee, A.K., Mukherjee, A., 2009. Evaluation of genotoxicity of coal fly ash in *Allium cepa* root cells by combining comet assay with the Allium test. *Environ. Monit. Assess.* 153, 351–357. <https://doi.org/10.1007/s10661-008-0361-z>.
- Chandler, J., Taylor Eighmy, T., Hartlen, J., Hjelm, O., Kosson, D., Sawel, S., van der Sloot, H., Vehlou, J., 1997a. Chemical aspects of leaching. *Stud. Environ. Sci.* 67, 507–578. <https://doi.org/10.12681/eadd/1834>.
- Chandler, J., Taylor Eighmy, T., Hartlen, J., Hjelm, O., Kosson, D., Sawel, S., van der Sloot, H., Vehlou, J., 1997b. Physical aspects of leaching. *Stud. Environ. Sci.* 67, 483–505.
- Chandler, J., Taylor Eighmy, T., Hartlen, J., Hjelm, O., Kosson, D., Sawel, S., van der Sloot, H., Vehlou, J., 1997c. Leaching modelling. *Stud. Environ. Sci.* 67, 607–636. <https://doi.org/10.1017/CBO9781107415324.004>.
- Chaturvedi, A., Bhattacharjee, S., Mondal, G.C., Kumar, V., Singh, P.K., Singh, A.K., 2019. Exploring new correlation between hazard index and heavy metal pollution index in groundwater. *Ecol. Indic.* 97, 239–246. <https://doi.org/10.1016/j.ecolind.2018.10.023>.
- Chmielewski, A.G., Licki, J., 2006. Stable isotopes of sulphur. *Environ. Protect. Eng.* 32, 1–6.
- Chu, L.M., 2008. Natural revegetation of coal fly ash in a highly saline disposal lagoon in Hong Kong. *Appl. Veg. Sci.* 11, 297–306. <https://doi.org/10.3170/2008.7-18427>.
- Civeira, M.S., Ramos, C.G., Oliveira, M.L.S., Kautzmann, R.M., Taffarel, S.R., Teixeira, E. C., Silva, L.F.O., 2016. Nano-mineralogy of suspended sediment during the beginning of coal rejects spill. *Chemosphere* 145, 142–147. <https://doi.org/10.1016/j.chemosphere.2015.11.059>.
- Coles, D.G., Ragaini, R.C., Ondov, J.M., 2002. Behavior of natural radionuclides in western coal-fired power plants. *Environ. Sci. Technol.* 12, 442–446. <https://doi.org/10.1021/es60140a007>.
- Coussy, S., Grangeon, S., Bataillard, P., Khodja, H., Maubec, N., Faure, P., Schwartz, C., Dagois, R., 2017. Evolution of iron minerals in a 100 years-old Technosol. *Consequences on Zn mobility. Geoderma* 290, 19–32. <https://doi.org/10.1016/j.geoderma.2016.12.009>.
- Crisan, M., Bakos, M.V., 2008. Groundwater monitoring in the proximity of an ash storage pit. In: BALWOIS 2008, Ohrid, Republic of Macedonia.

- Cui, Y., Zhu, Y.G., Zhai, R., Huang, Y., Qiu, Y., Liang, J., 2005. Exposure to metal mixtures and human health impacts in a contaminated area in Nanning, China. *Environ. Int.* 31, 784–790. <https://doi.org/10.1016/j.envint.2005.05.025>.
- da Silva, E.B., Li, S., de Oliveira, L.M., Gress, J., Dong, X., Wilkie, A.C., Townsend, T., Ma, L.Q., 2018. Metal leachability from coal combustion residuals under different pHs and liquid/solid ratios. *J. Hazard Mater.* 341, 66–74. <https://doi.org/10.1016/j.jhazmat.2017.07.010>.
- Davidson, G.R., Bassett, R.L., 1993. Application of boron isotopes for identifying contaminants such as fly ash leachate in groundwater. *Environ. Sci. Technol.* 27, 172–176. <https://doi.org/10.1021/es00038a020>.
- Debels, P., Figueroa, R., Urrutia, R., Barra, R., Niell, X., 2005. Evaluation of water quality in the Chillán River (Central Chile) using physicochemical parameters and a modified Water Quality Index. *Environ. Monit. Assess.* 110, 301–322. <https://doi.org/10.1007/s10661-005-8064-1>.
- Delgadillo, V., Verdejo, J., Mondaca, P., Verdugo, G., Gaete, H., Hodson, M.E., Neaman, A., 2017. Proposed modification to avoidance test with *Eisenia fetida* to assess metal toxicity in agricultural soils affected by mining activities. *Ecotoxicol. Environ. Saf.* 140, 230–234. <https://doi.org/10.1016/j.ecoenv.2017.02.038>.
- Ding, J., Ma, S., Shen, S., Xie, Z., Zheng, S., Zhang, Y., 2017. Research and industrialization progress of recovering alumina from fly ash: a concise review. *Waste Manag* 60, 375–387. <https://doi.org/10.1016/j.wasman.2016.06.009>.
- Dwivedi, S., Saquib, Q., Al-Khedhairi, A.A., Ali, A.Y.S., Musarat, J., 2012. Characterization of coal fly ash nanoparticles and induced oxidative DNA damage in human peripheral blood mononuclear cells. *Sci. Total Environ.* 437, 331–338. <https://doi.org/10.1016/j.scitotenv.2012.08.004>.
- Earthjustice, 2021. CCR Rule compliance [WWW Document]. URL 4.20.21. <https://docs.google.com/spreadsheets/d/1SF6KTLrFSKpJJaKQyN6ZKoYp6k6ZHqGVODCAGi7mg/edit#gid=0>.
- Edet, A.E., Offiong, O.E., 2002. Evaluation of water quality pollution indices for heavy metal contamination monitoring. A study case from Akpabuyo-Odukpani area, Lower Cross River Basin (southeastern Nigeria). *Geojournal* 57, 295–304. <https://doi.org/10.1023/B:GEJO.0000007250.92458.de>.
- El-Mogazi, D., Lisk, D.J., Weinstein, L.H., 1988. A review of physical, chemical, and biological properties of fly ash and effects on agricultural ecosystems. *Sci. Total Environ.* 74, 1–37.
- European Commission, 2020. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions: Critical Raw Materials Resilience: Charting a Path towards Greater Security and Sustainability [WWW Document]. COM/2020/474 Final. URL <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52020DC0474>. (Accessed 15 November 2021).
- Fiket, Ž., Medunić, G., Vidaković-Cifrek, Ž., Jezidžić, P., Cvjetko, P., 2020. Effect of coal mining activities and related industry on composition, cytotoxicity and genotoxicity of surrounding soils. *Environ. Sci. Pollut. Res.* 27, 6613–6627. <https://doi.org/10.1007/s11356-019-07396-w>.
- Fleming, L.N., Abinteh, H.N., Inyang, H.I., 1996. Leachant pH effects on the leachability of metals from fly ash. *Soil Sediment Contam* 5, 53–59. <https://doi.org/10.1080/15320389609383512>.
- Friedlingstein, P., et al., 2020. Global Carbon Budget 2020. *Earth Syst. Sci. Data* 12, 3269–3340. <https://doi.org/10.5194/essd-12-3269-2020>.
- Fu, B., Hower, J.C., Dai, S., Mardon, S.M., Liu, G., 2018. Determination of chemical speciation of arsenic and selenium in high-ash coal combustion ash by X-ray photoelectron spectroscopy: examples from a Kentucky stoker ash. *ACS Omega* 3, 17637–17645. <https://doi.org/10.1021/acsomega.8b02929>.
- Galhardi, J.A., García-Tenorio, R., Díaz Francés, I., Bonotto, D.M., Marcelli, M.P., 2017. Natural radionuclides in lichens, mosses and ferns in a thermal power plant and in an adjacent coal mine area in southern Brazil. *J. Environ. Radioact.* 167, 43–53. <https://doi.org/10.1016/j.jenvrad.2016.11.009>.
- Garrabrants, A., Kosson, D., DeLapp, R., Karier, P., Seignette, P., van der Sloot, H., Stefanski, L., Baldwin, M., 2012. Interlaboratory Validation of the Leaching Environmental Assessment Framework (LEAF) Method 1314 and Method 1315. U.S. Environmental Protection Agency, Washington, DC. EPA/600/R/12/623Garrabrants.
- Garrabrants, A.C., Kosson, D.S., DeLapp, R., van der Sloot, H.A., 2014. Effect of coal combustion fly ash use in concrete on the mass transport release of constituents of potential concern. *Chemosphere* 103, 131–139. <https://doi.org/10.1016/j.chemosphere.2013.11.048>.
- Garza-Mourino, G., Silva-Briano, M., Nandini, S., Sarma, S.S.S., Castellanos-Páez, M.E., 2005. Morphological and morphometrical variations of selected rotifer species in response to predation: a seasonal study of selected brachionid species from Lake Xochimilco (Mexico). *Hydrobiologia* 546, 169–179. <https://doi.org/10.1007/s10750-005-4114-5>.
- Ghazali, N., Muthusamy, K., Wan Ahmad, S., 2019. Utilization of fly ash in construction. *IOP Conf. Ser. Mater. Sci. Eng.* 601, 12–23. <https://doi.org/10.1088/1757-899X/601/1/012023>.
- Gilbert, E.S., 2009. International Journal of Radiation Biology Ionising radiation and cancer risks: what have we learned from epidemiology? Ionising radiation and cancer risks: what have we learned from epidemiology? *Int. J. Radiat. Biol.* 85, 467–482. <https://doi.org/10.1080/09553000902883836>.
- Global Monitor Energy, Sierra Club, CREA, GreenID, Climate Risk Horizons, GreenID, Ecosfer, 2021. Boom and Bust 2021: Tracking the Global Coal Plant Pipeline [WWW Document]. Glob. Coal Plant Tracker. URL <https://globalenergymonitor.org/projects/global-coal-plant-tracker/>.
- Gschwend, P.M., Backhus, D.A., MacFarlane, J.K., Page, A.L., 1990. Mobilization of colloids in groundwater due to infiltration of water at a coal ash disposal site. *J. Contam. Hydrol.* 6, 307–320. [https://doi.org/10.1016/0169-7722\(90\)90031-B](https://doi.org/10.1016/0169-7722(90)90031-B).
- Gupta, N., Yadav, K.K., Kumar, V., Kumar, S., Chadd, R.P., Kumar, A., 2019. Trace elements in soil-vegetables interface: translocation, bioaccumulation, toxicity and amelioration - a review. *Sci. Total Environ.* 651, 2927–2942. <https://doi.org/10.1016/j.scitotenv.2018.10.047>.
- Habib, M.A., Basuki, T., Miyashita, S., Bekeles, W., Nakashima, S., Tachato, K., Khan, R., Majlis, A.B.K., Phoungthong, K., 2019. Assessment of natural radioactivity in coals and coal combustion residues from a coal-based thermoelectric plant in Bangladesh: implications for radiological health hazards. *Environ. Monit. Assess.* 191 <https://doi.org/10.1007/s10661-018>.
- Haefner, R.J., 2001. Sulfur-isotope mixing model to trace leachate from pressurized fluidized bed combustion byproducts in an abandoned-coal-mine setting. *Fuel* 80, 829–836. [https://doi.org/10.1016/S0016-2361\(00\)00161-7](https://doi.org/10.1016/S0016-2361(00)00161-7).
- Harkness, J.S., Darrah, T.H., Moore, M.T., Whyte, C.J., Mathewson, P.D., Cook, T., Vengosh, A., 2017. Naturally occurring versus anthropogenic sources of elevated molybdenum in groundwater: evidence for geogenic contamination from southeast Wisconsin, United States. *Environ. Sci. Technol.* 51, 12190–12199. <https://doi.org/10.1021/acs.est.7b03716>.
- Harkness, J.S., Ruhl, L.S., Millot, R., Kloppman, W., Hower, J.C., Hsu-Kim, H., Vengosh, A., 2015. Lithium isotope fingerprints in coal and coal combustion residuals from the United States. *Procedia Earth Planet. Sci.* 13, 134–137. <https://doi.org/10.1016/j.proeps.2015.07.032>.
- Harkness, J.S., Sulkin, B., Vengosh, A., 2016. Evidence for coal ash ponds leaking in the southeastern United States. *Environ. Sci. Technol.* 50, 6583–6592. <https://doi.org/10.1021/acs.est.6b01727>.
- Harris, D., Heidrich, C., Feuerborn, J., 2019. Global aspects on coal combustion products. *VGB PowerTech* 25–33.
- Hassett, D.J., Pflughoeft-Hassett, D.F., Heebink, L.V., 2005. Leaching of CCBs: observations from over 25 years of research. *Fuel* 84, 1378–1383. <https://doi.org/10.1016/j.fuel.2004.10.016>.
- Hayes, S.M., Root, R.A., Perdrial, N., Maier, R.M., Chorover, J., 2014. Surficial weathering of iron sulfide mine tailings under semi-arid climate. *Geochim. Cosmochim. Acta* 141, 240–257. <https://doi.org/10.1016/j.gca.2014.05.030>.
- Hayes, S.M., White, S.A., Thompson, T.L., Maier, R.M., Chorover, J., 2009. Changes in lead and zinc lability during weathering-induced acidification of desert mine tailings: coupling chemical and micro-scale analyses. *Appl. Geochem.* 24, 2234–2245. <https://doi.org/10.1016/j.apgeochem.2009.09.010>.
- Healthy Energy Initiative, 2020. Coal Ash in India. A Compendium of Disasters [WWW Document]. URL. Environmental and Health Risks, 9.10.20. <http://www.healthyenergyinitiative.org/>.
- Hennebert, P., Avellan, A., Yan, J., Aguerre-Chariol, O., 2013. Experimental evidence of colloids and nanoparticles presence from 25 waste leachates. *Waste Manag* 33, 1870–1881. <https://doi.org/10.1016/j.wasman.2013.04.014>.
- Hopkins, W.A., Mendonça, M.T., Rowe, C.L., Congdon, J.D., 1998. Elevated trace element concentrations in southern toads, *Bufo terrestris*, exposed to coal combustion waste. *Arch. Environ. Contam. Toxicol.* 35, 325–329. <https://doi.org/10.1007/s002449900383>.
- Huang, J., Wang, Y., Zhou, G., Gu, Y., 2020. Exploring a promising technology for the extraction of gallium from coal fly ash. *Int. J. Coal Prep. Util.* 2699 <https://doi.org/10.1080/19392699.2020.1755662>.
- Hurst, R.W., Davis, T.E., Elseewi, A.A., 1991. Strontium isotopes as tracers of coal combustion residue in the environment. *Eng. Geol.* 30, 59–77. [https://doi.org/10.1016/0013-7952\(91\)90035-J](https://doi.org/10.1016/0013-7952(91)90035-J).
- International Energy Agency, 2020. Global energy review 2020 [WWW Document]. URL 8.29.20. <https://www.iea.org/reports/global-energy-review-2020>.
- Izquierdo, M., Querol, X., 2012. Leaching behaviour of elements from coal combustion fly ash: an overview. *Int. J. Coal Geol.* 94, 54–66. <https://doi.org/10.1016/j.coal.2011.10.006>.
- Jadhav, S.H., Sarkar, S.N., Patil, R.D., Tripathi, H.C., 2007. Effects of subchronic exposure via drinking water to a mixture of eight water-contaminating metals: a biochemical and histopathological study in male rats. *Arch. Environ. Contam. Toxicol.* 53, 667–677. <https://doi.org/10.1007/s00244-007-0031-0>.
- Jana, A., Ghosh, M., Sinha, S., Jothirajam, M., Nag, A., Mukherjee, A., 2017. Hazard identification of coal fly ash leachate using a battery of cyto-toxic and biochemical tests in *Allium cepa*. *Arch. Agron Soil Sci.* 63, 1443–1453. <https://doi.org/10.1080/03650340.2017.1280730>.
- Johnson, C.A., Kaeppli, M., Brandenberger, S., Ulrich, A., Baumann, W., 1999. Hydrological and geochemical factors affecting leachate composition in municipal solid waste incinerator bottom ash. *J. Contam. Hydrol.* 40, 239–259. [https://doi.org/10.1016/S0169-7722\(99\)00052-2](https://doi.org/10.1016/S0169-7722(99)00052-2).
- Jones, K.B., Ruppert, L.F., Swanson, S.M., 2012a. Leaching of elements from bottom ash, economizer fly ash, and fly ash from two coal-fired power plants. *Int. J. Coal Geol.* 94, 337–348. <https://doi.org/10.1016/j.coal.2011.10.007>.
- Jones, K.B., Ruppert, L.F., Swanson, S.M., 2012b. Leaching of elements from bottom ash, economizer fly ash, and fly ash from two coal-fired power plants. *Int. J. Coal Geol.* 94, 337–348. <https://doi.org/10.1016/j.coal.2011.10.007>.
- Jurković, L., Hiller, E., Veselská, V., Pet'Ková, K., 2011. Arsenic concentrations in soils impacted by dam failure of coal-ash pond in zemianske Kostolany, Slovakia. *Bull. Environ. Contam. Toxicol.* 86, 433–437. <https://doi.org/10.1007/s00128-011-0222-2>.
- Kadir, A.A., Hassan, M.I.H., Abdullah, M.M.A.B., 2016. Investigation on leaching behaviour of fly ash and bottom ash replacement in self-compacting concrete. *IOP Conf. Ser. Mater. Sci. Eng.* 133 <https://doi.org/10.1088/1757-899X/133/1/012036>.
- Kamran Haghighi, H., Irannajad, M., Fortuny, A., Sastre, A.M., 2018. Recovery of germanium from leach solutions of fly ash using solvent extraction with various extractants. *Hydrometallurgy* 175, 164–169. <https://doi.org/10.1016/j.hydromet.2017.11.006>.

- Kath, J., Dyer, F.J., 2017. Why groundwater matters: an introduction for policy-makers and managers. *Pol. Stud.* 38, 447–461. <https://doi.org/10.1080/01442872.2016.1188907>.
- Konstantinov, A., Novoselov, A., Konstantinova, E., Loiko, S., Kurasova, A., Minkina, T., 2020. Composition and properties of soils developed within the ash disposal areas originated from peat combustion (Tyumen, Russia). *Soil Sci. Annu.* 71, 3–14. <https://doi.org/10.37501/soilsa/121487>.
- Kosson, D.S., Garrabrants, A.C., DeLapp, R., van der Sloot, H.A., 2014. pH-dependent leaching of constituents of potential concern from concrete materials containing coal combustion fly ash. *Chemosphere* 103, 140–147. <https://doi.org/10.1016/j.chemosphere.2013.11.049>.
- Kosson, D.S., Garrabrants, A.C., Thorne, S.A., Fagnant, D., Helms, G., Connolly, K., Rodgers, M., 2019a. Leaching Environmental Assessment Framework (LEAF) How-To Guide. Appendices [WWW Document]. U.S. EPA. URL. 8.27.20. <https://www.epa.gov/hw-sw846/how-guide-leaching-environmental-assessment-framework>.
- Kosson, D.S., Garrabrants, A.C., Thorne, S.A., Fagnant, D., Helms, G., Connolly, K., Rodgers, M., 2019b. Leaching Environmental Assessment Framework (LEAF) How-To Guide [WWW Document]. U.S. EPA. URL. <https://www.epa.gov/hw-sw846/how-guide-leaching-environmental-assessment-framework>.
- Kosson, D.S., Van Der Sloot, H.A., Sanchez, F., Garrabrants, A.C., 2002. An integrated Framework for evaluating leaching in waste management and utilization of secondary materials. *Environ. Eng. Sci.* 19, 159–204. <https://doi.org/10.1089/109287502760079188>.
- Kosson, D.S., Sanchez, F., Kariher, P., Turner, L.H., DeLapp, R., Seignette, P.F.A.B., 2009. Characterization of Coal Combustion Residues from Electric Utilities - Leaching and Characterization Data. U.S. Environmental Protection Agency, Washington, DC. EPA/600/R-09/151.
- Kostić, O., Jarić, S., Gajić, G., Pavlović, D., Pavlović, M., Mitrović, M., Pavlović, P., 2018. Pedological properties and ecological implications of substrates derived 3 and 11 years after the revegetation of lignite fly ash disposal sites in Serbia. *Catena* 163, 78–88. <https://doi.org/10.1016/j.catena.2017.12.010>.
- Kravchenko, J., Lyster, H.K., 2018. The impact of coal-powered electrical plants and coal ash impoundments on the health of residential communities. *N. C. Med. J.* 79, 289–300.
- Kruger, R.A., 2017. Introduction to the utilization of coal combustion products. In: *Coal Combustion Products (CCPs): Characteristics, Utilization and Beneficiation*. Elsevier Ltd. <https://doi.org/10.1016/B978-0-08-100945-1.00004-6>.
- Lanno, R.P., Oorts, K., Smolders, E., Albanese, K., Chowdhury, M.J., 2019. Effects of soil properties on the toxicity and bioaccumulation of lead in soil invertebrates. *Environ. Toxicol. Chem.* 38, 1486–1494. <https://doi.org/10.1002/etc.4433>.
- Lauer, N., Vengosh, A., Dai, S., 2017. Naturally occurring radioactive materials in uranium-rich coals and associated coal combustion residues from China. *Environ. Sci. Technol.* 51, 13487–13493. <https://doi.org/10.1021/acs.est.7b03473>.
- Lauer, N.E., Hower, J.C., Hsu-Kim, H., Taggart, R.K., Vengosh, A., 2015. Naturally occurring radioactive materials in coals and coal combustion residuals in the United States. *Environ. Sci. Technol.* 49, 11227–11233. <https://doi.org/10.1021/acs.est.5b01978>.
- Lemly, A., 2015. Damage cost of the Dan River coal ash spill. *Environ. Pollut.* 197, 55–61. <https://doi.org/10.1016/j.envpol.2014.11.027>.
- Lemly, A.D., 2018a. Selenium poisoning of fish by coal ash wastewater in Herrington Lake, Kentucky. *Ecotoxicol. Environ. Saf.* 150, 49–53. <https://doi.org/10.1016/j.ecoenv.2017.12.013>.
- Lemly, A.D., 2018b. Selenium poisoning of fish by coal ash wastewater in Herrington Lake, Kentucky. *Ecotoxicol. Environ. Saf.* 150, 49–53. <https://doi.org/10.1016/j.ecoenv.2017.12.013>.
- Lemly, A.D., 2010. A White Paper on Environmental Damage from Coal Combustion Waste : the Cost of Poisoned Fish and Wildlife. Wake Forest University, Winston-Salem (NC). EPA-HQ-RCRA-2009-0640.
- León-Mejía, G., Silva, L.F.O., Civeira, M.S., Oliveira, M.L.S., Machado, M., Villela, I.V., Hartmann, A., Premoli, S., Corrêa, D.S., Da Silva, J., Henriques, J.A.P., 2016. Cytotoxicity and genotoxicity induced by coal and coal fly ash particles samples in V79 cells. *Environ. Sci. Pollut. Res.* 23, 24019–24031. <https://doi.org/10.1007/s11356-016-7623-z>.
- Li, J., Zhuang, X., Querol, X., Font, O., Moreno, N., 2018. A review on the applications of coal combustion products in China. *Int. Geol. Rev.* 60, 671–716. <https://doi.org/10.1080/00206814.2017.1309997>.
- Liu, G., Cai, Y., Hernandez, D., Schlau, J., Allen, M., 2016. Mobility and speciation of arsenic in the coal fly ashes collected from the Savannah River Site (SRS). *Chemosphere* 151, 138–144. <https://doi.org/10.1016/j.chemosphere.2016.02.071>.
- Loewen, T.N., Carriere, B., Reist, J.D., Halden, N.M., Anderson, W.G., 2016. Linking physiology and biomineralization processes to ecological inferences on the life history of fishes. *Comp. Biochem. Physiol. A* 202, 123–140. <https://doi.org/10.1016/j.cbpa.2016.06.017>.
- Luo, Y., Liang, J., Zeng, G., Chen, M., Mo, D., Li, G., Zhang, D., 2018. Seed germination test for toxicity evaluation of compost: its roles, problems and prospects. *Waste Manag.* 71, 109–114. <https://doi.org/10.1016/j.wasman.2017.09.023>.
- Madan, S., Hussain, A., 2014. Groundwater contamination due to fly ash disposal: a Review. *Int. J. Adv. Res. Biol. Sci.* 1, 143–147.
- Mahajan, V.E., Yadav, R.R., Dakshinkar, N.P., Dhoot, V.M., Bhojane, G.R., Naik, M.K., Shrivastava, P., Naoghare, P.K., Krishnamurthi, K., 2012. Influence of mercury from fly ash on cattle reared nearby thermal power plant. *Environ. Monit. Assess.* 184, 7365–7372. <https://doi.org/10.1007/s10661-011-2505-9>.
- Manerikar, R.S., Apte, A.A., Ghole, V.S., 2008. In vitro genotoxicity of fly ash leachate in earthworm coelomocytes. *Toxicol. Environ. Chem.* 90, 293–300. <https://doi.org/10.1080/02772240701458451>.
- Markad, V.L., Kodam, K.M., Ghole, V.S., 2012. Effect of fly ash on biochemical responses and DNA damage in earthworm, *Dichogaster curgensis*. *J. Hazard Mater.* 215–216, 191–198. <https://doi.org/10.1016/j.jhazmat.2012.02.053>.
- Masoum, H.G., Rastegar, S.O., Khamforoush, M., 2021. Ultrasound-Assisted leaching of vanadium and yttrium from coal ash: optimization, kinetic and thermodynamic study. *Chem. Eng. Technol.* 44, 2249–2256. <https://doi.org/https://doi.org/10.1002/ceat.202100297>.
- Mathews, T.J., Stevenson, L.M., Pickhardt, P.C., Murphy, C.A., Nisbet, R.M., Antczak, P., Garcia-Reyero, N., Gergs, A., 2020. The effect of dietary exposure to coal ash contaminants within food ration on growth and reproduction in *Daphnia magna*. *Environ. Toxicol. Chem.* 39, 1998–2007. <https://doi.org/10.1002/etc.4819>.
- Matzenbacher, C.A., Garcia, A.L.H., dos Santos, M.S., Nicolau, C.C., Premoli, S., Corrêa, D.S., de Souza, C.T., Niekaszewicz, L., Dias, J.F., Delgado, T.V., Kalkreuth, W., Grivicich, I., da Silva, J., 2017. DNA damage induced by coal dust, fly and bottom ash from coal combustion evaluated using the micronucleus test and comet assay in vitro. *J. Hazard Mater.* 324, 781–788. <https://doi.org/10.1016/j.jhazmat.2016.11.062>.
- Medunić, G., Ahel, M., Mihalčić, I.B., Srček, V.G., Kopjar, N., Fiket, Ž., Bituh, T., Mikac, I., 2016. Toxic airborne S, PAH, and trace element legacy of the superhigh-organic-sulphur Raša coal combustion: cytotoxicity and genotoxicity assessment of soil and ash. *Sci. Total Environ.* 566 (567), 306–319. <https://doi.org/10.1016/j.scitotenv.2016.05.096>.
- Medunić, G., Kuharić, Ž., Krivohlavek, A., Duroković, M., Dropučić, K., Radenović, A., Oberiter, B.L., Krizmanić, A., Bajramović, M., 2018. Selenium, sulphur, trace metal, and BTEX levels in soil, water, and lettuce from the Croatian raša bay contaminated by superhigh-organic-sulphur coal. *Geosci.* 8. <https://doi.org/10.3390/geosciences8110408>.
- Miljević, N., Golobčanin, D., 2007. Potential use of environmental isotopes in pollutant migration studies. *Arh. Hig. Rada. Toksikol.* 58, 251–262. <https://doi.org/10.2478/v10004-007-0015-5>.
- Minkina, T., Nevodimskaya, D., Shuvaeva, V., Bauer, T., Soldatov, A., Mandzhieva, S., Trigub, A., Zubavichus, Y., Ghazaryan, K., 2019. Molecular characterization of Zn in Technosols using X-ray absorption spectroscopy. *Appl. Geochem.* 104, 168–175. <https://doi.org/10.1016/j.apgeochem.2019.03.021>.
- Mortazavi, S., Mortazavi, G., Paknahad, M., 2016. Levels of arsenic, mercury, cadmium, copper, lead, zinc, and manganese in serum and whole blood of resident adults from mining and non-mining communities in Ghana. *Environ. Sci. Pollut. Res.* 23, 22220–22221. <https://doi.org/10.1007/s11356-016-7697-7>.
- Mtisi, M., Gwenzi, W., 2019. Evaluation of the phytotoxicity of coal ash on lettuce (*Lactuca sativa* L.) germination, growth and metal uptake. *Ecotoxicol. Environ. Saf.* 170, 750–762. <https://doi.org/10.1016/j.ecoenv.2018.12.047>.
- Neupane, G., Donahoe, R.J., 2013. Leachability of elements in alkaline and acidic coal fly ash samples during batch and column leaching tests. *Fuel* 104, 758–770. <https://doi.org/10.1016/j.fuel.2012.06.013>.
- OECD, 2012. OECD Environmental Outlook to 2050 [WWW Document]. OECD Publ. URL. 8.10.20. http://www.oecd-ilibrary.org/environment/oecd-environmental-outlook-to-2050_9789264122246-en.
- Orešćanin, V., Kollar, R., Buben, K., Mikelić, I.L., Kollar, K., Kollar, M., Medunić, G., 2012. Chemical and radiological characterization of fly and bottom ash landfill of the former sulfate pulp factory Plaski and its surroundings. *J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng.* 47, 1592–1606. <https://doi.org/10.1080/10934529.2012.680780>.
- Orešćanin, V., Mikelić, I., Lovrenčić, I., Barišić, D., Maćefat, M.R., Pavlović, G., Lulić, S., 2006. Chemical and radiological profile of the coal ash landfill in kastel gomilica. *Arh. Hig. Rada. Toksikol.* 57, 9–16.
- Pacwa-Płociniczak, M., Płociniczak, T., Yu, D., Kuroła, J.M., Sinkkonen, A., Piotrowska-Seget, Z., Romantschuk, M., 2018. Effect of silene vulgaris and heavy metal pollution on soil microbial diversity in long-term contaminated soil. *Water Air Soil Pollut.* 229. <https://doi.org/10.1007/s11270-017-3655-3>.
- Pandey, V., Ray, M., Kumar, V., 2020. Assessment of water-quality parameters of groundwater contaminated by fly ash leachate near Koradi Thermal Power Plant. *Nagpur. Environ. Sci. Pollut. Res.* 27, 27422–27434. <https://doi.org/10.1007/s11356-019-0616-x>.
- Parial, K., Guin, R., Agrahari, S., Sengupta, D., 2016. Monitoring of radionuclide migration around Kolaghat thermal power plant, West Bengal, India. *J. Radioanal. Nucl. Chem.* 307, 533–539. <https://doi.org/10.1007/s10967-015-4152-z>.
- Patel, P.M., Javad, R., Patel, K.P., 2016. The genotoxic effect of coal fly ash of thermal power plant on *Raphanus sativus* L. (Radish). *Int. J. Sci. Res. Sci. Technol.* 2, 555–561.
- Penniston-Dorland, S., Liu, X.M., Rudnick, R.L., 2017. Lithium isotope geochemistry. *Rev. Mineral. Geochem.* 82, 165–217. <https://doi.org/10.2138/rmg.2017.82.6>.
- Powers, M.B., 2020. Coal-ash spill cleanup workers reject reputed \$10M exposure settlement [WWW Document]. *Eng. News-Record*. URL. 4.22.20. <https://www.enr.com/articles/49225-coal-ash-spill-cleanup-workers-reject-reputed-10m-exposure-settlement>.
- Prasad, B., Bose, J.M., 2001. Evaluation of the heavy metal pollution index for surface and spring water near a limestone mining area of the lower himalayas. *Environ. Geol.* 41, 183–188. <https://doi.org/10.1007/s002540100380>.
- Prasad, B., Mondal, K.K., 2008. The impact of filling an abandoned open cast mine with fly ash on ground water quality: a case study. *Mine Water Environ.* 27, 40–45. <https://doi.org/10.1007/s10230-007-0021-5>.
- Prasad, B., Sangita, K., 2008. Heavy metal pollution index of ground water of an abandoned open cast mine filled with fly ash: a case study. *Mine Water Environ.* 27, 265–267. <https://doi.org/10.1007/s10230-008-0050-8>.

- Querol, X., Juan, R., Lopez-Soler, A., Fernandez-Turiel, J.L., Ruiz, C.R., 1996. Mobility of trace elements from coal and combustion wastes. *Fuel* 75, 821–838. [https://doi.org/10.1016/0016-2361\(96\)00027-0](https://doi.org/10.1016/0016-2361(96)00027-0).
- Radić, S., Medunić, G., Kuharić, Z., Roje, V., Maldini, K., Vujčić, V., Krivohavek, A., 2018. The effect of hazardous pollutants from coal combustion activity: phytotoxicity assessment of aqueous soil extracts. *Chemosphere* 199, 191–200. <https://doi.org/10.1016/j.chemosphere.2018.02.008>.
- Raimondo, S.M., Rowe, C.L., Congdon, J.D., 1998. Exposure to coal ash impacts swimming performance and predator avoidance in larval bullfrogs. *J. Herpetol.* 32, 289–292.
- Ramsey, A.B., Faiia, A.M., Szykiewicz, A., 2019. Eight years after the coal ash spill – fate of trace metals in the contaminated river sediments near Kingston, eastern Tennessee. *Appl. Geochem.* 104, 158–167. <https://doi.org/10.1016/j.apgeochem.2019.03.008>.
- Romero, F.M., Armienta, M.A., González-Hernández, G., 2007. Solid-phase control on the mobility of potentially toxic elements in an abandoned lead/zinc mine tailings impoundment, Taxco, Mexico. *Appl. Geochem.* 22, 109–127. <https://doi.org/10.1016/j.apgeochem.2006.07.017>.
- Rowe, C.L., Hopkins, W.A., Congdon, J.D., 2002. Ecotoxicological implications of aquatic disposal of coal combustion residues in the United States: a review. *Environ. Monit. Assess.* 80, 207–276. <https://doi.org/10.1023/A:1021127120575>.
- Rowe, C.L., Kinney, O.M., Fiori, A.P., Congdon, J.D., 1996. Oral deformities in tadpoles (*Rana catesbeiana*) associated with coal ash deposition: effects on grazing ability and growth. *Freshw. Biol.* 36, 723–730. <https://doi.org/10.1046/j.1365-2427.1996.00123.x>.
- Rowe, C.L., Kinney, O.M., Nagle, R.D., Congdon, J.D., 1998. Elevated maintenance costs in an anuran (*Rana catesbeiana*) exposed to a mixture of trace elements during the embryonic and early larval periods. *Physiol. Zool.* 71, 27–35. <https://doi.org/10.1086/515885>.
- Ruhl, L., Vengosh, A., Dwyer, G.S., Hsu-Kim, H., Schwartz, G., Romanski, A., Smith, S.D., 2012. The impact of coal combustion residue effluent on water resources: a North Carolina example. *Environ. Sci. Technol.* 46, 12226–12233. <https://doi.org/10.1021/es303263x>.
- Ruhl, L.S., Dwyer, G.S., Hsu-Kim, H., Hower, J.C., Vengosh, A., 2014. Boron and strontium isotopic characterization of coal combustion residuals: Validation of new environmental tracers. *Environ. Sci. Technol.* 48, 14790–14798. <https://doi.org/10.1021/es503746v>.
- Russ, A., Bernhardt, C., 2019. Coal's poisonous legacy [WWW Document]. *Environ. Integr. Proj.* URL 10.10.20. <https://environmentalintegrity.org/reports/coal-s-poisonous-legacy/>.
- Sahoo, S., Khaoash, S., 2020. Impact assessment of coal mining on groundwater chemistry and its quality from Brajrajnagar coal mining area using indexing models. *J. Geochem. Explor.* 215, 106559. <https://doi.org/10.1016/j.gexplo.2020.106559>.
- Sambandam, B., Devasena, T., Hairul Islam, V.I., Prakhyia, B.M., 2015. Characterization of coal fly ash nanoparticles and their induced in vitro cellular toxicity and oxidative DNA damage in different cell lines. *Indian J. Exp. Biol.* 53, 585–593.
- Sample, B.E., Suter II, G.W., 2002. Screening evaluation of the ecological risks to terrestrial Wildlife associated with a coal ash disposal site. *Hum. Ecol. Risk Assess.* 8, 637–656. <https://doi.org/10.1080/20028091057132>.
- Sanoamuang, L.O., 1993. The effect of temperature on morphology, life-history and growth-rate of *filinia terminalis* (plate) and *filinia cf. pejeri hutchinson* in culture. *Freshw. Biol.* 30, 257–267.
- Santamarina, J.C., Torres-Cruz, L.A., Bachus, R.C., 2019. Why coal ash and tailings dam disasters occur. *Science* 84 364, 526–528. <https://doi.org/10.1126/science.aax1927>.
- Schwartz, G.E., Hower, J.C., Phillips, A.L., Rivera, N., Vengosh, A., Hsu-Kim, H., 2018. Ranking coal ash materials for their potential to leach arsenic and selenium: relative importance of ash chemistry and site biogeochemistry. *Environ. Eng. Sci.* 35, 728–738. <https://doi.org/10.1089/ees.2017.0347>.
- Sears, C.G., Zierold, K.M., 2017. Health of children living near coal ash. *Glob. Pediatr. Heal.* 4. <https://doi.org/10.1177/2333794X17720330>.
- Shah, P., Strezov, V., Prince, K., Nelson, P.F., 2008. Speciation of As, Cr, Se and Hg under coal fired power station conditions. *Fuel* 87, 1859–1869. <https://doi.org/10.1016/j.fuel.2007.12.001>.
- Shi, Z., Tang, Z., Wang, C., 2017. A brief review and evaluation of earthworm biomarkers in soil pollution assessment. *Environ. Sci. Pollut. Res.* 24, 13284–13294. <https://doi.org/10.1007/s11356-017-8784-0>.
- Sierra Club, 2018. Dangerous Waters: America's Coal Ash Crisis [WWW Document]. URL, 6.10.20. <https://www.nrc.gov/docs/ML1821/ML1821A866.pdf>.
- Simsman, G.V., Chesters, G., Andren, A.W., 1987. Effect of ash disposal ponds on groundwater quality at a coal-fired power plant. *Water Res.* 21, 417–426. [https://doi.org/10.1016/0043-1354\(87\)90189-8](https://doi.org/10.1016/0043-1354(87)90189-8).
- Singh, P.K., Tripathi, P., Dwivedi, S., Awasthi, S., Shri, M., Chakrabarty, D., Tripathi, R. D., 2016. Fly-ash augmented soil enhances heavy metal accumulation and phytotoxicity in rice (*Oryza sativa* L.); A concern for fly-ash amendments in agriculture sector. *Plant Growth Regul.* 78, 21–30. <https://doi.org/10.1007/s10725-015-0070-x>.
- Singh, S.N., Kulshreshtha, K., Ahmad, K.J., 1997. Impact of fly ash soil amendment on seed germination, seedling growth and metal composition of *Vicia faba* L. *Ecol. Eng.* 9, 203–208. [https://doi.org/10.1016/S0925-8574\(97\)10004-0](https://doi.org/10.1016/S0925-8574(97)10004-0).
- Sloot, H.A., Van Der, Meeussen, J.C.L., Garabrant, A.C., Kossou, D.S., 2009. Review of the Physical and Chemical Aspects of Leaching Assessment. *Energy Res. Cent., Netherlands*.
- Smith, J.W., Batts, B.D., 1974. The distribution and isotopic composition of sulfur in coal. *Geochem. Cosmochim. Acta* 38, 121–133. [https://doi.org/10.1016/0016-7037\(74\)90198-7](https://doi.org/10.1016/0016-7037(74)90198-7).
- Smith, R.C., Taggart, R.K., Hower, J.C., Wiesner, M.R., Hsu-Kim, H., 2019. Selective recovery of rare earth elements from coal fly ash leachates using liquid membrane processes. *Environ. Sci. Technol.* 53, 4490–4499. <https://doi.org/10.1021/acs.est.9b00539>.
- Spadoni, M., Voltaggio, M., Sacchi, E., Sanam, R., Pujari, P.R., Padmakar, C., Labhasetwar, P.K., Wate, S.R., 2014. Impact of the disposal and re-use of fly ash on water quality: the case of the koradi and khaperkheda thermal power plants (Maharashtra, India). *Sci. Total Environ.* 159–170. <https://doi.org/10.1016/j.scitotenv.2014.01.111>, 479–480.
- Stanley, J.K., Kennedy, A.J., Bednar, A.J., Chappell, M.A., Seiter, J.M., Averett, D.E., Steevens, J.A., 2013. Impact assessment of dredging to remove coal fly ash at the Tennessee Valley Authority Kingston Fossil plant using fathead minnow elutriate exposures. *Environ. Toxicol. Chem.* 32, 822–830. <https://doi.org/10.1002/etc.2137>.
- Stevenson, L.M., Krattenmaker, K.E., Johnson, E., Bowers, A.J., Adeleye, A.S., McCauley, E., Nisbet, R.M., 2017. Standardized toxicity testing may underestimate ecotoxicity: environmentally relevant food rations increase the toxicity of silver nanoparticles to *Daphnia*. *Environ. Toxicol. Chem.* 36, 3008–3018. <https://doi.org/10.1002/etc.3869>.
- Stoy, L., Diaz, V., Huang, C.H., 2021. Preferential recovery of rare-earth elements from coal fly ash using a recyclable ionic liquid. *Environ. Sci. Technol.* 55, 9209–9220. <https://doi.org/10.1021/acs.est.1c00630>.
- Sun, X.-B., Liu, H.-Y., Li, Y.-C., Zhang, X.-P., 2007. Impact of heavy metals pollution on the community structure and spatial distribution of soil animals. *J. Appl. Ecol.* 18, 2080–2084.
- Surabhi, S., 2017. Fly ash in India: generation vis-à-vis utilization and global perspective. *Int. J. Appl. Chem.* 13, 29–52.
- Taggart, R.K., Hower, J.C., Dwyer, G.S., Hsu-Kim, H., 2016. Trends in the rare earth element content of U.S.-Based coal combustion fly ashes. *Environ. Sci. Technol.* 50, 5919–5926. <https://doi.org/10.1021/acs.est.6b00085>.
- Tanvir Rahman, M.A.T.M., Paul, M., Bhoomik, N., Hassan, M., Alam, M.K., Aktar, Z., 2020. Heavy metal pollution assessment in the groundwater of the Meghna Ghat industrial area, Bangladesh, by using water pollution indices approach. *Appl. Water Sci.* 10, 1–15. <https://doi.org/10.1007/s13201-020-01266-4>.
- Thorneloe, S.A., Kossou, D., Helms, G., Garabrant, A.C., 2009. Improved leaching test methods for environmental assessment of coal ash and recycled materials used in construction. In: *Proceedings Sardinia 2009, Twelfth International Waste Management and Landfill Symposium*. CISA Publisher, Cagliari, Italy.
- Tiwari, M.K., Bajpai, S., Dewangan, U.K., Tamrakar, R.K., 2015. Suitability of leaching test methods for fly ash and slag: a review. *J. Radiat. Res. Appl. Sci.* 8, 523–537. <https://doi.org/10.1016/j.jrras.2015.06.003>.
- Tso, M.Y.W., Leung, J.K.C., 1996. Radiological impact of coal ash from the power plants in Hong Kong. *J. Environ. Radioact.* 30, 1–14. [https://doi.org/10.1016/0265-931X\(95\)00042-9](https://doi.org/10.1016/0265-931X(95)00042-9).
- Turhan, S., Parmaksiz, A., Köse, A., Yüksel, A., Arıkan, I.H., Yücel, B., 2010. Radiological characteristics of pulverized fly ashes produced in Turkish coal-burning thermal power plants. *Fuel* 89, 3892–3900. <https://doi.org/10.1016/j.fuel.2010.06.045>.
- U.S. EPA, 2015. Hazardous and solid waste management system; disposal of coal combustion residuals from electric utilities.
- U.S. EPA, 2014. Human and ecological risk assessment of coal combustion wastes. *Fed. Regist.* 84, 409.
- U.S. EPA, 2012. *Edition of the Drinking Water Standards and Health Advisories*. Washington DC.
- Uddh Söderberg, T., Berggren Kleja, D., Åström, M., Jarsjö, J., Fröberg, M., Svensson, A., Augustsson, A., 2019. Metal solubility and transport at a contaminated landfill site – from the source zone into the groundwater. *Sci. Total Environ.* 668, 1064–1076. <https://doi.org/10.1016/j.scitotenv.2019.03.013>.
- Ukwattage, N.L., Ranjith, P.G., Bouazza, M., 2013. The use of coal combustion fly ash as a soil amendment in agricultural lands (with comments on its potential to improve food security and sequester carbon). *Fuel* 109, 400–408. <https://doi.org/10.1016/j.fuel.2013.02.016>.
- UNSCEAR, 2000. Sources and Effects of Ionizing Radiation, United Nations Scientific Committee on the Effects of Atomic Radiation UNSCEAR 2000 Report to the General Assembly, with Scientific Annexes, UNSCEAR 2000 Report.
- Us-Sakib, T., Sultana, S., Ahmed, A.N., Khan, A.A., Saha, M.S., 2018. Water quality of coal ash pond and its impact on adjoining surface and groundwater systems. *Aust. J. Water Resour.* 6, 176–180. <https://doi.org/10.12691/ajwr-6-4-5>.
- Uzarowicz, Ł., Skiba, M., Leue, M., Zagórski, Z., Gasiński, A., Trzcinski, J., 2018. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part II. Mineral transformations and soil evolution. *Catena* 162, 255–269. <https://doi.org/10.1016/j.catena.2017.11.005>.
- Uzarowicz, Ł., Zagórski, Z., 2015. Mineralogy and chemical composition of technogenic soils (Technosols) developed from fly ash and bottom ash from. *Soil Sci. Annu.* 66, 82–91. <https://doi.org/10.1515/ssa-2015-0023>.
- Uzarowicz, Ł., Zagórski, Z., Mendak, E., Bartmiński, P., Szara, E., Kondras, M., Oktaba, L., Turek, A., Rogoziński, R., 2017. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part I. Properties, classification, and indicators of early pedogenesis. *Catena* 157, 75–89. <https://doi.org/10.1016/j.catena.2017.05.010>.
- Valentin, B., Abagiu, A.T., Anghelescu, L., Flores, D., French, D., Gonçalves, P., Guedes, A., Popescu, L.G., Predeanu, G., Ribeiro, J., Santos, A.C., Slăvescu, V., Ward, C.R., 2019. Assessment of bottom ash landfilled at Căplea Valley (Romania) as a source of rare earth elements. *Int. J. Coal Geol.* 201, 109–126. <https://doi.org/10.1016/j.coal.2018.11.019>.
- Van Gestel, C.A.M., McGrath, S.P., Smolders, E., Ortiz, M.D., Borgman, E., Verweij, R.A., Buekers, J., Oorts, K., 2012. Effect of long-term equilibration on the toxicity of

- molybdenum to soil organisms. *Environ. Pollut.* 162, 1–7. <https://doi.org/10.1016/j.envpol.2011.10.013>.
- Vejahati, F., Xu, Z., Gupta, R., 2010. Trace elements in coal: associations with coal and minerals and their behavior during coal utilization - a review. *Fuel* 89, 904–911. <https://doi.org/10.1016/j.fuel.2009.06.013>.
- Vengosh, A., Cowan, E.A., Coyte, R.M., Kondash, A.J., Wang, Z., Brandt, J.E., Dwyer, G. S., 2019. Evidence for unmonitored coal ash spills in Sutton Lake, North Carolina: implications for contamination of lake ecosystems. *Sci. Total Environ* 686, 1090–1103. <https://doi.org/10.1016/j.scitotenv.2019.05.188>.
- Vengosh, A., Coyte, R., Karr, J., Harkness, J.S., Kondash, A.J., Ruhl, L.S., Merola, R.B., Dwyer, G.S., 2016. Origin of hexavalent chromium in drinking water wells from the piedmont aquifers of North Carolina. *Environ. Sci. Technol. Lett.* 3, 409–414. <https://doi.org/10.1021/acs.estlett.6b00342>.
- Vengosh, A., Heumann, K.G., Juraske, S., Kasher, R., 1994. Boron isotope application for tracing sources of contamination in groundwater. *Environ. Sci. Technol.* 28, 1968–1974. <https://doi.org/10.1021/es00060a030>.
- Vengosh, A., Lindberg, T.T., Merola, B.R., Ruhl, L., Warner, N.R., White, A., Dwyer, G.S., Di Giulio, R.T., 2013. Isotopic imprints of mountaintop mining contaminants. *Environ. Sci. Technol.* 47, 10041–10048. <https://doi.org/10.1021/es4012959>.
- Verma, C., Madan, S., Hussain, A., 2016. Heavy Metal Contamination of Groundwater Due to Fly Ash Disposal of Coal-Fired Thermal Power Plant. Parichha, Jhansi, India. <https://doi.org/10.1080/23311916.2016.1179243>. *Cogent Eng.*
- Vohra, K., Vodonos, A., Schwartz, J., Marais, E.A., Sulprizio, M.P., Mickley, L.J., 2021. Global mortality from outdoor fine particle pollution generated by fossil fuel combustion: Results from GEOS. *Chem. Environ. Res.* 195, 110754. <https://doi.org/10.1016/j.envres.2021.110754>.
- Voltaggio, M., Spadoni, M., Sacchi, E., Sanam, R., Pujari, P.R., Labhasetwar, P.K., 2015. Assessment of groundwater pollution from ash ponds using stable and unstable isotopes around the Koradi and Khaperkheda thermal power plants (Maharashtra, India). *Sci. Total Environ.* <https://doi.org/10.1016/j.scitotenv.2015.02.083>.
- Wagh, V.M., Panaskar, D.B., Mukate, S.V., Gaikwad, S.K., Muley, A.A., Varade, A.M., 2018. Health risk assessment of heavy metal contamination in groundwater of Kadava River Basin, Nashik, India. *Model. Earth Syst. Environ.* 4, 969–980. <https://doi.org/10.1007/s40808-018-0496-z>.
- Wang, Z., Coyte, R.M., Cowan, E.A., Stapleton, H.M., Dwyer, G.S., Vengosh, A., 2021. Evaluation and integration of geochemical indicators for detecting trace levels of coal fly ash in soils. *Environ. Sci. Technol.* 55, 10387–10397. <https://doi.org/10.1021/acs.est.1c01215>.
- Wang, Z., Dwyer, G.S., Coleman, D.S., Vengosh, A., 2019. Lead isotopes as a new tracer for detecting coal fly ash in the environment. *Environ. Sci. Technol. Lett.* 6, 714–719. <https://doi.org/10.1021/acs.estlett.9b00512>.
- Warner, N.R., Darrah, T.H., Jackson, R.B., Millot, R., Kloppmann, W., Vengosh, A., 2014. New tracers identify hydraulic fracturing fluids and accidental releases from oil and gas operations. *Environ. Sci. Technol.* 48, 12552–12560. <https://doi.org/10.1021/es5032135>.
- Williams, L.B., Hervig, R.L., 2004. Boron isotope composition of coals: a potential tracer of organic contaminated fluids. *Editorial handling by R.S. Harmon. Appl. Geochem.* 19, 1625–1636. <https://doi.org/10.1016/j.apgeochem.2004.02.007>.
- Wong, M.H., Wong, J.W.C., 1989. Germination and seedling growth of vegetable crops in fly ash-amended soils. *Agric. Ecosyst. Environ.* 26, 23–35. [https://doi.org/10.1016/0167-8809\(89\)90035-2](https://doi.org/10.1016/0167-8809(89)90035-2).
- World Coal Association, 2020. Coal and electricity [WWW Document]. URL 7.30.20. <https://www.worldcoal.org/>.
- Wu, X., Cobbina, S.J., Mao, G., Xu, H., Zhang, Z., Yang, L., 2016. A review of toxicity and mechanisms of individual and mixtures of heavy metals in the environment. *Environ. Sci. Pollut. Res.* 23, 8244–8259. <https://doi.org/10.1007/s11356-016-6333-x>.
- Xu, H., Liu, C., Mi, X., Wang, Z., Han, J., Zeng, G., Liu, P., Guan, Q., Ji, H., Huang, S., 2021. Extraction of lithium from coal fly ash by low-temperature ammonium fluoride activation-assisted leaching. *Separ. Purif. Technol.* 279, 119757. <https://doi.org/10.1016/J.SEPUR.2021.119757>.
- Xue, Y.H., Yang, X.X., Zhang, G., Xi, Y.L., 2017. Morphological differentiation of *Brachionus calyciflorus* caused by predation and coal ash pollution. *Sci. Rep.* 7, 1–8. <https://doi.org/10.1038/s41598-017-16192-w>.
- Yellishetty, M., Huston, D., Graedel, T.E., Werner, T.T., Reck, B.K., Mudd, G.M., 2017. Quantifying the potential for recoverable resources of gallium, germanium and antimony as companion metals in Australia. *Ore Geol. Rev.* 82, 148–159. <https://doi.org/10.1016/j.oregeorev.2016.11.020>.
- Zhai, Y., Ma, T., Zhou, J., Li, X., Liu, D., Wang, Z., Qin, Y., Du, Q., 2019. Impacts of leachate of landfill on the groundwater hydrochemistry and size distributions and heavy metal components of colloids: a case study in NE China. *Environ. Sci. Pollut. Res.* 26, 5713–5723. <https://doi.org/10.1007/s11356-018-4053-0>.
- Zhang, L., Song, Q., Xu, Z., 2021. Arsenic removal and recovery of germanium and tungsten in toxic coal fly ash from lignite by vacuum distillation with a sulfurizing reagent. *Environ. Sci. Technol.* 55, 4027–4036. <https://doi.org/10.1021/acs.est.0c08784>.
- Zhang, L., Xu, Z., 2016. An environmentally-friendly vacuum reduction metallurgical process to recover germanium from coal fly ash. *J. Hazard Mater.* 312, 28–36. <https://doi.org/10.1016/j.jhazmat.2016.03.025>.
- Zhang, S., Dai, S., Finkelman, R.B., Graham, I.T., French, D., Hower, J.C., Li, X., 2019. Leaching characteristics of alkaline coal combustion by-products: a case study from a coal-fired power plant, Hebei Province, China. *Fuel* 255, 115710. <https://doi.org/10.1016/j.fuel.2019.115710>.
- Zhang, X., 2014. Management of coal combustion wastes [WWW Document]. IEA Clean Coal Cent. URL 7.20.20. <https://www.iea-coal.org/report/management-of-coal-combustion-wastes-ccc-231/>.
- Zhao, L., Dai, S., Finkelman, R.B., French, D., Graham, I.T., Yang, Y., Li, J., Yang, P., 2020. Leaching behavior of trace elements from fly ashes of five Chinese coal power plants. *Int. J. Coal Geol.* 219, 103381. <https://doi.org/10.1016/j.coal.2019.103381>.
- Zhao, Y., Zhou, Y., Zhang, J., Zheng, C., 2019. Trace Element Resource Recovery from Coal and Coal Utilization By-Products, Emission and Control of Trace Elements from Coal-Derived Gas Streams. Elsevier Ltd. <https://doi.org/10.1016/B978-0-08-102591-8.00009-X>.



Physicochemical and mineral characteristics of soil materials developed naturally on two ~ 50 years old coal combustion residue disposal sites in Croatia

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ABSTRACT

Coal combustion has been one of the most dominant sources of energy for the last two centuries, generating tonnes of coal combustion residue (CCR). Rapid soil formation has been observed at old CCR disposal sites, altering the physicochemical and mineral properties of CCR, affecting contaminant release mechanisms and nutrient availability. Although ubiquitous, pedological properties of weathered CCR have been studied at only a small number of disposal sites. This study characterized two CCR landfills of similar age (~50 years) using a range of parameters, including pH, total nitrogen and organic carbon content, major oxides (Al₂O₃, CaO, and SiO₂), and macronutrients (Ca, K, Mg, P, and S), as well as textural and mineralogical data. In addition, specific surface area and cation exchange capacity were determined to assess particle properties, and ¹³C and ²⁹Si NMR spectra were examined to characterize the organic matter and degree of polymerization of the coal ash glassy phase. Such comprehensive approach aimed to determine indicators of soil formation and to characterize the capacity of such landfills to retain water, nutrients, and contaminants. Both landfills displayed evidence of pedogenesis reflected in the pH decrease, formation of secondary minerals (such as ettringite, hydrotalcite, gypsum, and calcite), and changes in the C:N ratio. The Plaški landfill seems to have a better capacity to hold water, nutrients, and contaminants evident by higher clay content, CEC, and SSA values, possibly explaining why it developed more rapidly than Štrmac despite their similar age. The presence of montmorillonite in Plaški could be one of the main factors accelerating pedogenesis. ¹³C NMR spectra point to the unburned coal particles as the main origin of organic matter and ²⁹Si NMR spectra showed higher depolymerization of a non-crystalline fraction in bare ash samples than in vegetated ash samples.

1. Introduction

Coal combustion produces nearly 1 billion tonnes of coal combustion residuals (CCR) annually, of which 40–50% is disposed of in landfills or surface impoundments (Harris et al., 2019; Kruger, 2017). The total number of CCR disposal sites worldwide is not known (Petrović and Fiket, 2022). Such information is publicly available only for the U.S., where there are >1 000 CCR disposal sites, out of which ~ 450 are unlined, and for 235 the lining status is unknown (Earthjustice, 2021).

Although precise data on the number of such landfills are not

available, the literature undoubtedly suggests that pollution near CCR disposal sites can persist for decades in different environmental compartments. In Croatia (Europe), elevated levels of trace elements were found in soil, vegetables, water, sediment, and non-migratory birds, decades after CCR disposal (Crnić et al., 2022; Medunić et al., 2018a, 2018b). Similar observations were made for Poland, India and the United States (Brandt et al., 2017, 2018; Lemly, 2018; Pacwa-Plóciniczak et al., 2018; Verma and Madan, 2016). In addition to pollution, old CCR disposal sites represent a unique matrix of altered physicochemical properties of the original ash due to long-term exposure to

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environmental conditions (Uzarowicz and Zagorski, 2015). Changes in waste properties directly affect nutrient availability and contaminant release, affecting the rate of natural succession of such deposits (Kanbar et al., 2020; Ugolini et al., 2020).

To date, only a few studies investigated the aging of coal ash and the associated changes of physicochemical properties (Konstantinov et al., 2020; Uzarowicz et al., 2018a; Uzarowicz et al., 2018b; Uzarowicz et al., 2017; Uzarowicz and Zagorski, 2015; Zikeli et al., 2005, 2004, 2002). A common characteristic is accelerated soil formation, typical of human artefacts exposed to environmental conditions due to a strong imbalance between the waste and environment (Leguëdois et al., 2016; Séré et al., 2010). Early pedogenetic processes such as oxidation, formation of secondary minerals, root development, and even humus formation can be observed on coal ash landfills, even though they are <200 years old. Such processes can take hundreds and thousands of years in natural soils (Leguëdois et al., 2016; Séré et al., 2010). Soils containing 20% or more artefacts (such as sludge, cinders, mine spoils and ashes) are called Technosols (IUSS Working Group WRB, 2022).

The evolution of CCR landfills can be categorized into four main phases based on changes in pH and main mineral phases (Uzarowicz et al., 2018b). In the first phase, ash is generated in thermal power plants and not yet exposed to environmental conditions, thus pH and mineralogy reflect the type of coal combusted (Uzarowicz et al., 2018a).

In the second phase, waste is disposed of and exposed to environmental conditions which causes the dissolution of some primary minerals and crystallization of secondary mineral phases (Uzarowicz et al., 2018b). Due to the dissolution and crystallization, pH drops to 9–10 if the waste was highly alkaline ($\text{pH} > 11$). Which secondary mineral phases will form depends on the type of 'fresh' ash (fly or bottom ash) and the type of coal burned (lignite or bituminous). These changes are more dynamic in lignite ashes than in bituminous because lignite ashes contain more highly reactive mineral phases (e.g. lime, periclase, anhydrite) which easily transform during weathering (Uzarowicz et al., 2018b). Typically, a variety of secondary minerals (calcite, bassanite, gypsum, ettringite, hydrotalcite, and brucite) will form in the 2nd phase of ash evolution (Uzarowicz et al., 2018b; Uzarowicz and Zagorski, 2015).

The third phase is early pedogenesis as the changes are controlled by both abiotic and biotic processes. In this phase, further crystallization of calcite occurs, while gypsum and ettringite are leached out. All of that is followed by a drop in pH to 6–8 (Uzarowicz et al., 2018b). In this phase, an increase in organic matter content can be observed which is usually expressed by the ratio of total organic carbon (TOC) and total nitrogen (N_t) (C:N) (Kostić et al., 2018; Uzarowicz et al., 2018b; Zikeli et al., 2002). TOC cannot be solely used as an indicator of newly formed organic matter since coal ashes can have large amounts of unburned carbon, significantly increasing TOC values (Zikeli et al., 2002). Besides an increase in organic matter, increase in clay content and formation of scattered vegetation is a typical feature of coal ash Technosols (Chu, 2008; Kostić et al., 2018).

The fourth phase is final phase, as the Technosols are developed into another soil formation. However, categorization of newly formed Technosols according to World reference base for soil resources was found to be tricky due to a lack of Protocalcic, Ferritic, Fractic, and Limnic qualifiers in the supplementary list for Technosols (Uzarowicz et al., 2017).

One interesting feature of coal ash landfills is cementation. Due to high content of lime, coal ash tends to cement when exposed to rainfall. Although useful in cement industry, these features slow the natural succession since water and roots cannot penetrate the landfill (Zikeli et al., 2002). In coal ash Technosol in Poland, after 40 years of disposal, mineral assemblage from 2nd phase of landfill evolution persisted in the cemented subsoil of CCR landfill which was hardly affected by soil-forming processes (Uzarowicz et al., 2018b).

To date, only relatively small number of aged coal ash landfills were investigated in context of soil formation (5 in Germany (Zikeli et al.,

2002), 7 in Poland (Uzarowicz et al., 2017), 3 in Serbia (Kostić et al., 2018), 1 in Hong Kong (Chu, 2008). Of these, 4 of the 16 analysed coal ash Technosols were dry landfills, while the others were settling ponds (wet disposal method).

This study, therefore, aims to contribute to better understanding of dry coal ash evolution in the environment. To this end, the specific objectives of this study include characterization of a) physical and chemical properties of coal ash Technosols, b) mineral assemblages and c) ash's capacity to hold water, nutrients and contaminants. In addition to commonly used parameters, such as pH, total organic carbon, total nitrogen and macronutrient (Ca, K, Mg, P, and S) content as well as mineralogical composition, this study also included analyses of specific surface area (SSA), cation exchange capacity (CEC), ^{13}C NMR, and ^{29}Si NMR. Both SSA and CEC are not commonly measured while characterizing aged waste characteristics, and to the best of our knowledge this is the first study to use ^{13}C NMR and ^{29}Si NMR spectra for characterisation of organic matter and degree of glass polymerization, respectively.

Moreover, this study investigates pedological and ecological evolution of two alkaline coal ash landfills developed under the different climatic conditions. First landfill (in Štrmac, Croatia) is situated in an area characterized by Mediterranean climate conditions with hot summers, while the second one (in Plaški, Croatia) is situated in an area characterized by temperate humid climate with fresh summers.

2. Methods

2.1. LANDFILLS description and sampling

This study regards two unlined coal ash landfills located in villages Štrmac and Plaški in Croatia (Europe) (Fig. 1.a).

First landfill (LŠ) is situated in Štrmac, a village on Istrian peninsula, the westernmost part of Croatia (Fig. 1.b). The area is characterized by Mediterranean climate conditions with hot summers (Csa according to the Köppen Classification) (Filipčić, 2001; Šegota and Filipčić, 2003). The average annual air temperature is 14.8°C (Zaninović et al., 2008) and total annual precipitation is 900 – 1100 mm (Gajić-Čapka et al., 2003). The landfill lays on well-permeable foraminiferal limestones covered with brown soils, belonging to the class of Chromic Cambisols (Miko et al., 2003; Šikić et al., 1969). The landfill consists of coal bottom ash and slag disposed in 1960 s by a local foundry and covers the area of $\sim 17\,000\text{ m}^2$. The nearest residents are $\sim 12\text{ m}$ away. The top of the landfill is covered with planted conifers, while the slope is bare, with patches of naturally growing grass and several other pioneer plant species (Fig. 1.). The type of coal used was local Raša coal, a super-high-organic-sulphur coal enriched in S, Se, Mo, U, V and Re (Medunić et al., 2016b). A detailed description of geological and geochemical characteristics of Raša coal can be found elsewhere (Medunić et al., 2018; Medunić et al., 2016b), as well as environmental pollution caused by its combustion (Fiket et al., 2020; Medunić et al., 2016a; Radić et al., 2018).

The second landfill (LP) is situated in Plaški, a village in Lika Region (Fig. 1.c). The area is characterized by a temperate humid climate with fresh summer (Cfc according to the Köppen Classification) (Filipčić, 2001; Šegota and Filipčić, 2003). The average annual air temperature is 10.25°C (Zaninović et al., 2008) and total annual precipitation is 1600 – 1700 mm (Gajić-Čapka et al., 2003). The landfill lays on Quaternary sediments which consist of poorly bound to unbound detritus of limestones, dolomites, and cherts mixed with humus, sand, gravel, and mud (Velić and Sokač, 1981). The landfill consists of $70,000\text{ m}^3$ of fly and bottom ash disposed of by the former sulfate pulp factory which operated from 1965 to 1991. The height of the landfill varies from 3.5 to about 13 m (Oreščanin et al., 2012). The top of the landfill is covered with naturally growing grass, while the slopes are bare, with patches of pioneer plant species (Fig. 1.c). The ash was not fertilized. Slopes are cemented, which is often found in such landfills (Weber et al., 2015). The type of coal burned in the factory is unknown to us, but residents

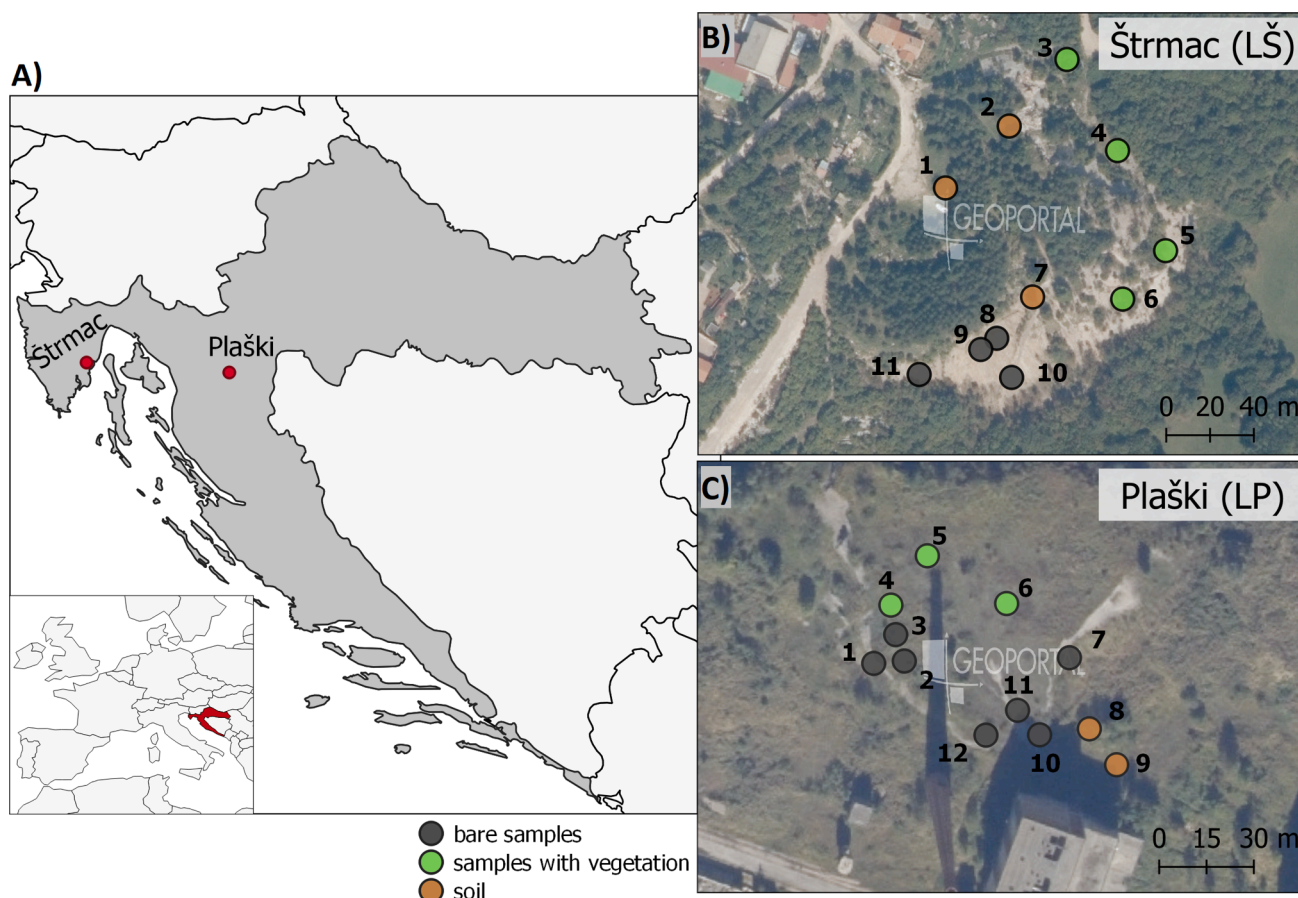


Fig. 1. Study area: A) map of Croatia and locations of two landfills; B) sampling locations at the Štrmac landfill; C) sampling locations at the Plaški landfill. At each location, several samples with varying depth were taken (detailed in 2.2.).

told us it came from Bosnia and Herzegovina.

2.2. Sampling and sample preparation

The sampling campaign was conducted in July 2020 (LŠ) and May 2021 (LP). In total, 70 samples were collected with the sampling shovel and stored in a plastic bag. On both landfills, coal ash samples with and without vegetation were sampled along with soil samples (Fig. 1.).

In Štrmac, a total of 30 samples with varying depths were taken at 11 locations. At 9 locations (LŠ1, LŠ3-6, LŠ8-11) samples were taken at three different depths (0–10 cm, 10–20 cm, and 20–30 cm), on 1 location (LŠ2) at two depths (0–10, 10–20 cm), and at LŠ7 only surface sample was taken.

In Plaški, 40 samples were taken at 12 locations. At LP1 and LP5 locations, samples were taken up to 70 cm and 50 cm, respectively, at 2 locations (LP4, LP6) up to 40 cm, and at 3 (LP7, LP8, LP9) up to 30 cm. On cemented part of the landfill, 1–4 cemented samples were taken at 5 locations (LP2, LP3, LP10, LP11, LP12).

In the laboratory, bulk samples were separated for granulometric analysis, and for all other analyses, samples were dried, uncemented were sieved through a 2 mm sieve to remove the gravel fraction and cemented were crushed with a hammer. Both types of samples were stored until further analysis. For XRD, XRF, HR-ICP-MS, NMR, C_{tot} , and N_{tot} analysis, samples were ground and homogenized in an agate mill.

2.3. Sample analysis

To detect early pedogenesis, common indicators were measured – pH, mineralogy, organic matter (C:N and solid-state ^{13}C NMR), and macronutrients (Ca, K, Mg, P, and S).

For pH measurements, ash samples were mixed with Mili-Q water at 1:5 ratio and left 30 min to settle. pH of eluates was measured using Thermo Scientific™ Orion™ Versa Star Pro™ pH meter.

Mineral composition of samples was assessed by X-ray diffraction using a Philips PW3710 X-ray diffractometer equipped with CuK α radiation.

Simultaneous analysis for C, H, N was performed using an Elemental vario Micro cube CHNS/O analyzer. Catalytic combustion was performed at a continuous temperature of 1050 °C in a pure oxygen environment using tungsten oxide as catalyst. Subsequently, the reduction of the combustion gases was carried out on hot copper in a second furnace. The formed analytical gases N $_2$, CO $_2$, H $_2$ O gases remaining in the He carrier gas were then separated into their components on a column by temperature programmed desorption (TPD) and then fed into a thermal conductivity detector (TCD). The precision of the measurements expressed as standard deviation was 3–5%. The reference material we used to verify our measurements was the “High organic sediment standard OAS; Cert. No.: 175032”, with certified values of $N_{tot} = 0.57 \pm 0.02$ wt% and $C_{tot} = 7.17 \pm 0.09$.

Mineral composition, C_{tot} , N_{tot} , and XRF analysis were performed on selected samples (Table S1, S2, S3, S4).

For identification of dominant organic phases, solid-state NMR experiments of three surface samples (LŠ5, LŠ7, LŠ10) were performed on a Bruker AVANCE NEO 400 MHz NMR spectrometer using a 4 mm CP-MAS probe. The sample spinning frequency was 15 kHz. The 1H - ^{13}C CP-MAS NMR experiments consisted of excitation of protons with p/2 pulse of 3.0 μ s, CP block of 3 ms, and signal acquisition with high-power proton decoupling. A total of ca. 5,700 to 17,000 scans were accumulated with the repetition delay of 5 s. ^{29}Si MAS NMR spectra were acquired using one pulse sequence with p/2 pulse of 4.0 μ s and with high-

power proton decoupling during acquisition. A total of ca. 7,400 to 8,500 scans were accumulated with the repetition delay of 10 s. Larmor frequencies for ^{13}C and ^{29}Si were 100.63 MHz and 79.50 MHz. The chemical shifts were referenced externally using adamantane.

For content of major oxides (Al_2O_3 , CaO and SiO_2), L55 (1–3), L57, L510 (1–3), and L511 (1–3) were first dried in an exhaust air dryer for 24 h at 50 °C and were then pelletized using the hand press pelletizer, a PVC tube and a torque wrench of 2 T for XRF analyzes. All pellets were analyzed for major and minor element concentrations in a portable stand using a handheld XRF analyzer NITON XL5+. All readings were obtained using the instrument's default mining mode settings (Cu/Zn) and calibrations corrected by Compton Normalization. By using the four filters, the analyzer can evaluate over thirty elements, from Mg (lightest) to U (heaviest). For each measurement, the three filters run once for 40 s and the last filter (Light) runs for 90 s for a total run time of 210 s. Data are interpreted by the analyzer system software in parts per million and percent, with detection limits (LOD) determined by continuously averaging the detected energy for each element. Concentrations falling below 2-sigma are considered to be below the detection limits (-). Quality control was performed by analyzing duplicate samples, while quality assurance was performed by measuring 22 internal reference materials to generate internal calibration curves.

Macronutrients (Ca, K, Mg, P, and S) of ash samples were measured by High-Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) using Element 2 instrument (Thermo, Bremen, Germany). Typical instrument conditions and measurement parameters used throughout the work were reported earlier (Fiket et al., 2016).

The granulometric analysis of ashes was carried out using a laser diffraction particle size analyzer (LS 13320, Beckman Coulter, Brea, CA, USA). Prior to measurement, samples were soaked in deionized water and treated with ultrasound for 5 min. The particle size was classified into clay (<2 μm), silt (2–63 μm), and sand (>63 μm) (Wentworth, 1922). Specific surface area (SSA) was measured by nitrogen adsorption using the FlowSorb II 2300 instrument (Micromeritics, I.C.). Cation exchange capacity (CEC) was determined with an ammonium-selective electrode (Busenberg and Clemency, 1973).

2.4. Statistics

Nonparametric methods were employed for statistical analysis using R, including Mann Whitney test for comparing the difference between bare and vegetated samples, with significance level set at $p < 0.05$.

3. Results & discussion

3.1. Indicators of early pedogenesis

Specific indicators were used to detect early pedogenesis including pH, mineral assemblage, total organic carbon, total nitrogen content, and macronutrient content (Mg, P, S, Ca, K). By comparing samples with and without vegetation we tried to identify characteristics of 'evolved' part of the landfills and determine the main evolution phase of both landfills.

3.1.1. Decrease in pH

The pH of samples collected at the Štrmac landfill ranged from 8.7 to 12.6, with an average of 10.2, and at the Plaški landfill from 8.2 to 10.4, with an average of 9.1 (Table 1). In Štrmac, bare samples had significantly higher ($p < 0.05$) pH values (12.1 ± 0.5) than samples with vegetation (9.2 ± 0.2), while in Plaški values were similar (9.0 ± 0.4 for bare samples and 9.1 ± 0.2 for vegetated samples). At both localities no trend was observed with increasing depth.

Initial pH of CCR disposed in Štrmac was 13.5 (Lieberman et al., 2020), while the initial pH of ash disposed in Plaški is unknown as there is no record of the origin of the coal used. Most likely it was more alkaline than today as suggested by the mineralogy discussed in more

Table 1

Average pH values and average mineral content (%) in samples collected at Štrmac (LŠ) and Plaški (LP) landfills, grouped according to sample characteristics – bare* are samples without vegetation, veg** are samples with vegetation, and soil*** are soil samples collected around the landfills. Data for every sample collected is available in Supplementary Table 1 and 2.

	LŠ - bare	LŠ - veg	LŠ - soil	LP - bare	LP - veg	LP - soil
pH	12.1	9.2	8.9	9.0	9.1	9.0
Calcite	26.8	79.3	6.60	57.5	58.6	22.5
Gypsum	7.86	0.35	10.9	6.66	1.65	3.07
Portlandite	16.1	0.20	nd	0.60	nd	0.10
Ettringite	20.5	0.82	nd	11.3	1.43	3.48
Hematite	0.20	0.57	2.97	1.47	1.78	4.08
Hydrotalcite	1.42	0.37	nd	2.24	1.08	1.80
Graphite 2H	0.56	2.01	6.40	4.48	7.86	15.1
Pyrite	0.10	0.18	0.25	0.13	0.34	0.20
Dolomite	1.99	1.64	nd	2.37	0.93	5.15
Illite 2 M1	1.53	4.75	24.6	2.68	nd	9.60
Kaolinite 2 M	0.10	1.79	11.7	5.30	0.60	nd
Montmorillonite	nd	nd	nd	8.84	13.3	21.8
Anorthite, sodian	nd	2.97	0.50	2.81	4.34	6.42
Tridymite	0.42	1.98	2.10	0.38	0.70	0.75
Quartz low	0.30	4.83	43.2	7.10	9.24	18.2
Amorph. fraction	43.9	20.5	59.6	Nd	nd	Nd
Sulphur	nd	nd	nd	0.20	0.60	0.25

*LŠ8 (1–3), LŠ9 (1–3), LŠ10 (1–3), LŠ11 (1–3), LP1 (1–6), LP3 (1–4), LP12 (1–4).

**LŠ3 (1–3), LŠ4 (1–3), LŠ5 (1–3), LŠ6 (1–3), LP5 (1–5).

***LŠ2 (1–2), LŠ7, LP8 (1–3), LP9 (1–3).

nd - not determined.

detail later. In short, ettringite was found in cemented bare samples in Plaški (in LP11 up to 43.3%). Although pH stability of ettringite in this exact context was not studied, ettringite forms in very alkaline environments ($\text{pH} > 11$) (Hassett et al., 2005) indicating more alkaline initial pH of Plaški ash.

Therefore, a decrease in pH over time is indicated at both landfills which is consistent with the literature of coal ash and similar Technosols (Daniell and van Deventer, 2018; Konstantinov et al., 2020; Séré et al., 2010; Uzarowicz et al., 2017), and also suggests an onset of pedogenetic processes. Typically, pH equal or lower than 9 of previously alkaline ashes ($\text{pH} > 11$) indicates early pedogenesis (3rd phase of landfill evolution) (Uzarowicz et al., 2018b). Since part of the Štrmac landfill has a pH higher than 10, the landfill, based solely on pH, is characterized by both 2nd and 3rd phase of landfill evolution (Uzarowicz et al., 2018b), meaning that at bare parts of the landfills, abiotic processes are still predominant. The Plaški landfill, even though it has bare parts, is characterized by a 3rd phase (early pedogenesis).

3.1.2. Formation of secondary minerals

Both landfills had the same mineral composition, but with varying relative abundance, except for montmorillonite and elemental sulfur found only in the Plaški samples.

Abundance of following minerals was similar in bare and vegetated samples in Štrmac samples, respectively: hematite (0.20% and 0.57%), pyrite (0.10 and 0.18%), and dolomite (1.99 and 1.64%); and in Plaški samples: calcite (57.5 and 58.6%), hematite (1.47 and 1.78%), pyrite (0.13 and 0.34%), tridymite (0.38 and 0.70%), and sulphur (0.20 and 0.60%). However, abundance of following minerals differed in bare and vegetated samples in Štrmac samples, respectively: calcite (26.8 and 79.3%), gypsum (7.86 and 0.35%), portlandite (16.13 and 0.20%), ettringite (20.5 and 0.82%), hydrotalcite (1.42 and 0.37%), graphite (0.56 and 2.01%), illite (1.53 and 4.75%), kaolinite (0.10 and 1.79%), anorthite (n.d. and 2.97%), tridymite (0.42 and 1.98%), quartz (0.30 and 4.83%); and in Plaški samples: gypsum (6.66 and 1.65%), portlandite (0.60% and n.d.), ettringite (11.3 and 1.43%), hydrotalcite (2.24 and 1.08%), graphite (4.48 and 7.86%), illite (2.68% and n.d.), kaolinite (5.30 and 0.60%), anorthite (2.81 and 4.34%), quartz (7.10

and 9.24%) (Table 1).

Most of the minerals observed in studied landfills were also found in weathered alkaline coal ash in Poland (Uzarowicz et al., 2018b), but in different quantities. Most noticeable is the difference in quartz (up to 88.1% in Poland), ettringite (2.5%), and calcite (1.0%) content in Poland samples, while these minerals amount to 20.4%, 41.3%, and 94% in our samples, respectively. The differences most probably result from the type of coal burned, furnace conditions, type of ash disposed of, and waste age (Van Dyk et al., 2009).

In coal ash Technosols minerals can be inherited from original ash (either formed during coalification or combustion), formed by pedogenesis, have allochthonous origins, or even several different origins. To distinguish between secondary minerals formed during initial disposal (2nd stage of landfill evolution) and minerals formed during the 3rd phase (early pedogenesis), differences between bare and vegetated samples were investigated.

Bare samples at the Štrmac landfill had significantly higher levels of ettringite, gypsum, and portlandite than vegetated samples ($p < 0.05$; Table 1). These minerals form after fresh ash encounters rainwater (e.g. ettringite, gypsum) or are inherited from the ash (e.g., portlandite, gypsum) and are consistent with the 2nd phase of coal ash landfill evolution (Uzarowicz et al., 2018b). Ettringite is a typical secondary mineral that forms whenever alkaline coal ash comes into contact with water, even under laboratory conditions (Hassett et al., 2005; Izquierdo and Querol, 2012; Johnson et al., 1999). Its precursors are anhydrite, which was found in fresh Raša ash (Lieberman et al., 2020), and aluminosilicate glass (as a source of Al). All these minerals were also found in bare samples from the Plaški landfill, but their values were not significantly higher ($p < 0.05$) than in vegetated samples, which is consistent with the pH value.

In addition to ettringite, portlandite, and gypsum, hydrotalcite seems to be a typical secondary mineral formed during 2nd phase of coal ash landfill evolution. It was observed in both studied landfills, as well as in Poland (Uzarowicz et al., 2018b), but its values were not significantly higher ($p < 0.05$) in bare samples compared to vegetated ones. This is most likely due to its better stability compared to ettringite and gypsum (Grünwald et al., 2007). Therefore, once formed, it stays stable despite decreasing pH. Ettringite and gypsum, on the other hand, are more stable under highly alkaline conditions; therefore, they are almost completely leached out in samples affected by pH decrease. This is evident in samples with vegetation, where the percentage of ettringite and gypsum was much lower (e.g., bare samples from the Štrmac landfill had 20.5% ettringite, while vegetated samples contained 0.3%).

Once these minerals are leached out, they are replaced by other minerals, usually calcite. Calcite is a typical secondary mineral formed from both bituminous and lignite ashes (Uzarowicz et al., 2018b), although it can also be inherited from the original ash. Fresh Raša ashes contain calcite as one of the main constituents (Lieberman et al., 2020), but the increase in calcite content from an average of 26.8% in the LŠ bare samples to 79.3% in the vegetated samples (in LŠ3-1 94%) also indicates a pedogenic origin of calcite. In Plaški, calcite content was similar in the bare and vegetated samples, but a decrease with depth was observed in the vegetated ones. This is consistent with the observations in previous studies that calcite is leached from the topsoil as pedogenesis progresses (Uzarowicz et al., 2018b).

Some minerals, such as dolomite, tridymite, pyrite, quartz, and sulfur, most likely originate from original ashes. Pyrite and quartz are typical primary minerals of coal ashes (Hower et al., 2017a; Van Dyk et al., 2009; Verma et al., 2015), and tridymite is formed at temperatures above 867 °C (Hower et al., 2017b; White and Case, 1990).

For some minerals, their origin cannot be distinguished with certainty. Hematite, anorthite and graphite were not found in fresh Raša ashes (Lieberman et al., 2020), but they are usually a primary mineral in coal ashes (Hower et al., 2017b). In addition, some clay minerals, such as kaolinite, illite, and montmorillonite, can originate from fresh ashes, but can also be formed by weathering or can have allochthonous origin

(Uzarowicz et al., 2018b). Montmorillonite was found in every Plaški sample, and its content reaches up to 27.5%. Considering that montmorillonite can be found in fresh ashes, it could be inherited from the original coal and ash in Plaški samples (Barnes et al., 1986; Vassilev and Vassileva, 1996). In addition, its content decreases with increasing depth and is more abundant in samples with vegetation. Therefore, it is likely that it was formed by weathering of Plaški samples as well. Montmorillonite typically forms by weathering in alkaline environments and requires abundance of silica. It also forms by weathering of volcanic ash (Ferris, 2006), and coal ash has been compared to volcanic ash, namely in pH values and silica content (Krishnan et al., 2017). Nevertheless, future studies should deal with developing a method for distinguishing the origin of selected minerals.

The results suggest that, despite differences in type of coal burned, furnace conditions, and climate, several secondary minerals, such as ettringite, hydrotalcite, gypsum, and calcite, form during weathering of alkaline coal ash, and their content changes as soil formation progresses. In addition, mineralogy of bare and vegetated samples points to the same conclusion observed by difference in pH. Štrmac landfill is characterized by both 2nd and 3rd stage of landfill evolution, while in Plaški, characteristics of bare sample are similar to vegetated samples, characterizing it as 3rd stage.

3.1.3. Contribution of non-crystalline fraction

The ^{29}Si NMR was used to characterize the level of glass depolymerization in selected samples (LŠ10-1, LŠ7, and LŠ5-1). Typically, coal fly and bottom ash contain significant content of amorphous phase (>60%) (Chancey et al., 2010), which mainly consist of aluminosilicate glass, organic matter and unburnt coal (Uzarowicz et al., 2018). Aluminosilicate glass is formed during combustion when silicate minerals from coal decompose due to high temperature and then, due to rapid cooling, form amorphous glassy particles instead of crystals. The glass structure can become depolymerized if there is a large presence of oxides of alkali and alkaline earth metals (Hemmings and Berry, 1987). The degree of glass depolymerization impacts the reactivity of glassy phase, thus impacting nutrient and pollutant release (Aughenbaugh et al., 2013; Hemmings and Berry, 1987).

Considering that the amorphous fraction reaches up to 60% in our samples, we have acquired ^{29}Si NMR spectra of selected samples. Since ^{29}Si NMR can be used for both characterization of minerals and amorphous fraction (Barnes et al., 1986), we chose three samples that do not have or have minor content of silicate minerals to focus on amorphous phase (LŠ5-1, LŠ7, LŠ10-1). We did not observe any signals in ^{29}Si CP-MAS NMR spectra indicating the absence of any hydrated silicates. This confirmed that there are no hydrated clay minerals in our chosen Štrmac samples. Therefore, a single-pulse excitation ^{29}Si MAS NMR experiments were conducted, and the corresponding spectra are shown in Fig. 3.b.

^{29}Si MAS NMR spectrum of bare sample LŠ10-1 exhibits two signals at $\delta -71.1$ ppm and $\delta -85.5$ ppm, which are on the broad hump between ca. $\delta -60$ and -105 ppm. The resonance at $\delta -71.1$ ppm is assigned to the coordination units of Q^0 (Monomer) and Q^1 (Si end group), while the signal at $\delta -85.5$ ppm belongs to the coordination unit of Q^2 (Si middle group). Based on the broad hump we could also conclude that Si branching groups Q^3 are present in sample LŠ10-1, however to a lesser extent (Netzel, 1991).

^{29}Si MAS NMR spectrum of a vegetated sample (LŠ5-1) exhibits one signal at $\delta -91.1$ ppm and a shoulder at ca. $\delta -85.5$ ppm, which belong to coordination units of Q^2 (Si middle group). All signals are on the broad hump, which is in the case of sample LŠ5-1 slightly shifted upfield in comparison to sample LŠ10-1 and is between ca. $\delta -70$ and -120 ppm. Hence, the Si with coordination unit of Q^3 and with Q^4 (Si cross-linking group) are also present in sample LŠ5-1. The presence of Si with coordination unit of Q^0 and Q^1 is much smaller in comparison to sample LŠ10-1.

The least intense signals were observed for soil sample LŠ7. Only a

broad hump was observed in ^{29}Si MAS NMR spectrum of sample LŠ7 which, however, extends as in the LŠ5-1 sample between δ ca. -70 and -120 ppm indicating the presence of the Si with coordination units of Q^0 , Q^1 , Q^3 and Q^4 . It should be mentioned that signals corresponding to Q^0 and Q^1 are slightly more intense than in sample LŠ5-1.

The less intense signals in LŠ7 were expected considering that the measured sample is soil, having the least amount of aluminosilicate glass in its amorphous fraction. That soil sample was collected on the edge of the upper part of the landfill (Fig. 1.b.), thus some peaks were similar to ash samples most likely due to presence of ash particles.

The ^{29}Si NMR results of ash samples (LŠ5-1, LŠ10-1) indicate the co-existence of different aluminosilicate glasses, from highly polymerized to highly depolymerized with many non-binding oxygens. However, peaks of Si groups that indicate the higher degree of depolymerization (Q^0 and Q^1) dominated the bare sample LŠ10-1 (Fig. 2). Therefore, glassy phase in bare samples is more depolymerized than in vegetated sample (LŠ5-1). Typically, the reason for depolymerization of silicate chains in ash samples is high content of CaO. The SiO_2 , Al_2O_3 , and CaO ratio in our samples (Table 2) further confirms the cause of higher degree of glass depolymerization in bare samples. Bare samples had up to 38.5% CaO, 4.73% Al_2O_3 and 4.08% SiO_2 (Table 2). However, vegetated sample also had high content of CaO (up to 45%) and yet, the degree of glass depolymerization is lower. Therefore, it is likely that pedogenic process that lowered the pH and changed the mineral assemblage, also changed the glass structure. It is generally accepted that glass reactivity increases with increasing depolymerization of the glass structure (Hemmings and Berry, 1987), therefore the depolymerized glasses were likely attacked first by soil forming processes in vegetated sample.

For the environmental management of coal ash, the rate of release of potentially toxic elements will also be influenced by the ways in which they are incorporated in the non-crystalline parts of coal ash (Choi et al., 2002). Future studies should address both the distribution and release mechanism of trace elements from the glassy phase of coal ash considering its abundant content in ash.

3.1.4. Increase in pedogenic organic matter

Increase in organic matter content is one of the main indicators of early pedogenesis. However, coal ashes usually contain high amount of unburned carbon which hinders the use of total organic matter as an indicator. The latter was confirmed by the obtained results as the average content of total organic carbon (TOC) at Štrmac and Plaški landfills was 14.1% (± 1.21) and 8.07% (± 2.20), respectively, and there was no statistically significant difference ($p < 0.05$) in TOC content between bare and vegetated samples. For comparison, in the study of three coal ash landfills in Serbia, TOC values ranged from 1.46% at landfills with abundant vegetation to 3.19% for recently disposed ash (Kostić et al., 2018). In landfills in Poland, values ranged from 1.7% for fresh ashes, up to 13.7% (2.1% on average) in soils developed from lignite ashes and up to 19.9% (5.7% on average) in soils developed from bituminous coal ashes (Uzarowicz et al., 2017). Higher values of TOC in our samples most likely stem from insufficient burning time and temperature. This is likely for both of studied landfills because ashes originate from small-scale power plants used solely by a foundry (Štrmac) and a sulfate pulp factory (Plaški) without developed advanced combustion technologies.

To get a better insight into the nature of the carbon atoms as well as identification of existing functional groups and consequently the chemical structure of waste material we have acquired ^{13}C CP-MAS NMR spectra of selected Štrmac samples (LŠ5-1, LŠ7, LŠ10-1). ^{13}C CP-MAS NMR spectra of samples LŠ10-1 and LŠ5-1 exhibit broad signals between δ 0 and 50 ppm and between δ 100 and 160 ppm. Based on the literature data, the following carbon atoms can be present within the broad signals between δ 0 and 50 ppm: aliphatic CH_3 carbons (δ 0–16 ppm), aromatic CH_3 carbons (δ 16–25 ppm), CH and CH_2 carbons (25–36 ppm), and quaternary carbon (36–51 ppm). Broad signals between δ 100 and 160 ppm reflect the presence of protonated and non-protonated aromatic carbon atoms (Netzel, 1991). In addition, quite an intense signal at δ 168.5 ppm was observed for sample LŠ10-1 corresponding to carbonyl/carboxyl carbon atoms. This signal was much

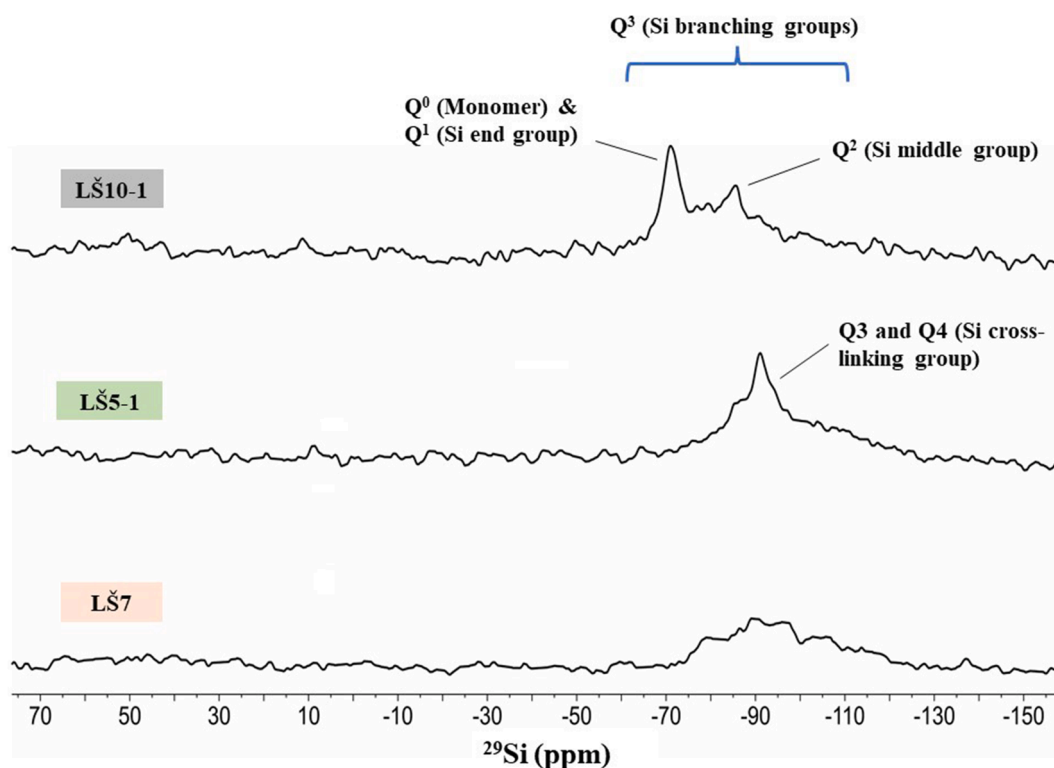


Fig. 2. ^{29}Si NMR spectra of three surface samples from Štrmac landfill with different characteristics (LŠ10 has no vegetation, LŠ5 has vegetation, and LŠ7 is soil partially mixed with ash).

Table 2

Average content of major oxides (Al_2O_3 , CaO and SiO_2), macronutrients (Ca, K, Mg, P, and S), total organic carbon (TOC), total nitrogen (N_{tot}), C/N ratio, clay content (%), cation exchange capacity (CEC, $\text{cmol}_+ \text{kg}^{-1}$), and specific surface area (SSA, m^2/g) in samples collected at Štrmac (LŠ) and Plaški (LP) landfills, grouped according to sample characteristics (total, bare, vegetated, soil). Data for every sample collected is available in [Supplementary Table 3 and 4](#).

	SiO_2	Al_2O_3	CaO	Mg	P	S	Ca	K	TOC	N_{tot}	C/N	Clay	CEC	SSA
LŠ	4.11	6.08	35.2	1.10	0.02	2.61	26.0	0.08	14.1	0.16	249	4.87	18	10.5
LŠ - bare	3.04	3.90	35.0	1.46	0.01	4.33	23.5	0.05	13.4	0.16	196	3.81	25	10.9
LŠ - veg	5.17	7.39	42.7	0.75	0.03	0.89	28.6	0.11	15.3	0.16	342	5.92	10	10.1
LŠ - soil	7.37	15.3	13.3	0.70	0.05	1.89	9.86	0.77	9.05	0.28	31	9.96	29	16.9
LP	–	–	–	1.12	0.05	0.54	14.7	0.50	7.62	0.07	630	6.81	62	29.3
LP - bare	–	–	–	1.22	0.05	0.72	15.8	0.47	7.84	0.09	503	7.51	64	31.9
LP - veg	–	–	–	1.01	0.05	0.37	13.6	0.52	7.01	0.03	986	5.94	59	25.6
LP - soil	–	–	–	0.96	0.04	0.49	7.34	0.79	13.6	0.30	45	7.33	41	21.6

weaker for sample LŠ5-1. The least intense signals for carbon atoms were found in sample LŠ7 indicating the lowest amount of such molecules containing carbon atoms (Fig. 3.).

The peaks observed are similar to ^{13}C NMR spectra for SHOS (super-high-organic-sulfur) Chinese coals (Wei, 2018). Typically, coal contains a higher proportion of hydrophobic moieties, such as alkyl C ($0\text{--}45 \text{ cm}^{-1}$) and aromatic C ($110\text{--}140 \text{ cm}^{-1}$). Since the Štrmac ash originates from SHOS Croatian coals (Medunić et al., 2016b), our peaks indicate that the organic matter observed in samples originates from unburned coal particles. Although Dick et al. (2006) noted that peaks between 60 and 90 ppm point to the accumulated organic matter (corresponding to O-alkyl carbon), no peaks were observed in this range. At this point, we could not identify any C atoms corresponding to accumulated organic matter. However, we observed a decrease in the intensity of signals in the vegetated sample (LŠ5-1), which could point to the degradation or transformation of unburned particles during natural succession.

Nitrogen content is also an indicator of accumulation of organic matter since it is typically not abundant in coal ash but increases with formation of pedogenic organic matter (Chu, 2008; Kostić et al., 2018; Šourková et al., 2005). The average content of total nitrogen (N_{tot}) at Štrmac and Plaški landfills was $0.16 (\pm 0.05)$ and $0.10\% (\pm 0.09)$, respectively. The values were similar to those reported for coal ash Technosols in Poland (0.13%) (Uzarowicz et al., 2017) and Serbia (0.02 to 0.19%), although in those studies a clear increase in nitrogen content was observed as soils and vegetation developed. In our study, there was

no statistically significant difference ($p < 0.05$) in N_{tot} content between bare and vegetated samples. Cemented samples at the Plaški landfill had the lowest nitrogen content (0.001%), but other bare samples had N_{tot} similar to vegetated ones. This suggests the formation of pedogenic matter even in unvegetated samples, further confirming the 3rd stage of landfill evolution. Cemented samples seem to be hardly affected by soil-forming as found for Technosols in Poland (Uzarowicz et al., 2018) and most likely reflect original N_{tot} values. This is also confirmed by high ettringite content in cemented samples (up to 43.3%).

As other authors mentioned, decrease in C:N ratio is a great indicator of accumulation of organic matter in coal ash Technosols. Typically, total nitrogen content increases with pedogenesis and therefore C:N ratio lowers from a value of several hundred to approximately a dozen (Kostić et al., 2018; Uzarowicz et al., 2017). Average C:N was 86 and 82 in bare samples at Štrmac and Plaški landfill, respectively, and 94 and 72 in samples with vegetation. However, the values are highly heterogeneous and reach up to 1532 (Table S4) which is high considering values reported in the literature (up to 336) (Kostić et al., 2018; Uzarowicz et al., 2017). Lower C:N values in vegetated samples at Plaški landfill point to the accumulation of organic matter. However, lower C:N values in bare Štrmac samples is contradictory. ^{13}C CP-MAS NMR spectra could resolve the inconclusive C:N ratios. The peak at 168.5 corresponds to amides (type of carboxyl C), which contain nitrogen. All three samples (LŠ10-1, LŠ5-1, and LŠ7) had similar N_{tot} content (0.25, 0.20, 0.35, respectively) but no (intense) peaks at 168.5 were observed in LŠ5-1 and

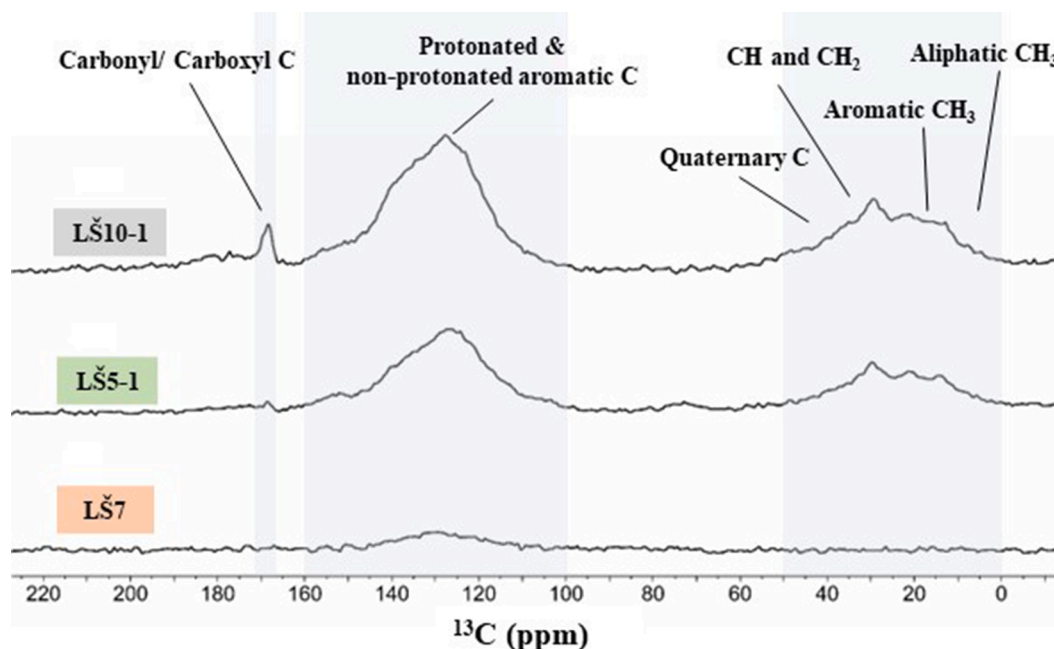


Fig. 3. ^{13}C NMR spectra of three surface samples from Štrmac landfill with different characteristics (LŠ10 has no vegetation, LŠ5 has vegetation, and LŠ7 is soil partially mixed with ash).

LŠ7 samples. This could point to the different origins of N_{tot} . In LŠ10-1, a bare sample from Štrmac landfill, N_{tot} probably originates from amides inherited from the Raša coal, while in other samples, vegetated and soil samples, most likely from the accumulation of organic matter.

3.2. Capacity of aged coal ash to hold water, nutrients, and contaminants

3.2.1. Content of macronutrients (Ca, K, Mg, P, and S)

The concentrations of the measured macronutrients (Ca, K, Mg, P, and S; Table 2) did not follow the same distribution in both landfills. In the Štrmac samples, Mg and S were 2 to 4 times higher in the bare samples than in the samples with vegetation, while P and K were 3 times higher in samples with vegetation. In the Plaški samples, only S content was 2 times higher in bare samples, while other elements had similar distribution in both types of samples.

The decrease in sulfur content is consistent with the leaching of sulphate minerals (gypsum and ettringite) previously discussed, while the increase in phosphorus content seems to be typical of soil formation on various human artefacts as found in soils developed on spoil heaps after brown-coal mining in the Czech Republic (Šourková et al., 2005). High sulfur content in Štrmac samples is a legacy of Raša coal, a coal with one of the highest organic-sulfur-content in the world (Medunić et al., 2016b; Sinninghe Damsté et al., 1999). Such high sulfur content could increase soil salinity and limit plant growth (Chu, 2008) which could be one of the reasons why Štrmac evolves more slowly than Plaški. In addition, Plaški samples have higher P and K content, which are typically scarce and insoluble in coal ash yet essential for plant growth (Izquierdo and Querol, 2012).

3.2.2. Texture, clay content, CEC, and SSA

The texture of ash is important for supporting plant communities as it affects water and nutrient holding capacity. Plaški samples had finer grain texture ranging from silty loam to sandy loam texture, compared to Štrmac samples exhibiting predominately sandy loam texture (Table S3 and S4). The difference in texture between these two landfills is likely the result of the type of coal burned and ash disposed of. A similar observation was made by Uzarowicz et al. (2017) where layers with high proportion of the silt fraction were composed of fly ash and those with a texture of sand were composed of bottom ash. In Plaški, it is not known what type of ash was disposed of, but it could be a mixture of fly ash and bottom ash, while in Štrmac bottom ash was disposed predominantly, corresponding to a sandy loam texture.

Both landfills had higher clay content than landfills described in the literature. The average clay content of previously investigated coal ash Technosols ranged from 2 to 3% (Kostić et al., 2018; Uzarowicz et al., 2017; Zikeli et al., 2005) while studied landfills had 4.87% (Štrmac) and 6.81% (Plaški). In Štrmac, the vegetated samples had a higher clay content (5.92%) than the bare samples (3.81%), while in Plaški bare samples had a higher clay content (7.51%) than the vegetated samples (5.94%). An increase in clay content is a typical feature of aged coal ash landfills (Kostić et al., 2018; Uzarowicz et al., 2017; Zikeli et al., 2005), so it is unusual for samples with vegetation in Plaški to have lower clay content.

Values of cation exchange capacity (CEC) ranged from 2.79 to 44.6 $\text{cmol}_+ \text{kg}^{-1}$ (avg. 17.8 $\text{cmol}_+ \text{kg}^{-1}$) in Štrmac samples and from 30.2 to 89.3 $\text{cmol}_+ \text{kg}^{-1}$ (avg. 61 $\text{cmol}_+ \text{kg}^{-1}$) in Plaški samples (Table 2, Table S3 and S4). Lower values in Štrmac samples could be caused by higher pH of Štrmac samples and high content of montmorillonite in Plaški samples.

At Štrmac landfills, bare samples had higher CEC values than vegetated ones (25 $\text{cmol}_+ \text{kg}^{-1}$ bare, 10 $\text{cmol}_+ \text{kg}^{-1}$ vegetated) while in Plaški values were similar (64 $\text{cmol}_+ \text{kg}^{-1}$ bare, 59 $\text{cmol}_+ \text{kg}^{-1}$ vegetated). The literature reports conflicting observations with no obvious trends in the change of CEC values with coal ash age. Increase in CEC values from 36.8 to 68.7 $\text{cmol}_+ \text{kg}^{-1}$ was observed in coal ash landfills in Serbia (Kostić et al., 2018), while decrease in CEC values was found in lignite-

ash-derived soils from Germany (Zikeli et al., 2004).

Lower CEC values in Štrmac vegetated samples could be caused by multiple factors, such as decrease in pH as proposed for lignite-ash-derived soils in Germany (Zikeli et al., 2004). In addition to pH, an increase in pedogenic organic matter could potentially decrease CEC in vegetated samples. While organic matter can contribute to higher CEC values, it can also promote aggregation of clay mineral particles, thus limiting availability of their surfaces, and lowering CEC values (Ivanić et al., 2020).

Specific surface area (SSA) values ranged from 5.4 to 18.6 m^2/g in Štrmac samples and from 13.1 to 40.8 m^2/g in Plaški samples (Table 2, Table S3 and S4). At both landfills, there was no observable difference between bare and vegetated samples, while in Plaški, the bare samples had higher SSA values. Higher SSA values in Plaški, compared to Štrmac, are most likely due to several factors. One factor that leads to higher SSA values is the presence of montmorillonite, which was determined only in Plaški samples. Of all the observed clay minerals, montmorillonite has the highest SSA value (Kabata-Pendias, 2010) and was present in Plaški samples up to 27.5%. In addition, unburned carbon can increase SSA due to the well-developed porosity of the carbon particles (Yeboah et al., 2014) which depends on the coal rank, i.e. the higher the coal rank, the lower the SSA values (Bartoňová, 2015; Hower et al., 2017b). The Raša coal is bituminous coal (Medunić et al., 2016b), while coal combusted in Plaški is unknown. However, due to the higher degree of cementation at the Plaški landfill and its faster development, Plaški CCR seems to originate from lower rank coal, and thus has higher SSA values. This is consistent with the literature, which found that ashes from lower ranked coals tend to cement and are more reactive than ashes from higher ranked coals (Uzarowicz et al., 2018).

Since Plaški landfill has higher clay content, CEC, and SSA values, it has a better capacity to hold nutrients and water and support plant communities. This could be one of the reasons why Plaški landfill seems to develop faster, despite the similar age of the waste deposits. Almost all samples collected at the Plaški landfill could be characterized by the 3rd phase of landfill evolution, regardless of presence of vegetation. In comparison, Štrmac samples show greater differences between the bare and vegetated samples. Despite the lower ability of Štrmac to retain water and nutrients, Štrmac also has a high content of leachable sulfur (Petrović et al., 2022) which can increase electroconductivity (EC). The high EC values were found to be a limiting factor for vegetation in coal ash Technosol in Hong Kong (Chu, 2008), so future studies should address this issue.

4. Conclusions

In summary, weathering of the alkaline coal combustion residues studied resulted in a decrease in pH and precipitation of secondary minerals such as ettringite, gypsum, hydrotalcite, and calcite, despite differences in the type of coal burned, furnace conditions, and climate. The mineralogy and high pH indicate that the bare part of the Štrmac landfill is still dominated by abiotic processes (2nd stage of landfill evolution), while both the bare and vegetated samples from the Plaški landfill show signs of early pedogenesis (3rd stage), probably due to combustion of lower rank coal in Plaški. Furthermore, the high sulfur content in the Štrmac landfill, originating mainly from superhigh-organic-sulfur Raša coal, proves to be an aggravating parameter, increasing the salinity of the soil and limiting plant growth, contributing to slower development than in Plaški. Although values for SSA and CEC were highly heterogenous, they showed trends between bare and vegetated samples. Overall, Plaški has better capacity to retain water, nutrients, and pollutants due to its higher clay content and CEC and SSA values, which is likely caused by multiple factors, such as high content of montmorillonite and unburned carbon originating from lower rank coal. The presence of clay minerals, especially montmorillonite, may even be crucial for pedogenesis, as they contain both water and nutrients in their structure. In addition, the Plaški landfill has a greater capacity to adsorb

contaminants, and therefore probably has a lower impact on the environment, which should be investigated in further studies through leaching tests. The data obtained from this study not only improved our understanding of how particle properties, as indicated by CEC and SSA, change with waste age, but also illuminated the additional insights that NMR spectra can provide, improving our understanding of the pedogenesis of widespread coal ash landfills.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catena.2023.107338>.

References

- Aughenbaugh, K.L., Stutzman, P., Juenger, M.C.G., 2013. Assessment of the glassy phase reactivity in fly ashes used for geopolymer cements. *ASTM Spec. Tech. Publ.* 1566 STP, 11–20. <https://doi.org/10.1520/stp156620120105>.
- Barnes, J.R., Clague, A.D.H., Clayden, N.J., Dobson, C.M., Jones, R.B., 1986a. The application of ^{29}Si and ^{27}Al solid state n.m.r. spectroscopy to characterising minerals in coals. *Fuel* 65, 437–441. [https://doi.org/10.1016/0016-2361\(86\)90311-X](https://doi.org/10.1016/0016-2361(86)90311-X).
- Bartoňová, L., 2015. Unburned carbon from coal combustion ash: an overview. *Fuel Process. Technol.* 134, 136–158. <https://doi.org/10.1016/j.fuproc.2015.01.028>.
- Brandt, J.E., Bernhardt, E.S., Dwyer, G.S., Di Giulio, R.T., 2017. Selenium ecotoxicology in freshwater lakes receiving coal combustion residual effluents: a north carolina example. *Environ. Sci. Technol.* 51, 2418–2426. <https://doi.org/10.1021/acs.est.6b05353>.
- Brandt, J.E., Lauer, N.E., Vengosh, A., Bernhardt, E.S., Di Giulio, R.T., 2018. Strontium isotope ratios in fish otoliths as biogenic tracers of coal combustion residual inputs to freshwater ecosystems. *Environ. Sci. Technol. Lett.* 5, 718–723. <https://doi.org/10.1021/acs.estlett.8b00477>.
- Busenberg, E., Clemency, C.V., 1973. Determination of the cation exchange capacity of clays and soils using an ammonia electrode. *Clays Clay Miner.* 21, 213–217. <https://doi.org/10.1346/CCMN.1973.0210403>.
- Chancey, R.T., Stutzman, P., Juenger, M.C.G., Fowler, D.W., 2010. Cement and concrete research comprehensive phase characterization of crystalline and amorphous phases of a Class F fly ash. *Cem. Concr. Res.* 40, 146–156. <https://doi.org/10.1016/j.cemconres.2009.08.029>.
- Choi, S.K., Lee, S., Song, Y.K., Moon, H.S., 2002. Leaching characteristics of selected Korean fly ashes and its implications for the groundwater composition near the ash disposal mound. *Fuel*. [https://doi.org/10.1016/S0016-2361\(02\)00006-6](https://doi.org/10.1016/S0016-2361(02)00006-6).
- Chu, L.M., 2008. Natural revegetation of coal fly ash in a highly saline disposal lagoon in Hong Kong. *Appl. Veg. Sci.* 11, 297–306. <https://doi.org/10.3170/2008-7-18427>.
- Crnić, A.P., Damijanić, D., Bilandžić, N., Sedak, M., Medunić, G., 2022. Enhanced levels of hazardous trace elements (Cd, Cu, Pb, Se, Zn) in bird tissues in the context of environmental pollution by Raša coal. *Rud. Geol. Naft. Zb.* 37, 19–30. <https://doi.org/10.17794/rgn.2022.1.3>.
- Daniell, A., van Deventer, P.W., 2018. An overview of pedogenesis in Technosols in South Africa. *South African J. Plant Soil* 35, 281–291. <https://doi.org/10.1080/02571862.2018.1470265>.
- Dick, D.P., Knicker, H., Ávila, L.G., Inda, A.V., Giasson, E., Bissani, C.A., 2006. Organic matter in constructed soils from a coal mining area in southern Brazil. *Org. Geochem.* 37, 1537–1545. <https://doi.org/10.1016/j.orggeochem.2006.06.017>.
- Earthjustice, 2021. CCR Rule Compliance [WWW Document]. accessed 4.20.21. <https://docs.google.com/spreadsheets/d/1SF6KTLrFSkPgJJaKQyN6ZKoYp6k6ZHQVdCAGi7rng/edit#gid=0>.
- Ferris, J.P., 2006. Montmorillonite-catalysed formation of RNA oligomers: the possible role of catalysis in the origins of life. *Philos. Trans. R. Soc. B* 361, 1777–1786. <https://doi.org/10.1098/rstb.2006.1903>.
- Fiket, Ž., Medunić, G., Vidaković-Cifrek, Ž., Jezidžić, P., Cvjetko, P., 2020. Effect of coal mining activities and related industry on composition, cytotoxicity and genotoxicity of surrounding soils. *Environ. Sci. Pollut. Res.* 27, 6613–6627. <https://doi.org/10.1007/s11356-019-07396-w>.
- Fiket, Z., Mikac, N., Kniewald, G., 2016. Mass fractions of forty-six major and trace elements, including rare earth elements, in sediment and soil reference materials used in environmental studies. *Geostand. Geoanalytical Res.* 41, 123–135. <https://doi.org/10.1111/ggr.12129>.
- Filipčić, A., 2001. Boundary separation of Köppen's climatic types Cf and Cs in Croatia. *Acta Geogr. Croat.* 35, 7–18. Croatian.
- Gajić-Čapka, M., Perčec Tadić, M., Patačić, M., 2003. Digital annual precipitation map of Croatia/Digitalna godišnja oborinska karta Hrvatske. *Hrvat. Meteorološki Casopis* 38, 21–33.
- Grünwald, G., Kaiser, K., Jahn, R., 2007. Alteration of secondary minerals along a time series in young alkaline soils derived from carbonatic wastes of soda production 71, 487–496. <https://doi.org/10.1016/j.catena.2007.03.022>.
- Harris, D., Heidrich, C., Feuerborn, J., 2019. Global aspects on Coal Combustion Products. *VGB Power tech* 25–33.
- Hassett, D.J., Pflughoeft-Hassett, D.F., Heebink, L.V., 2005. Leaching of CCBs: observations from over 25 years of research. *Fuel* 84, 1378–1383. <https://doi.org/10.1016/j.fuel.2004.10.016>.
- Hemmings, R.T., Berry, E.E., 1987. On the glass in coal fly ashes: recent advances. *MRS Proc.* 113 <https://doi.org/10.1557/proc-113-3>.
- Hower, J.C., Groppo, J.G., Graham, U.M., Ward, C.R., Kostova, I.J., Maroto-Valer, M.M., Dai, S., 2017a. Coal-derived unburned carbons in fly ash: A review. *Int. J. Coal Geol.* 179, 11–27. <https://doi.org/10.1016/j.coal.2017.05.007>.
- J.C. Hower K.R. Henke S. Dai C.R. Ward D. French S. Liu U.M. Graham Generation and nature of coal fly ash and bottom ash 2017 Characteristics, Utilization and Beneficiation. Elsevier Ltd. Coal Combustion Products (CCPs) 10.1016/B978-0-08-100945-1.00002-2.
- IUSS Working Group WRB, 2022. World Reference Base for Soil Resources. International soil classification system for naming soils and creating legends for soil maps, 4th ed. International Union of Soil Sciences (IUSS), Vienna, Austria.
- Ivanić, M., Durn, G., Škapin, S.D., Sondi, I., 2020. Size-related mineralogical and surface physicochemical properties of the mineral particles from the recent sediments of the Eastern Adriatic Sea. *Chemosphere* 249, 126531. <https://doi.org/10.1016/j.chemosphere.2020.126531>.
- Izquierdo, M., Querol, X., 2012. Leaching behaviour of elements from coal combustion fly ash: An overview. *Int. J. Coal Geol.* 94, 54–66. <https://doi.org/10.1016/j.coal.2011.10.006>.
- Johnson, C.A., Kaeppli, M., Brandenberger, S., Ulrich, A., Baumann, W., 1999. Hydrological and geochemical factors affecting leachate composition in municipal solid waste incinerator bottom ash. *J. Contam. Hydrol.* 40, 239–259. [https://doi.org/10.1016/S0169-7722\(99\)00052-2](https://doi.org/10.1016/S0169-7722(99)00052-2).
- Kabata-Pendias, A., 2010. Trace Elements in Soils and Plants, 4th ed. CRC Press.
- Kanbar, H.J., Matar, Z., Saha, G.A.A.H., Kazzard, V., 2020. Selective metal leaching from technosols based on synthetic root exudate composition. *J. Environ. Sci. (China)* 96, 85–92. <https://doi.org/10.1016/j.jes.2020.04.040>.
- Konstantinov, A., Novoselov, A., Konstantinova, E., Loiko, S., Kurasova, A., Minkina, T., 2020. Composition and properties of soils developed within the ash disposal areas originated from peat combustion (Tyumen, Russia). *Soil Sci. Annu.* 71, 3–14. <https://doi.org/10.37501/soilsa/121487>.
- Kostić, O., Jarić, S., Gajić, G., Pavlović, D., Pavlović, M., Mitrović, M., Pavlović, P., 2018. Pedological properties and ecological implications of substrates derived 3 and 11 years after the revegetation of lignite fly ash disposal sites in Serbia. *Catena* 163, 78–88. <https://doi.org/10.1016/j.catena.2017.12.010>.
- Krishnan, G., Achyuthan, H., Siva, V.H.R., 2017. Comparative Petrophysical and Geochemical Characteristics of Thermal and Volcanic Ash from Southeastern India 90, 20–24. <https://doi.org/10.1007/s12594-017-0659-y>.
- Kruger, R.A., 2017. Introduction to the utilization of coal combustion products: Characteristics, Utilization and Beneficiation. Elsevier Ltd. Coal Combustion Products (CCPs). <https://doi.org/10.1016/B978-0-08-100945-1.00004-6>.
- Leguédols, S., Séré, G., Auclerc, A., Cortet, J., Huot, H., Ouvrard, S., Watteau, F., Schwartz, C., Morel, J.L., 2016. Modelling pedogenesis of Technosols. *Geoderma* 262, 199–212. <https://doi.org/10.1016/j.geoderma.2015.08.008>.
- Lemly, A.D., 2018. Selenium poisoning of fish by coal ash wastewater in Herrington Lake, Kentucky. *Ecotoxicol. Environ. Saf.* 150, 49–53. <https://doi.org/10.1016/j.ecoenv.2017.12.013>.
- Lieberman, N.R., Izquierdo, M., Muñoz-Quiros, C., Cohen, H., Chenery, S.R., 2020. Geochemical signature of superhigh organic sulphur Raša coals and the mobility of toxic trace elements from combustion products and polluted soils near the Plomin coal-fired power station in Croatia. *Appl. Geochemistry* 114, 104472. <https://doi.org/10.1016/j.apgeochem.2019.104472>.
- Medunić, G., Ahel, M., Mihaljić, I.B., Srček, V.G., Kopjar, N., Fiket, Ž., Bituh, T., Mikac, I., 2016a. Toxic airborne S, PAH, and trace element legacy of the superhigh-organic-sulphur Raša coal combustion: Cytotoxicity and genotoxicity assessment of soil and ash. *Sci. Total Environ.* 566–567, 306–319. <https://doi.org/10.1016/j.scitotenv.2016.05.096>.
- Medunić, G., Kuharić, Ž., Krivohlavek, A., Fiket, Ž., Radenović, A., Gödel, K., Kampić, Š., Kniewald, G., 2018. Geochemistry of Croatian superhigh-organic-sulphur Raša coal, imported low-S coal and bottom ash: Their se and trace metal fingerprints in seawater, clover, foliage and mushroom specimens copyright. *Int. J. Oil, Gas Coal Technol.* 18, 3–24. <https://doi.org/10.1504/IJOGCT.2018.091517>.
- Medunić, G., Radenović, A., Bajramović, M., Švec, M., Tomac, M., 2016b. Once grand, now forgotten: What do we know about the superhigh-organic-sulphur Raša coal? *Rud. Geol. Naft. Zb.* 31, 27–45. <https://doi.org/10.17794/rgn.2016.3.3>.

- Medunić, G., Kuharić, Ž., Fiket, Ž., Bajramović, M., Singh, A.L., Krivohlavek, A., Kniewald, G., Dujmović, L., 2018a. Selenium and other potentially toxic elements in vegetables and tissues of three non-migratory birds exposed to soil, water, and aquatic sediment contaminated with seleniferous Raša coal. *Rud. Geol. Naft. Zb.* 33, 53–62. <https://doi.org/10.17794/rgn.2018.3.6>.
- Medunić, G., Kuharić, Ž., Krivohlavek, A., Đuroković, M., Dropučić, K., Radenović, A., Oberiter, B.L., Krizmanić, A., Bajramović, M., 2018b. Selenium, sulphur, trace metal, and BTEX levels in soil, water, and lettuce from the Croatian Raša bay contaminated by superhigh-organic-sulphur coal. *Geosci.* 8 <https://doi.org/10.3390/geosciences8110408>.
- Miko, S., Durn, G., Adamcová, R., Čović, M., Dubíková, M., Skalský, R., Kapelj, S., Ottner, F., 2003. Heavy metal distribution in karst soils from Croatia and Slovakia. *Environ. Geol.* 45, 262–272. <https://doi.org/10.1007/s00254-003-0878-y>.
- Netzel, D.A., 1991. Multinuclear NMR Approach Coal Fly Ash Characterization. DOE/MC/11076-3200. <https://www.osti.gov/servlets/purl/6687192> (2.5.2023.).
- Oreščanin, V., Kollar, R., Buben, K., Mikelić, I.L., Kollar, K., Kollar, M., Medunić, G., 2012. Chemical and radiological characterization of fly and bottom ash landfill of the former sulfate pulp factory Plaški and its surroundings. *J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng.* 47, 1592–1606. <https://doi.org/10.1080/10934529.2012.680780>.
- Pacwa-Płociniczak, M., Płociniczak, T., Yu, D., Kurola, J.M., Sinkkonen, A., Piotrowska-Seget, Z., Romantschuk, M., 2018. Effect of *Silene vulgaris* and Heavy Metal Pollution on Soil Microbial Diversity in Long-Term Contaminated Soil. *Water. Air. Soil Pollut.* 229 <https://doi.org/10.1007/s11270-017-3655-3>.
- Petrović, M., Fiket, Ž., 2022. Environmental damage caused by coal combustion residue disposal: A critical review of risk assessment methodologies. *Chemosphere* 299, 134410. <https://doi.org/10.1016/j.chemosphere.2022.134410>.
- Petrović, M., Fiket, Ž., Medunić, G., Chakravarty, S., 2022. Mobility of metals and metalloids from SHOS coal ash and slag deposit: mineralogical and geochemical constraints. *Environ. Sci. Pollut. Res.* 29, 46916–46928. <https://doi.org/10.1007/s11356-022-19074-5>.
- Radić, S., Medunić, G., Kuharić, Ž., Roje, V., Maldini, K., Vujčić, V., Krivohlavek, A., 2018. The effect of hazardous pollutants from coal combustion activity: Phytotoxicity assessment of aqueous soil extracts. *Chemosphere* 199, 191–200. <https://doi.org/10.1016/j.chemosphere.2018.02.008>.
- Šegota, T., Filipčić, A., 2003. Köppen's classification of climates and the problem of corresponding Croatian terminology. *Geoadria* 8, 17–37.
- Séré, G., Schwartz, C., Ouyard, S., Renat, J.C., Watteau, F., Villemain, G., Morel, J.L., 2010. Early pedogenic evolution of constructed Technosols. *J. Soils Sediments* 10, 1246–1254. <https://doi.org/10.1007/s11368-010-0206-6>.
- Šikić, D., Polšak, A., Magaš, N., 1969. Osnovna geološka karta SFRJ 1:100 000, List Labin L33–101. Institut za geološka istraživanja, Zagreb.
- Sinninghe Damsté, J.S., White, C.M., Green, J.B., De Leeuw, J.W., 1999. Organosulfur compounds in sulfur-rich Raša coal. *Energy and Fuels* 13, 728–738. <https://doi.org/10.1021/ef980236c>.
- Šourková, M., Frouz, J., Šantrůčková, H., 2005. Accumulation of carbon, nitrogen and phosphorus during soil formation on alder spoil heaps after brown-coal mining, near Sokolov (Czech Republic). *Geoderma* 124, 203–214. <https://doi.org/10.1016/j.geoderma.2004.05.001>.
- Ugolini, F., Baronti, S., Lanini, G.M., Maenza, A., Ungaro, F., Calzolari, C., 2020. Assessing the influence of topsoil and technosol characteristics on plant growth for the green regeneration of urban built sites. *J. Environ. Manage.* 273, 111168 <https://doi.org/10.1016/j.jenvman.2020.111168>.
- Uzarowicz, L., Skiba, M., Leue, M., Zagórski, Z., Gasiński, A., Trzcinski, J., 2018b. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part II. Mineral transformations and soil evolution. *Catena* 162, 255–269. <https://doi.org/10.1016/j.catena.2017.11.005>.
- Uzarowicz, L., Zagórski, Z., 2015. Mineralogy and chemical composition of technogenic soils (Technosols) developed from fly ash and bottom ash from. *Soil Sci. Annu.* 66, 82–91. <https://doi.org/10.1515/ssa-2015-0023>.
- Uzarowicz, L., Zagórski, Z., Mendak, E., Bartmiński, P., Szara, E., Kondras, M., Oktaba, L., Turek, A., Rogoziński, R., 2017. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part I. properties, classification, and indicators of early pedogenesis. *Catena* 157, 75–89. <https://doi.org/10.1016/j.catena.2017.05.010>.
- Uzarowicz, L., Kwasowski, W., Spiewak, O., Switonak, M., 2018a. Indicators of pedogenesis of Technosols developed in an ash settling pond at the Belchatów thermal power station (central Poland). *Soil Sci. Annu.* 69, 49–59. <https://doi.org/10.2478/ssa-2018-0006>.
- Van Dyk, J.C., Benson, S.A., Laumb, M.L., Waanders, B., 2009. Coal and coal ash characteristics to understand mineral transformations and slag formation. *Fuel*. <https://doi.org/10.1016/j.fuel.2008.11.034>.
- Vassilev, S.V., Vassileva, C.G., 1996. Occurrence, abundance and origin of minerals in coals and coal ashes 48, 85–106.
- Verma, C., Madan, S., Hussain, A., 2016. Heavy metal contamination of groundwater due to fly ash disposal of coal-fired thermal power plant, Parichha, Jhansi, India. *Cogent. Eng.* doi:10.1080/23311916.2016.1179243.
- Velić, I., Sokač, B., 1981. Osnovna geološka karta SFRJ 1:100.000, List Ogulin L33–103. Geološki zavod – OOUR za geologiju i paleontologiju.
- Verma, S.K., Masto, R.E., Gautam, S., Choudhury, D.P., Ram, L.C., Maiti, S.K., Maity, S., 2015. Investigations on PAHs and trace elements in coal and its combustion residues from a power plant. *Fuel* 162, 138–147. <https://doi.org/10.1016/j.fuel.2015.09.005>.
- Weber, J., Straczyńska, S., Kocowicz, A., Gilewska, M., Bogacz, A., Gwizdz, M., Debicka, M., 2015. Properties of soil materials derived from fly ash 11years after revegetation of post-mining excavation. *Catena* 133, 250–254. <https://doi.org/10.1016/j.catena.2015.05.016>.
- Wei, Q., 2018. Study on Structure Evolution Characteristics of High-Organic-Sulfur Coals from Typical Chinese Areas. <https://doi.org/10.3390/min8020049>.
- Wentworth, C.K., 1922. A scale of grade and class terms for clastic sediments. *J. Geol.* 30, 377–392. <https://doi.org/10.1086/622910>.
- White, S.C., Case, E.D., 1990. Characterization of fly ash from coal-fired power plants. *J. Mater. Sci.* 25, 5215–5219. <https://doi.org/10.1007/BF00580153>.
- Yeboah, N.N.N., Shearer, C.R., Burns, S.E., Kurtis, K.E., 2014. Characterization of biomass and high carbon content coal ash for productive reuse applications. *Fuel* 116, 438–447. <https://doi.org/10.1016/j.fuel.2013.08.030>.
- Zaninović, K., Gajić-Čapka, M., Perčec Tadić, M., Al, E., 2008. Climate atlas of Croatia / Klimatski atlas Hrvatske 1961–1990, 1971–2000. Državni hidrometeorološki zavod, Zagreb, Croatia.
- Zikeli, S., Jahn, R., Kastler, M., 2002. Initial soil development in lignite ash landfills and settling ponds in Saxony-Anhalt. Germany. *J. Plant Nutr. Soil Sci.* 165, 530–536. [https://doi.org/10.1002/1522-2624\(200208\)165:4<530::AID-JPLN530>3.0.CO;2-J](https://doi.org/10.1002/1522-2624(200208)165:4<530::AID-JPLN530>3.0.CO;2-J).
- Zikeli, S., Kastler, M., Jahn, R., 2004. Cation exchange properties of soils derived from lignite ashes. *J. Plant Nutr. Soil Sci.* 167, 439–448. <https://doi.org/10.1002/jpln.200421361>.
- Zikeli, S., Kastler, M., Jahn, R., 2005. Classification of anthrosols with vitric/andic properties derived from lignite ash. *Geoderma* 124, 253–265. <https://doi.org/10.1016/j.geoderma.2004.05.004>.



Research Paper

Changes in the mobility of oxyanions from coal combustion residues after 50 years of natural weathering

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ABSTRACT

Coal combustion residues (CCR) disposal sites are widespread, yet the influence of pedogenesis on oxyanion mobility remains poorly understood. This study investigates how weathering and early soil formation modify the release of oxyanion-forming elements from two CCR landfills in Croatia, representing different stages of pedogenesis. Four standardized leaching methods (EN 12457-2, TCLP-2, EPA 1313, and 1316), supported by SEM-EDS and FTIR characterization of the samples, were used to quantify pH-dependent and L/S-dependent leaching from vegetated and non-vegetated CCR. Across tests, Plaški samples consistently exhibited higher relative mass leached (RML) compared to Štrmac samples (<10 %), reflecting the greater reactivity and finer texture of the Plaški CCR. EPA 1313 results revealed that pedogenesis modified how elements respond to changing pH. In the vegetated Štrmac sample, As, V and P remained low until pH ~ 10.5, after which their concentrations increased sharply. In contrast, the bare material showed much smaller variations because Ca-bearing phases continued to buffer the system. EPA 1316 results further pointed out that pedogenesis caused a shift in leaching behaviour of certain oxyanions (As, V and P), which leaching pattern changed from available-content to solubility limited leaching. These results demonstrate the importance of incorporating such data into the long-term management plans for these and similar landfills to ensure environmental protection and regulatory compliance.

1. Introduction

About 1.1 billion tons of coal combustion residue (CCR) are generated annually in coal-fired thermal power plants (TPP), with half being disposed of in ponds and landfills (BP, 2020; Harris et al., 2019; Kruger, 2017). These disposal sites serve as final repositories for CCR, which include four types of coal combustion by-products: fly ash, bottom ash, boiler slag, and flue gas desulphurization (FGD) residues (Harris et al., 2019). Even if coal combustion ceases, its legacy will remain in the environment as CCR disposal sites. These materials contain a mixture of inorganic compounds, trace elements, and radionuclides that have the potential to leach into the environment (Petrović and Fiket, 2022).

A critical aspect of CCR environmental assessment is evaluating the release of elements that tend to form oxyanions (e.g. As, Cr, Mo, Se, Sb, V, etc.). These elements are more mobile in an alkaline environment, a common characteristic of CCR, therefore they usually leach in more significant concentrations than commonly investigated heavy metals

(Hassett et al., 2005; Izquierdo and Querol, 2012; Wang, 2007; Zhang et al., 2019). For example, CCR effluents discharging from CCR disposal ponds to lakes in North Carolina (U.S.) were enriched in the mentioned oxyanion species (Ruhl et al., 2012). In addition, these oxyanions can harm biota. Elevated Se concentrations from CCR effluents have caused various deformities in fish and aquatic birds, such as spinal curvatures and abnormal fin, head, and mouth development (Brandt et al., 2017; Lemly, 2018).

The mobility of these elements from CCR is determined by a complex interplay of geochemical processes (Petrović et al., 2022). Key factors affecting element mobility include pH, which alters the speciation of elements and affect their solubility; redox conditions, which affects the valence state of elements; mineralogy, which can adsorb or release elements; and the presence of other ions that can compete for binding sites or affect ion exchange processes. In addition, organic matter and microbial activities within the landfill influence the mobility of the elements through complex interactions (Deonarine et al., 2021; Petrović

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et al., 2022; Petrović and Fiket, 2022; Wang et al., 2022).

However, one factor rarely accounted for in leaching studies is the significant change in coal ash physicochemical characteristics during long-term weathering. After only a few decades of disposal, early pedogenesis and pioneer vegetation have been observed on coal ash disposal sites, causing a decrease in pH and change in mineral and organic matter (Chu, 2008; Kostić et al., 2018; Petrović et al., 2023; Uzarowicz et al., 2018, 2017; Zikeli et al., 2002). For example, a study investigating the two landfills from this study found that pH significantly decreased during weathering from > 12 to 9 (Petrović et al., 2023). In addition, various secondary minerals precipitated, and a decrease in C:N ratio pointed to the accumulation of newly formed organic matter. A decrease in the C:N ratio reflects the input of nitrogen-rich compounds from plant litter and microbial activity into the initially carbon-rich, nitrogen-poor ash, where even small increases in N markedly lower the overall C:N ratio (Kostić et al., 2018; Petrović et al., 2023; Uzarowicz et al., 2017; Zikeli et al., 2002). Considering that pH, mineralogy, and organic matter significantly affect the mobility of trace elements, it is crucial to understand changes in the mobility of elements from materials impacted by long-term weathering. To date, there have been only a few studies addressing the mobility in context of pedogenesis. For example, a decrease in the total content of As, B, Cr, Cu, Mn, Ni and Zn and their mobility was observed in CCR ponds in Serbia after 3 and 11 years revegetation (Kostić et al., 2018). However, that study addressed landfills after engineered, and not natural revegetation.

Considering the lack of leaching studies of naturally weathered CCR and oxyanions, the main objectives of this study are: 1) to quantify the concentrations and leaching behavior of elements prone to form oxyanions, including As, Cr, Mo, P, S, Se, Sb, U and V, within CCR deposits

that have experienced varying degrees of pedogenesis.; 2) to elucidate the mechanisms and factors influencing their mobility in the presence of pedogenetic transformations. By achieving these objectives, our aim is to provide a comprehensive analysis of the long-term dynamics of oxyanions within weathered coal ash deposits, offering insights that can inform environmental management practices and enhance our understanding of contaminant behavior in complex soil systems.

2. Materials and methods

2.1. Study area

This study regards two unlined CCR landfills located in villages Štrmac and Plaški in Croatia (Europe) (Fig. 1) which descriptions are detailed in Petrović et al. (2023).

Briefly, first landfill (LŠ) is situated in Štrmac, a village on Istrian peninsula, the westernmost part of Croatia. It consists of coal bottom ash and slag disposed in 1960 s by a local foundry and covers the area of $\sim 17\,000\text{ m}^2$. The top of the landfill is covered with soil and planted conifers, while the slope is bare, with patches of grass and several other pioneer plant species. The type of coal used was local super-high-organic-sulphur Raša coal, enriched in S, Se, Mo, U, V and Re (Medunić et al., 2018; Medunić et al., 2016).

The second landfill (LP) is situated in Plaški, a village in Lika Region. The landfill consists of $70,000\text{ m}^3$ of fly ash and bottom ash disposed of by the former sulphate pulp factory which operated from 1965 to 1991. The top of the landfill is covered with naturally growing grass, while the slopes are bare, with patches of pioneer plant species. Slopes are cemented, which is often found in such landfills (Weber et al., 2015).

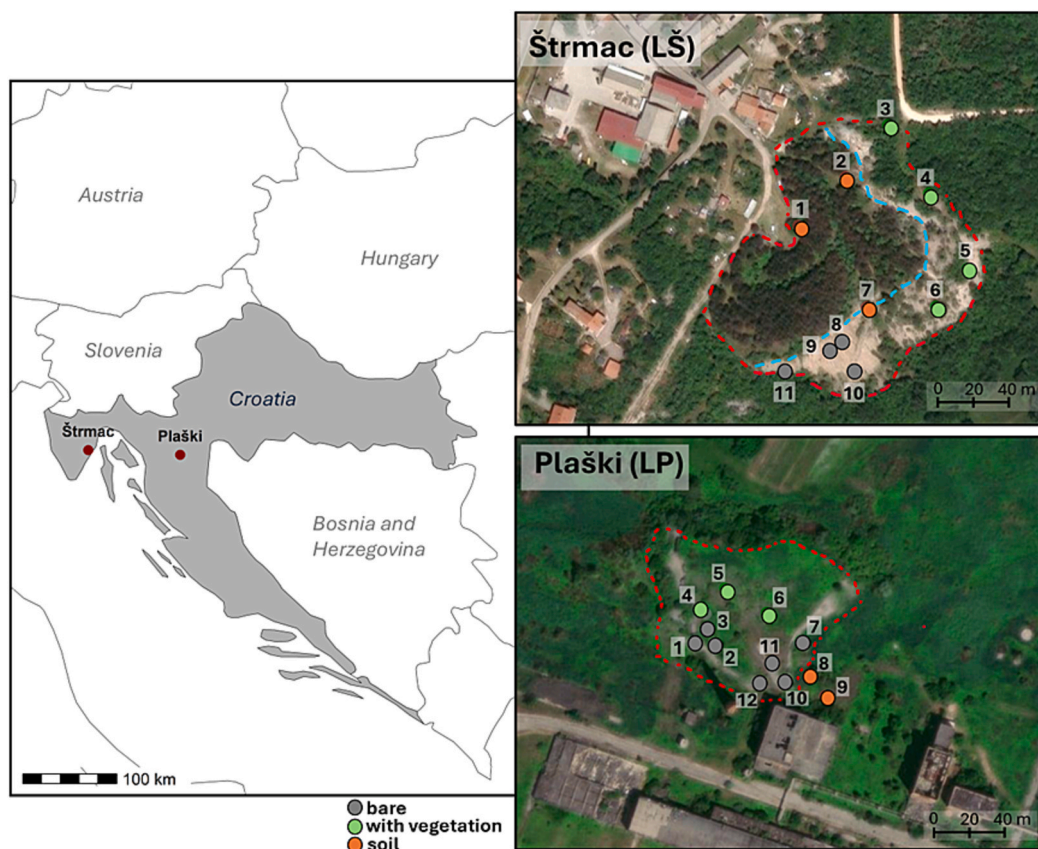


Fig. 1. Study area: map of Croatia and locations of two landfills; sampling locations at the Štrmac landfill; sampling locations at the Plaški landfill. Red dashed lines indicate the approximate boundaries of the landfill areas. In the Štrmac site, an additional blue dashed line marks the boundary between the exposed ash deposit and the section of the landfill that has been covered with soil and planted with conifers. Photographs of representative bare ash, vegetated ash, and soil sampling locations are provided in the Supplementary Material (Fig. S1).

The type of coal burned in the factory is publicly unknown.

A detailed characterization of the physicochemical and mineralogical properties of the samples from these two landfills can be found in Petrović et al. (2023). According to this study, the bare section of the Štrmac landfill is primarily influenced by abiotic processes (2nd stage of landfill evolution), while the vegetated areas show early signs of pedogenesis (3rd stage). In contrast, both the bare and vegetated samples of the Plaški landfill show signs of early pedogenesis (3rd stage).

2.2. Sampling and sample preparation

The sampling campaign was conducted in July 2020 (LŠ) and May 2021 (LP). At both landfills, 69 CCR samples with and without vegetation, hereafter referred to as vegetated and bare samples, were taken together with soil samples. In Štrmac, a total of 29 samples with varying depths were taken at 11 locations (Fig. 1, Table S1). In Plaški, a total of 40 samples with varying depths were taken at 12 locations (Fig. 1, Table S2). The landfill boundaries were identified in the field based on prior site investigation (Medunić et al., 2018) and/or verified visually by distinct differences in vegetation cover and surface morphology compared to the surrounding natural soils.

To clarify, in the following text the superscript numbers accompanying sample names denote the depth of the subsurface layer, such as LŠ1₁ indicating a sample from location LŠ1 taken at a depth of 0 to 10 cm, and LŠ1₂ representing a sample from location LŠ1 taken at a depth of 10 to 20 cm, and so forth.

In the laboratory, all samples were dried in an exhaust air dryer for 24 h at 50 °C, sieved through a 2 mm sieve to remove the gravel fraction and stored until further analysis. For total element and FTIR analysis samples were ground and homogenized in an agate mill. For extraction, sieved samples (<2 mm) were mixed with a specified extraction medium.

2.3. Determination of pH

Two types of pH measurements were performed. The pH of the dry ash material was determined by rehydrating approximately 10 g of sample with 50 mL of Milli-Q water (solid-to-liquid ratio = 1:5, w/v), allowing the suspension to settle for 30 min, and measuring the supernatant pH with a Thermo Scientific™ Orion™ Versa Star Pro™ pH meter, following ISO 10390:2021 guidelines. The pH of the leachates was measured directly in the collected eluate using the same instrument. Before measurement, the pH meter was calibrated with standard buffer solutions with pH values of 4.0, 7.0 and 10.0.

2.4. Sample preparation for total element analysis

For total element analysis, sub-samples (0.05 g), previously homogenized in an agate mill, were subjected to a total digestion in the microwave oven (Multiwave 3000, Anton Paar, Graz, Austria) in a two-step procedure. The latter consisted of digestion with a mixture of 4 mL nitric acid (HNO₃, 65 %, pro analysi, Kemika, Zagreb, Croatia) – 1 mL hydrochloric acid (HCl) – 1 mL hydrofluoric acid (HF, 48 %, pro analysi, Kemika, Zagreb, Croatia) followed by addition of 6 mL of boric acid (H₃BO₃, Fluka, Steinheim, Switzerland). Prior to analysis, digests were 10-fold diluted, acidified with 2 % (v/v) HNO₃ (65 %, supra pur, Fluka, Steinheim, Switzerland) and In (1 µg L⁻¹) as internal standard was added.

2.5. Leachate preparation

Four leaching methods were used to evaluate the mobility of the elements from selected samples. A water extraction was performed using the European Standard Batch Leaching Test (EN 12457–2, CEN, 2002). Milli-Q (MQ) water with a liquid-to-solid ratio of 10:1 (10 mL MQ, 1 g sample) was the extraction medium.

An acid extraction was performed using a modified TCLP-2 method (USEPA, 2015). The extraction solution was prepared by mixing 2.85 mL of acetic acid (CH₃COOH) with 500 mL of Milli-Q water. To ensure comparability with the water extraction and address one of the method's limitations, the liquid-to-solid ratio was adjusted from 20:1 to 10:1 (Petrović and Fiket, 2022). Although the TCLP procedure was originally developed for municipal solid-waste environments, it has been widely applied to coal ash materials, and its use for fresh ash has been criticized (Petrović and Fiket, 2022). In this study, however, weathered ash was tested, and the method serves as a practical analogue for localized acidification in vegetated landfill areas, where root exudates and microbial activity can release low-molecular-weight organic acids that temporarily lower pH. At the end of the extraction time, the EN 12457–2 and TCLP-2 leachates were subjected to sequential filtration using acetate-cellulose filters of different pore sizes (0.45, 0.22 and 0.10 µm).

EPA Method 1313 (USEPA, 2017a), a batch-leaching method consisting of nine parallel extractions was performed on selected samples, at a ratio of liquid to solid of 10 mL/g to reach the target pH values of 2, 4, 5.5, 7, 8, 9, 10.5, 12, and 13.

EPA Method 1316 (USEPA, 2017b) is a parallel batch leaching method which reaches the target L/S ratios over a range from 1 to 10 mL/g. The procedure was conducted on selected samples and included weighing 4 g, 10 g, 20 g, and 40 g of the dry sample and addition of the appropriate amount of ultra-pure water to achieve the target liquid–solid ratios.

Prior to analysis, all leachates were 100-fold diluted, acidified with 2 % (v/v) HNO₃ (65 %, supra pur, Fluka, Steinheim, Switzerland) and In (1 µg L⁻¹) as internal standard was added.

2.6. Multielement analysis

Multielement analysis of the prepared total digests and leachates was performed by an inductively coupled plasma triple quadrupole mass spectrometer (model 8900, Agilent, USA). All samples were analyzed for a total concentration of 9 elements (As, Cr, Mo, P, S, Sb, Se, U, and V).

Quality control of the analytical procedure was performed by simultaneous analysis of the blank sample and certified reference material for soil (NCS DC 77302, China National Analysis Center for Iron and Steel, Beijing, China). For all elements, good agreement was obtained between the analyzed and certified concentrations within the analytical uncertainties (<10 %).

2.7. FTIR analysis

Nine samples from the Štrmac landfill (LŠ5₁₋₃, LŠ10₁₋₃, LŠ11₁₋₃) and eleven samples from the Plaški landfill (LP3₁₋₄, LP5₁₋₅, LP10₁₋₂) were analyzed using Fourier transform infrared spectroscopy (FTIR) with a Bruker Alpha FTIR spectrophotometer model 11,795,252 in Massachusetts, USA. Prior to analysis, samples were finely ground. To prepare pastilles, 1 mg of each sample and 200 mg KBr were weighed. After mixing the powdered sample with KBr, the mixture was homogenized in a mortar and then pressed into a pellet using a press. The IR spectra were recorded in the range from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹.

The total organic carbon (TOC) and total nitrogen (Nt) contents of all samples were determined previously and are reported in detail in Petrović et al. (2023). These data are again mentioned in Supplementary Material of the present study (Table S3–S5) to allow easier following of the paper and to support the interpretation of FTIR spectra and are also in Supplementary Material (Table S3–S5).

2.8. SEM/EDS analysis

Two samples from the Štrmac landfill (LŠ3₃, LŠ8₃) and two samples from the Plaški landfill (LP3₃, LP5₃) were analyzed using SEM Thermo Fisher Scientific model Axia™ ChemiSEM™. Sieved samples were put on top of carbon tape to characterize the morphology and qualitative

and quantitative elemental distribution by SEM equipped with Energy Dispersive X-ray Spectroscopy (EDS). Elemental maps were exported from the SEM-EDS software and combined in ImageJ by assigning each element to a separate RGB channel (e.g., Ca = red, S = green). Co-localized signal appears as mixed colors (e.g., yellow for Ca-S), allowing qualitative identification of major-element associations.

2.9. Statistical analysis

The data were statistically analyzed using STATISTICA 7.0 (StatSoft, Inc, Tulsa, OK, USA). Correlation analysis was performed using Pearson correlations to determine the relationships between element concentrations in samples and literature data on pH, physicochemical properties and mineral composition from (Petrović et al., 2023). Differences between groups (sample types and locations) were tested using the Mann Whitney *U* test or Kruskal-Wallis analysis of variance (ANOVA), followed by pairwise comparison using the Dunn method, with the significance level set at $p < 0.05$.

3. Results and discussion

3.1. Accumulation of pedogenic organic matter and mineral content of weathered coal ash

Certain elements are bound to coal organic matter (e.g., N, S, Be, B,

Ge, V, W, Zr) (Vejahati et al., 2010), so transformations of organic matter (OM) during weathering can influence the leaching behavior of these elements. In addition, organic matter can modulate the mobility of elements not inherently bound to coal OM through complexation and adsorption (Lewińska et al., 2018; Palansooriya et al., 2020). However, the nature and extent of these OM transformations in coal ash remain insufficiently understood. In our previous study, we showed through C:N ratios and ^{13}C NMR spectra that weathering promotes both the formation of new organic matter and the degradation of unburned coal particles, respectively (Petrović et al., 2023). Building on those findings, FTIR analysis was applied here to further characterize the composition and functional groups of OM in weathered coal ash.

3.1.1. Organic matter transformation and formation of pedogenic OM

Small peaks of aromatic OM ($\text{WN } 1620 \text{ cm}^{-1}$), from the structural vibration of aromatic $\text{C}=\text{C}$, were observed in all bare samples but were absent in Štrmac vegetated samples. Small peaks of aliphatic OM ($\text{WN } 3000\text{--}2800 \text{ cm}^{-1}$), belonging to aliphatic C-H stretches, were observed in vegetated samples but typically not in bare samples (Fig. 2). Since coal consists mainly of aromatic OM (Dick et al., 2006), the presence of aliphatic OM in vegetated samples suggests the formation of pedogenic OM. This is consistent with C:N ratios and ^{13}C NMR which pointed to the formation of new OM and degradation of unburned coal particles, respectively (Petrović et al., 2023) (Table S3). However, C:N ratios were useful only in Plaški samples, while high amide content in Štrmac

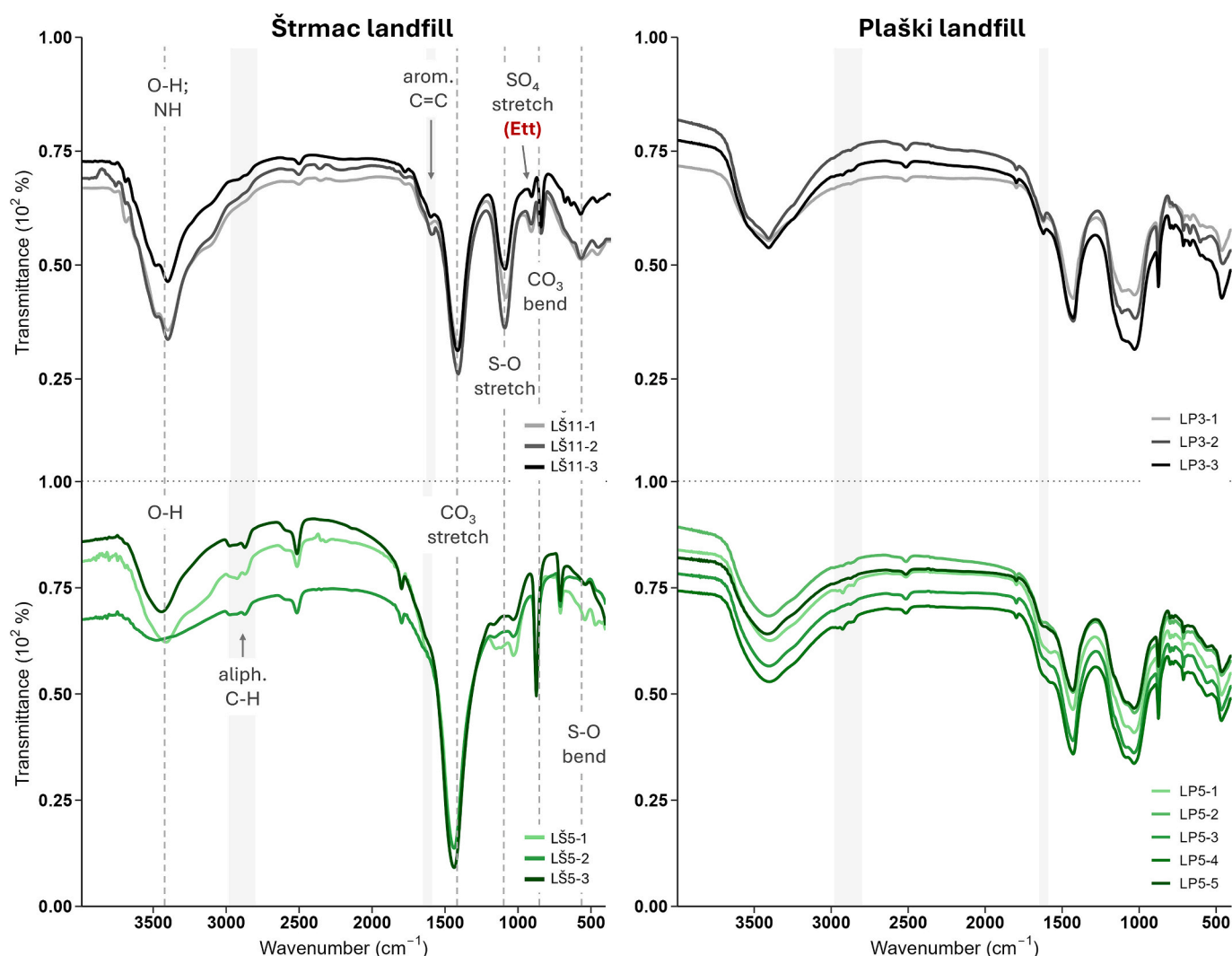


Fig. 2. FTIR spectra of bare and vegetated coal ash samples. Gray lines highlight peaks distinctive of aliphatic and aromatic organic matter. Ett = ettringite.

samples hindered C:N ratio as an indicator of soil formation. In addition, ^{13}C NMR didn't show newly formed organic matter in Štrmac samples but only decrease in the abundance of unburned coal particles. Therefore, we find that FTIR analysis of weathered CCR is a reliable method for assessing pedogenic organic matter even in CCR with high amide content.

3.1.2. Mineral composition identified by FTIR

Besides organic matter, FTIR has typically been used to determine main mineral phases in coal ash (Uzarowicz et al., 2018; Yin et al., 2019).

The most intense peaks were associated with water, calcite, and gypsum. The broad peak at 3400 cm^{-1} corresponds to O–H stretching

vibrations in water molecules but cannot be definitively assigned to a single mineral. It is likely a combination of signals from organic matter and water-containing minerals such as gypsum, portlandite, ettringite, kaolinite, and montmorillonite, all of which were identified by XRD analysis in these samples (Petrović et al., 2023) (Table S4 and S5). However, in LŠ11 samples this band appears narrower, indicating contributions from NH groups (amides) (Horgnies et al., 2013). Elevated N contents previously measured in Štrmac bare samples support this interpretation, along with ^{13}C NMR spectra, which also confirmed the presence of amide structures in LŠ11 (Petrović et al., 2023). These amide groups most likely represent residual nitrogen-bearing organic compounds inherited from unburned Raša coal particles (Petrović et al., 2023).

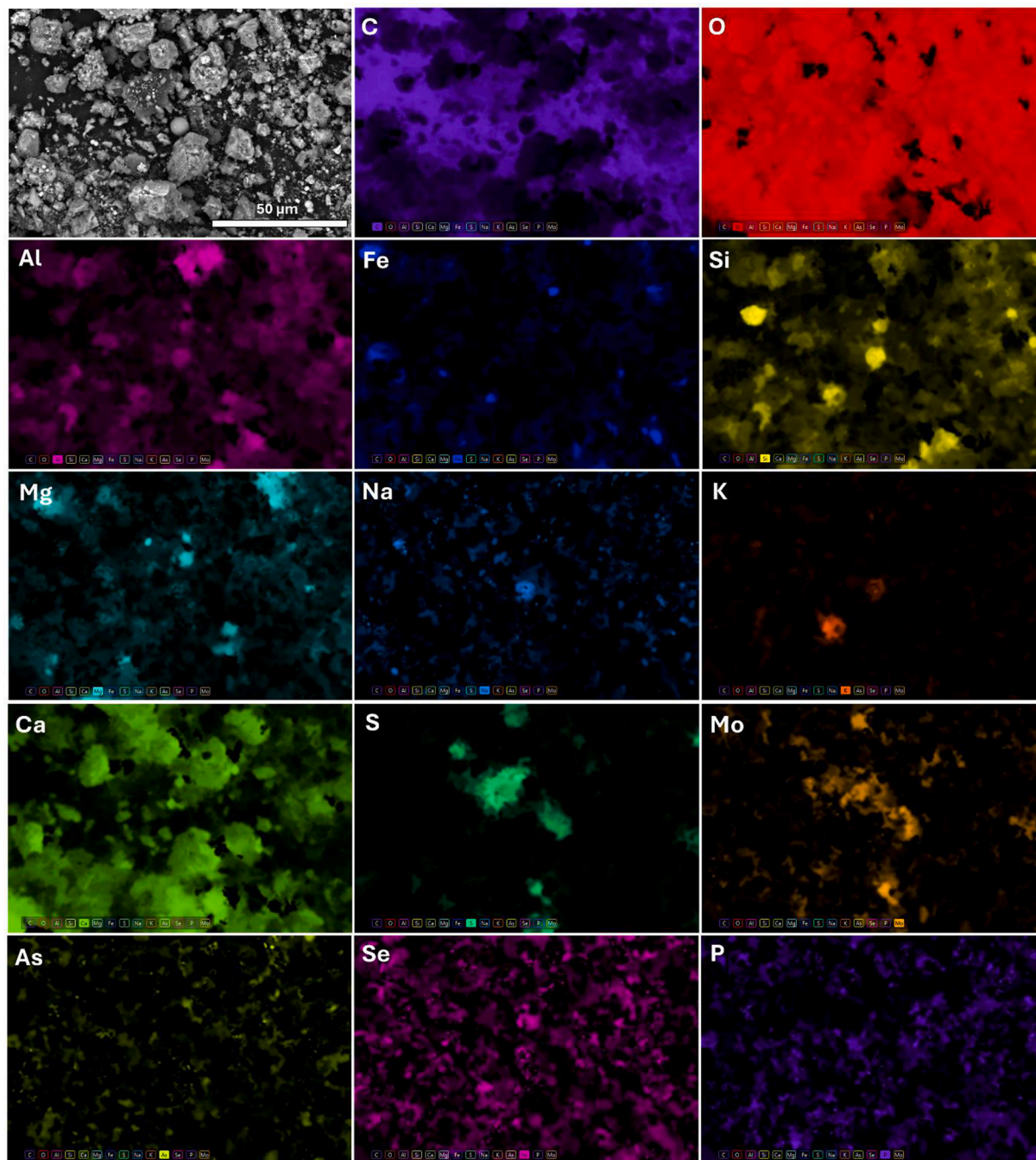


Fig. 3. Quantitative elemental maps for one representative LŠ8 (bare) BSE image. Elemental overlaps and maps for the rest of the samples are in the Supplementary material (Figs. S2-S5).

Peaks at 1429 cm^{-1} and 874 cm^{-1} are attributed to CO_3 asymmetric stretching and out-of-plane CO_3 bending, respectively, therefore these peaks are typically assigned to calcite (Uzarowicz et al., 2018). Similarly, a strong peak at 1114 cm^{-1} corresponds to S-O stretching vibrations associated with gypsum (Uzarowicz et al., 2018). The peak at 601 cm^{-1} , typically associated with gypsum (Uzarowicz et al., 2018) was not detected in Plaški samples, despite XRD analysis indicating the presence of gypsum in those samples. All samples contained, besides calcite and gypsum, ettringite as one of the main mineral phases (Petrović et al., 2023). Ettringite, being a water- and sulfate-containing mineral, has overlapping bands with calcite and gypsum. A distinctive peak for ettringite could be at 950 cm^{-1} , corresponding to the stretching vibrations of sulfate groups within its structure (Uzarowicz et al., 2018). However, this peak was only detected in Štrmac bare samples, which contain significant ettringite concentrations, but not in other samples, even though XRD detected ettringite as one of the mineral phases in the samples (Petrović et al., 2023).

Overall, FTIR analysis identified two distinct OM sources in weathered CCR: (i) pedogenic OM, expressed as aliphatic structures in vegetated samples, and (ii) coal inherited OM expressed as aromatic structures in bare sample and amide-rich compounds in Štrmac bare samples inherited from Raša coal. While FTIR provides valuable insight into the transformation of both OM and mineral components during ash weathering, overlapping spectral bands within mineral groups and the heterogeneous nature of CCR limit its ability to unambiguously distinguish specific mineral phases.

3.2. Morphology and element distribution

SEM analysis of the CCR samples revealed a heterogeneous morphology characterized by a broad particle size distribution ranging from submicron to approximately $50\text{ }\mu\text{m}$ (Fig. 3, S2-4). At both sites, vegetated samples had finer particle texture. All samples consisted predominantly of irregular, angular, and porous particles. The rough surface textures and agglomerated structures suggest secondary mineral formation, in agreement with previous XRD analysis (Petrović et al., 2023). Occasional spherical particles (cenospheres) were also observed, indicative of fly ash particles. This morphology reflects a predominantly bottom ash material with a minor presence of fly ash.

SEM-EDS elemental mapping revealed a complex and heterogeneous distribution of both major and trace elements (Fig. 3, S2-S4), reflecting the presence of multiple mineral and non-mineral phases. In Štrmac samples, Ca-rich regions formed the most prominent component of the mapped areas (Fig. 3, S2, S5), while in Plaški samples, Ca- and Si-rich regions were evenly dominant (Fig. 3, S2-S4). Silicon and aluminium were broadly co-distributed across the mapped areas, representing widespread aluminosilicate material (Fig. S5). These regions cannot be conclusively identified as glass, however, their diffuse Si-Al overlap (Fig. S5), together with XRD evidence of high amorphous content (Petrović et al., 2023), suggests that they comprise a mixture of aluminosilicate glass and fine crystalline aluminosilicate phases. Isolated Si-rich clusters were also identified, likely representing quartz (Fig. S5).

In both Štrmac and Plaški, S occurred in Ca-poor regions, indicating that a substantial portion of S is associated with residual organic matter. This interpretation is supported by the co-occurrence of S and C in the C-S maps (Fig. S5). This was more pronounced in Štrmac samples, which is consistent with the high organic sulfur characteristic of Raša coal (Medunić et al., 2016). However, at both landfills, Ca and S overlapped in small, discrete patches, interpreted as secondary sulfate phases such as gypsum or ettringite. Much of the Ca signal occurred independently of S, consistent with the presence of additional Ca-bearing phases such as calcite and portlandite (Fig. S5) detected in the previous XRD analysis (Petrović et al., 2023).

Trace elements (Mo, Se, As) exhibited heterogeneous but generally low-intensity spatial patterns. In the Štrmac samples, Mo appeared co-localized with S particles identified as unburned carbon particles in

maps overlay (Fig. S5). This is in the agreement with the enrichment of Mo in Raša coal combusted at the Štrmac location (Medunić et al., 2018; Petrović et al., 2023). In the Plaški vegetated samples, Mo was instead associated with Ca-S phases, identified as secondary sulfates (Fig. S5), in agreement with previous observations of Mo incorporation into Ca-S-Al phases in CCR (Mohebbi et al., 2022). Selenium was dispersed across the aluminosilicate matrix, with some enrichments near S-rich micro-domains, although SEM-EDS resolution limits definitive interpretation. Arsenic occurred at very low count rates and displayed a diffuse, scattered distribution. Although Fe- and Mg-bearing particles often act as potential sorptive hosts for As in CCR (Mohebbi et al., 2022), no such associations can be made here. Because the X-ray signals of As and Se were extremely weak, reliable map overlap could not be performed, and no definitive microscale host phases can be identified for these elements.

3.3. Enrichment of oxyanion-forming elements in bare and vegetated CCR samples

Total concentrations of elements (As, Cr, Mo, P, S, Se, Sb, U, and V) analyzed in bare, vegetated, and soil samples from the Plaški and Štrmac disposal sites are shown in Supplementary Material (Tables S1 and S2). To evaluate the enrichment of elements in analysed samples, the mean element concentrations in bare and vegetated samples are compared to the world average (Clarke) values for coal ash (Ketris and Yudovich, 2009) (Fig. 4). Štrmac samples are slightly enriched in Mo, U, and Se in bare samples, within typical levels for Cr and V, and depleted in As, P, and Sb no matter the sample type. Plaški samples are slightly enriched in Cr, Mo, and U, within typical levels for As and V and depleted in P, Sb, and Se in both bare and vegetated samples. Clarke values for sulphur do not exist but Štrmac samples are typically enriched in S due to originating from high-sulfur coal, while the Plaški samples are within typical levels of S in coal ash (Fig. S6, Tables S1 and S2) (Petrović et al., 2023).

The distribution and concentrations of elements in CCR are dependent on the properties of the original coal (Izquierdo and Querol, 2012). However, even though Štrmac samples originate from unique Raša coal enriched in S, Se, Mo, U, and V (Medunić et al., 2018; Medunić et al., 2016), all these elements, except S and Se, are less enriched in Štrmac compared to the Plaški samples. In our previous work, we found that the texture of these CCRs differs. CCR disposed in Štrmac has a coarser texture (sandy loam), and Plaški has a finer texture; therefore, we hypothesised that the Plaški CCR could be a mix of both fly and bottom ash. Since fly ash typically has a higher enrichment in trace elements, this could be the reason for Plaški being enriched in Mo, U, and V. However, SEM analysis did not confirm this hypothesis (Fig. 3, S2-S4), therefore the enrichment likely stems from the type of coal combusted in Plaški, which is unknown.

When comparing the element enrichment and concentration between different sample types (bare and vegetated), it can be observed that the differences between these sample types are much more pronounced at the Štrmac site than at the Plaški site (Fig. 4 and S6, Table S1 and S2). Most elements were more abundant in bare samples; however, vegetated samples from the Štrmac site had significantly higher concentrations of As, P, and Sb, and from the Plaški site of V ($p < 0.05$). The higher concentrations of these elements in vegetated samples could be related to changes that occur as vegetation develops. Vegetated areas contain more organic matter and a greater proportion of fine, weathered material, including newly formed Fe/Al (oxyhydr)oxides (Uzarowicz et al., 2018). Because these phases have a strong affinity for oxyanions (Mohebbi et al., 2022), they may promote greater retention of elements such as As, Se, and Mo in vegetated zones.

Following the above it can be concluded that landfill evolution, i.e. pedogenesis, leads to certain changes in the redistribution of elements between the individual components of the landfill itself in a relatively short period of only a few decades.

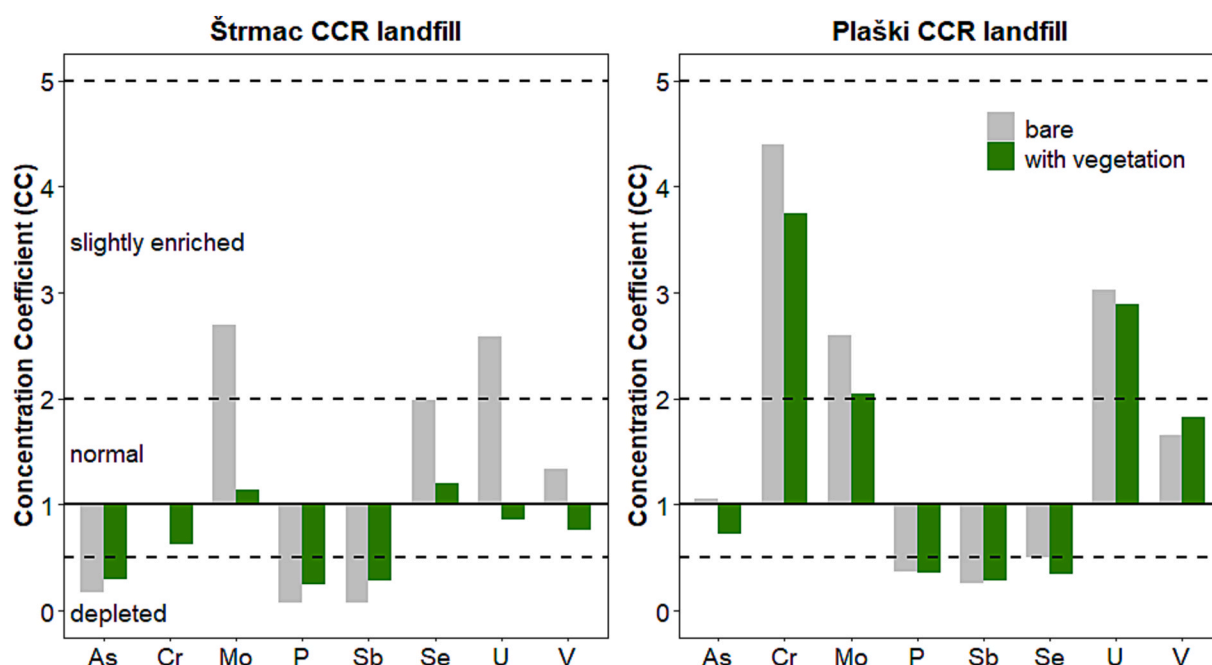


Fig. 4. Concentration coefficient (CC): mean element concentrations (in mg/kg) in all Štrmac and Plaški samples versus the average world (Clarke) values for coal ash.

3.4. Effect of early pedogenesis on leaching of oxyanions under different pH conditions

Early pedogenesis substantially modifies the geochemical environment of deposited CCR. Previous work (Petrović et al., 2023) demonstrated that the natural pH of vegetated Štrmac samples decreased from highly alkaline values (>12) to 8–9 due to carbonation and weathering. In contrast, bare samples retained their strong alkaline character from the original ash. At Plaški, bare and vegetated samples exhibit similar pH levels (~ 9) and mineralogy, suggesting that the landfill has undergone substantial weathering, even in its bare parts. Because many oxyanion-forming elements reach elevated mobility in the neutral to mildly alkaline range (7–10) (Izquierdo and Querol, 2012; Wang et al., 2022; Zhao et al., 2020), such pH changes are expected to influence their leaching behavior.

To evaluate this effect, bare and vegetated samples from both Štrmac and Plaški landfills were subjected to leaching in water (EN 12457-2) and an acidic medium (TCLP-2), simulating natural infiltration and localized acidification in vegetated landfill zones. The concentrations measured in eluates are provided in Table S6 and S7.

At both landfills, bare samples consistently released significantly higher concentrations ($p < 0.05$) of Cr, Mo, S and Se than vegetated samples, regardless of leaching medium. Sb and V showed no significant differences between sample types, whereas P and As were more mobile in vegetated Štrmac samples. Acidic conditions moderately enhanced the leaching of S, Se and U at both sites, and increased As and Cr release in Plaški samples (Table S6 and S7). When compared against regulatory criteria, most EN 12457-2 eluates remained well below the EU non-hazardous waste acceptance limits (Table S8). When evaluated against the more stringent WHO drinking-water guideline values, exceedances occurred for As (LP1₁, LP3₁, LP5₁, LŠ5₃), U (LP3₁), and Mo (LP3₁, LŠ11₁₋₃) (Table S8). TCLP-2 eluates showed higher concentrations, and several additional samples exceeded WHO guideline values for As (LP1₁, LP3₁, LP5₁, LP8₁, LP9₁, LŠ5₁₋₃), U (LP1₁, LP3₁, LP10₁, LŠ11₂₋₃), and Mo (LP3₁, LŠ11₁₋₃). In contrast, Cr, Sb, Se, and V remained consistently below both thresholds.

The relative mass leached (RML) was calculated for each element to assess what % of the total element is available to leach in different

media and sample types. Higher average mass leached was found for the Plaški landfill than for the Štrmac landfill indicating that the elements are more mobile at the Plaški site (Fig. 5, Table S10). This difference is likely related to the greater reactivity of the Plaški material, as previously proposed by Petrović et al. (2023), who suggested that Plaški ash originated from lower-rank coal and has undergone more extensive weathering. Plaški CCR has finer particle size, higher specific surface area ($13.1\text{--}40.8\text{ m}^2\text{ g}^{-1}$ vs. $5.4\text{--}18.6\text{ m}^2\text{ g}^{-1}$ in Štrmac), and higher CEC ($30.2\text{--}89.3$ vs. $2.79\text{--}44.6\text{ cmol(c) kg}^{-1}$), lower alkalinity, and reduced

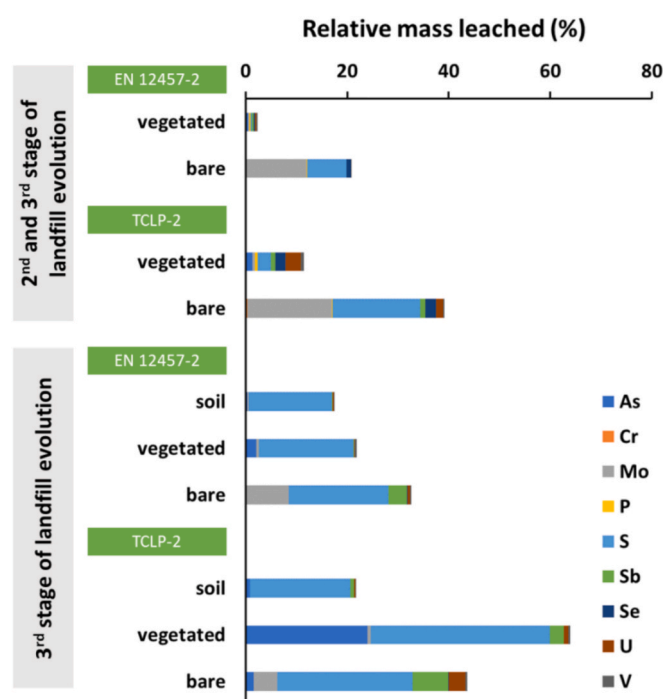


Fig. 5. The total relative leached masses of elements from different coal ash landfills.

amount of buffering phases (e.g. ettringite, portlandite) than Štrmac (Petrović et al., 2023), all of which increase dissolution rates and the amount of material available for leaching. Together, all mentioned Plaški properties provide a plausible explanation for the higher RML values observed at that CCR landfill.

Sulfur also provides a clear example of how mode of occurrence influences mobility. Although Štrmac samples contain higher total sulfur due to the high-organic-sulfur Raša coal (Medunić et al., 2016), Plaški samples exhibited substantially higher sulfur mobility (16.3–35.3 %). SEM-EDS confirmed that much of the sulfur in Štrmac is organically bound and retained within unburned coal (Fig. S5) that dissolve more slowly and thus limit S release. In contrast, Plaški sulfur is dominated by inorganic sulfate minerals (Fig. S5) that dissolve more readily than unburned coal.

When comparing RML across different sample types, Štrmac consistently showed several-fold higher RML in bare ash than in vegetated ash, regardless of leachate pH (Table S9–10), indicating that pedogenesis increased the retention capacity of the vegetated material. In contrast, Plaški exhibited the opposite pattern: under acidic conditions, the highest RML values were generally observed in vegetated materials, with exceptions for Mo, Sb and U, which leached more readily from bare ash (Fig. 5, Table S10). These contrasting patterns underscore that pedogenesis modifies leaching behavior differently depending on the initial ash composition and mineralogy.

4. .

To better understand the processes governing oxyanion release, pH-dependent leaching curves were obtained using EPA 1313 method for a representative pair of Štrmac samples: the alkaline bare material (LŠ8-3) and the more weathered vegetated material (LŠ3-3) (Fig. 6).

In bare LŠ8-3 sample, Mo and S occur at high but only weakly pH-dependent concentrations, whereas V, As, Se, U and Cr remain low across the tested range. A shallow minimum near pH ~ 10 occurs for several oxyanions (As, Se, U, Cr) but is not pronounced. This behaviour corresponds well with the mineralogy of LŠ8-3, which contains abundant ettringite (25 wt%), portlandite (36 wt%) and measurable gypsum (7.1 wt%) (Petrović et al., 2023). These phases act as both structural hosts and reactive sinks: they incorporate oxyanions through substitution (particularly ettringite) and they maintain a highly alkaline pore-water environment that favours incorporation rather than desorption (Hassett et al., 2005; Izquierdo and Querol, 2012; Wang et al., 2022). The slight dip near pH ~ 10 is fully consistent with the known stability window of ettringite, which remains persistent until approximately pH 10–11 before undergoing gradual destabilisation. Although this behaviour resembles the Type III ettringite-dominated systems described by Wang et al. (2022), the LŠ8-3 response does not show the deep concentration minima typical of fully equilibrated Type III behaviour. A plausible explanation is kinetic where ettringite phase may not fully dissolve and recrystallise within the 24-h EPA 1313 equilibration time,

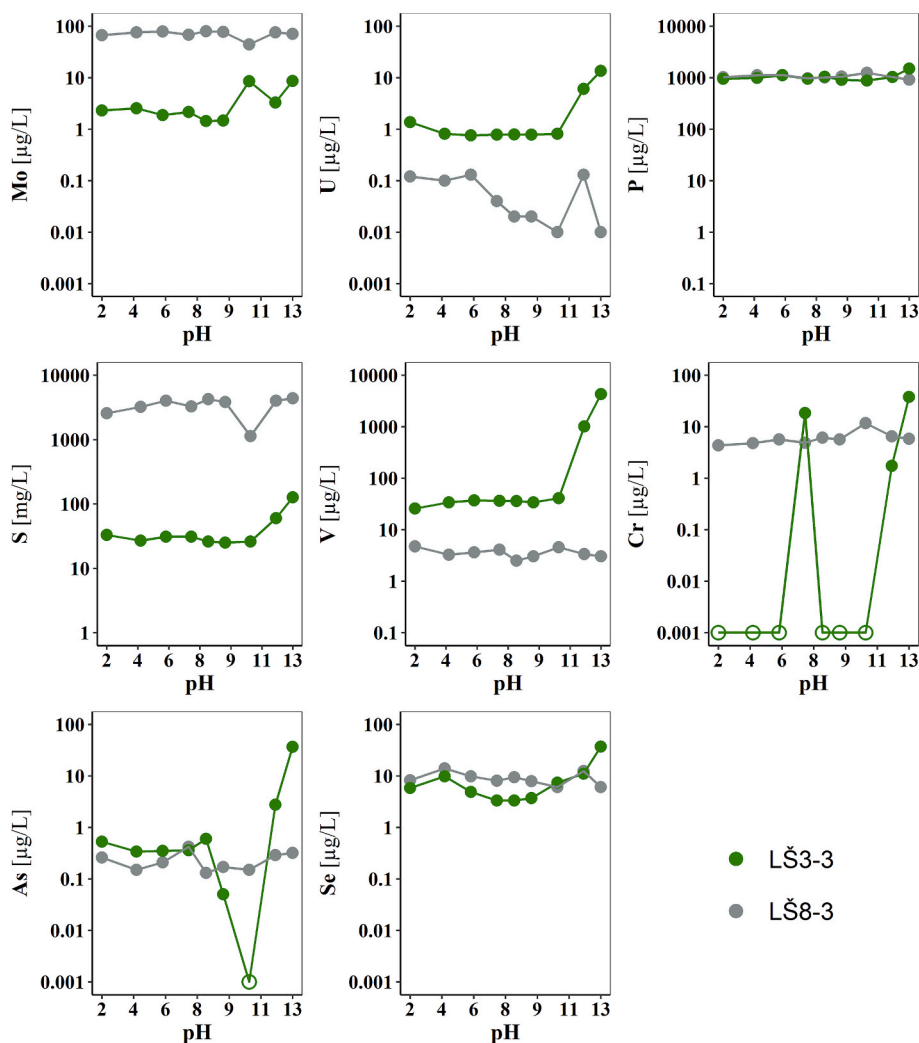


Fig. 6. Ph-dependent leaching of oxyanion-forming elements in EPA 1313 eluates from selected bare and vegetated štrmac samples. Solid circles represent detected concentrations, while open circles indicate values below the method detection limit.

which is also noted as a limitation in Wang et al. (2022) for high-Ca ashes.

In contrast to bare sample, the vegetated sample LŠ3-3 showed very low oxyanion concentrations from pH 2 to ~ 10.5, followed by sharp increases, often several orders of magnitude, at higher pH. This behaviour is consistent with mineralogical changes induced by pedogenesis, which markedly reduced ettringite and portlandite (to < 0.4 wt%) and led to a matrix dominated by calcite, and minor increase in Fe/Al (oxyhydr)oxides, clays and organic matter (Petrović et al., 2023). These phases provide strong sorption capacity in the acidic to mildly alkaline range, but their surfaces deprotonate at high pH (>10.5), releasing previously sorbed oxyanions into solution. In this sense, the EPA 1313 results for LŠ3-3 reflect a mineralogical system that no longer contains sufficient ettringite or other Ca-S-Al phases to buffer oxyanion release at high pH; instead, solubility is controlled by the progressive loss of Fe/Al sorption sites. This is consistent with the observed mineralogical differences between bare and vegetated Štrmac materials and aligns with the general behaviour noted for intermediate-Ca ashes undergoing natural weathering in Wang et al. (2022).

Together, these results show that simply adjusting the pH of the system does not reproduce the same leaching pattern in bare and vegetated materials. A notable outcome of this EPA 1313 experiment is that the early pedogenesis modifies the mineralogical controls on oxyanion mobility more strongly than it modifies bulk chemical composition. Even though the two Štrmac samples share similar major-element chemistry (CaO , Fe_2O_3 , $\text{SiO}_2 + \text{Al}_2\text{O}_3$; Fig. S7), their leaching patterns differ fundamentally because their mineral assemblages, and therefore their dominant retention mechanisms, are no longer the same. Pedogenesis seem to reduce the influence of Ca-bearing buffering minerals and increases the role of Fe/Al surface processes, resulting in a shift from Ca-phase-controlled behaviour in the bare ash to sorption-desorption control in the vegetated material.

4.1. Influence of mineral content on leaching properties

To further clarify the factors controlling oxyanion release, element leaching was compared with bulk mineralogical and physicochemical properties previously reported for the same samples (Petrović et al., 2023) (Table S11).

The strongest positive correlations were observed between leached Cr, Mo, S and Se and the abundance of gypsum, portlandite and ettringite. Specifically, Cr and Mo showed strong positive correlations with gypsum ($r = 0.76$ and $r = 0.90$), and Cr, Mo, S and Se correlated significantly with portlandite ($r = 0.54$ – 0.79). Cr and S also showed positive correlations with ettringite ($r = 0.76$ and $r = 0.65$). These associations agree well with the mineralogy of the Štrmac bare samples, where these Ca-S-Al phases occur in appreciable quantities and can contribute oxyanions during dissolution. Gypsum dissolves up to pH ~ 11, and both portlandite and ettringite progressively dissolve as pH decreases from strongly alkaline to neutral conditions, providing plausible sources for S, Mo and, given its behaviour under alkaline conditions, Cr. The additional positive correlation of Cr, S and Se with the amorphous fraction ($r = 0.58$ – 0.89), which includes aluminosilicate glass, unburned coal and organic-rich material, suggests that non-crystalline matrices may also contribute to oxyanion release.

In contrast, As and Sb correlate most strongly with calcite (positive), and with several minor phases including hematite, hydrotalcite, pyrite, graphite and montmorillonite (Table S4, S5, S11). Although these correlations are moderate, they indicate that As and Sb mobility is influenced by a wider suite of phases and by surface-controlled processes rather than by dissolution of a dominant host.

Phosphorus shows a positive correlation only with total organic carbon (TOC), implying that its release is mainly controlled by dissolution or desorption of organic-associated P. Uranium exhibits a significant negative correlation with leachate pH ($r = -0.80$), supporting the interpretation that U becomes more mobile at higher pH due to

desorption or dissolution of U-bearing phases, as also observed in the EPA 1313 leaching curves.

Taken together, these relationships demonstrate that the mineralogy of the CCR, particularly the proportions of Ca-S-Al phases, Fe/Al-bearing sorptive phases, clays and organic matter, plays a key role in governing oxyanion mobility. Cr, Mo, S and Se are primarily controlled by dissolution of Ca-rich and amorphous phases, whereas As, Sb and V are more strongly influenced by secondary minor phases and pH-dependent sorption-desorption, while the mobility of some elements is exclusively related to the organic matter in the samples (e.g., P). These mineralogical controls align with the EPA 1313 observations and provide a coherent explanation for the contrasting leaching behaviour of bare and vegetated materials, confirming that early pedogenesis fundamentally alters the dominant mechanisms of oxyanion release.

4.2. Effect of early pedogenesis on leaching of oxyanions under different liquid-solid ratios

One of the main factors influencing the leaching rate of elements, after pH and mineralogy, is the L/S ratio (Kosson et al., 2019; Wang et al., 2023; Zhang et al., 2019). Typically, leaching tests have a set L/S which can limit the understanding of whether the leaching is solubility-dependent or controlled by available content (Kosson et al., 2019). Therefore, the samples were tested by the EPA 1316 to reach the target L/S ratio at 1, 2, 5, and 10.

Studied oxyanions behave differently with increasing L/S ratio and sample type (Fig. 7). Their liquid-to-solid partitioning (LSP) curves can be categorized into three patterns: decrease in concentration as the L/S increases, first increase then decrease in concentration as the L/S increases, and increase in concentration as the L/S increases.

The majority of LSP curves fit the first pattern where oxyanion concentration decreases as the L/S increases no matter the sample type. This is true for As, Cr, Mo, Sb, U, and V in Štrmac samples, and Mo, S, Sb, Se, and U in Plaški samples. This indicates that these elements are controlled by the available content. As the L/S ratio increases, a larger volume of liquid interacts with the same amount of available fraction of the element, resulting in a dilution effect and lower element concentrations in the leachate (Kosson et al., 2019). The second pattern, where oxyanion concentration first increases and then decreases as L/S increases, was observed for Se in the vegetated Štrmac samples. The third pattern, where oxyanion concentrations increase as the L/S increases was observed for As, V, and P in vegetated Plaški samples. This indicates that the leaching of these elements is controlled by solubility because there is more available fraction to leach out when increasing the volume of the eluate. Since the third pattern emerged only in vegetated Plaški samples, it can be stated that their leaching pattern changed from available-content limited to solubility limited leaching when compared to bare samples.

Together with the EPA 1313 results, which showed enhanced high-pH release in the vegetated materials due to reduced Ca-phase buffering and increased reliance on Fe/Al sorption processes, the EPA 1316 results confirm that early pedogenesis modifies both the magnitude and the mechanisms of oxyanion release. Solubility-limited behavior of As and V in vegetated Plaški samples suggests that these elements may become progressively more mobile during continued weathering, especially if associated with weakly bound or newly formed secondary phases.

4.3. Changes in leaching characteristics with depth

If, in addition to the different leaching solution ratios (L/S) and the presence or absence of vegetation, the sampling depth was also taken into account, the following trends can be observed (Fig. 8).

For most elements (As, Cr, Mo, S, Se and Sb), a consistent decrease in concentrations with increasing L/S ratio was observed, as mentioned in previous chapter. V, As, and P had more unique behaviour, showing an

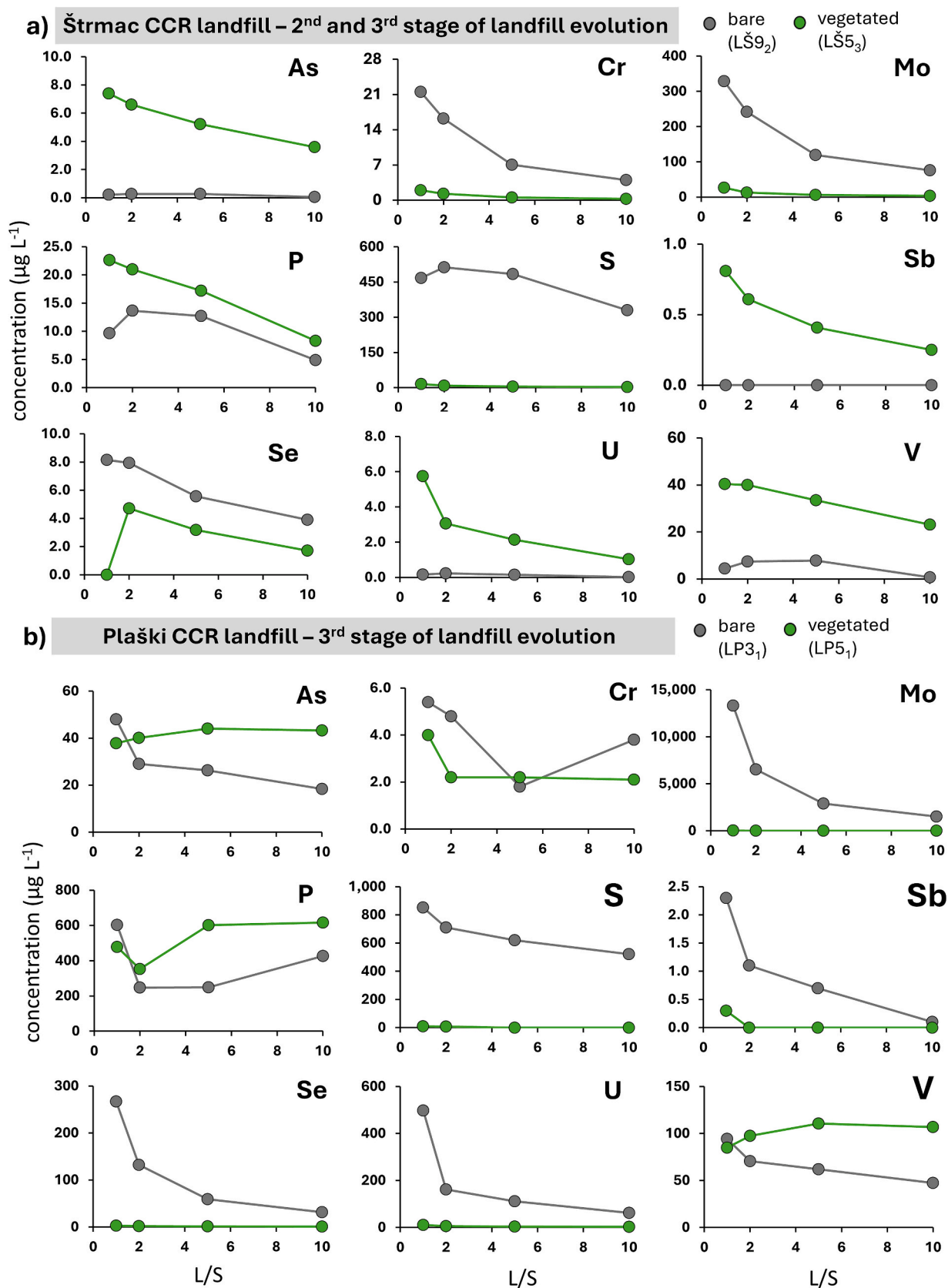


Fig. 7. Element concentrations in EPA 1316 eluates vs. L/S ratio for a) Štrmac and b) Plaški.

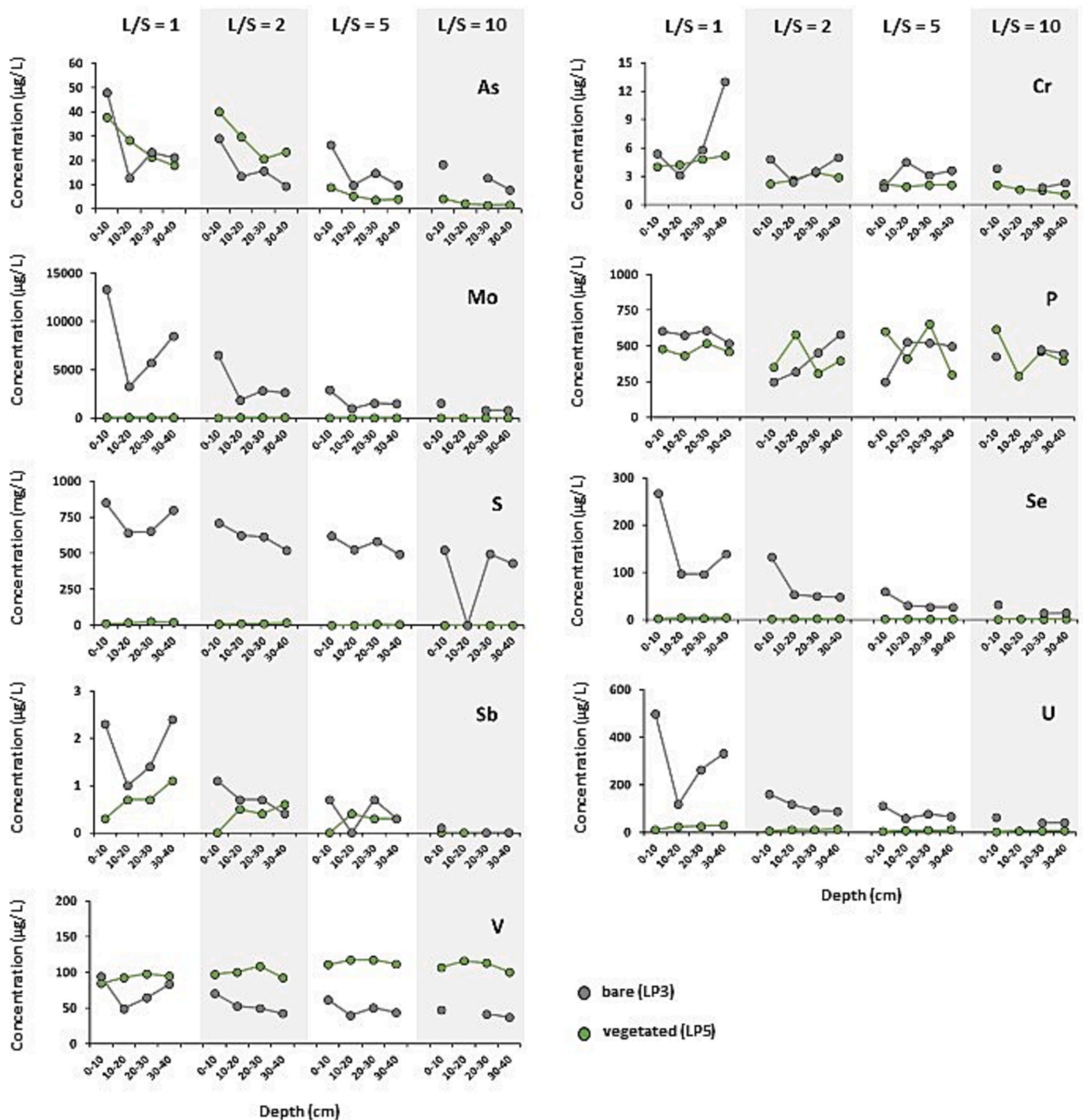


Fig. 8. Leaching concentrations in EPA 1316 eluates from Plaški landfill in relation to L/S ratio and sampling depth. The missing values are due to lack of sample, they are not values below the limit.

increase in concentration in vegetated samples compared to unvegetated samples and across all L/S ratios. However, different patterns were observed with respect to the increase in depth for the elements studied, which were most pronounced at $L/S = 1$. In general, most elements showed higher concentrations at shallower depths and at higher L/S ratios, suggesting that leachate mobility and element concentrations may be higher near the surface and at larger volumes of leachate. There is a general trend of decreasing element concentration with increasing depth, which may be due to several factors including absorption, precipitation or dilution effects in the subsurface environment.

These depth-dependent trends in element concentrations, together with the influence of the existing vegetation cover, i.e. the pedogenesis stage, can have a significant impact on the root zone of vegetation in coal ash landfills.

4.4. Distribution of elements in different size fractions

In this study, we define large colloids as particles retained at $0.45 \mu\text{m}$ (e.g., mineral aggregates, clay particles), while small colloids refer to particles passing through $0.45 \mu\text{m}$ but retained at $0.1 \mu\text{m}$ (e.g.,

nanoparticles, metal–organic complexes). Particles passing through 0.1 μm are considered part of the dissolved fraction, consisting mainly of free ions and very small molecular complexes.

The average distribution of elements in the different size fractions ($<0.22\ \mu\text{m}$ and $<0.10\ \mu\text{m}$) in the samples from the Štrmac and Plaški landfills was similar (Fig. S8), with concentrations approaching 100 % of those analyzed in the 0.45 μm size fraction. This indicates that they occur predominantly either in colloidal or dissolved state.

In some cases, however, different patterns occurred. The recovery of As and U in Štrmac samples was slightly lower in fractions 0.22 μm and 0.10 μm , both in the EN 12457–2 (78 % and 81 % for As and 77 % and 78 % for U, respectively,) and TCLP-2 (71 % and 82 % for As and 91 % and 86 % for U, respectively) eluates, indicating a possible association with larger colloids. Similar trends were observed for antimony (Sb), particularly in the EN 12457–2 eluates, which accounted for 80 % and 58 % in the fractions of 0.22 μm and 0.10 μm , respectively. The same was, however, not observed for Sb in the TCLP-2 eluates. For P, the differences were more pronounced in the 0.22 μm and 0.10 μm fractions of EN 12457–2 (62 % and 63 %, respectively) compared to TCLP-2 (90 % in both fractions), suggesting that both P and Sb were related to phases that do not readily dissolve under acidic conditions.

In Plaški, the presence of P and Se in the size fractions of 0.22 and 0.10 μm was below the detection limit in water eluates. Cr appeared in Plaški in lower proportions in the EN 12457 eluates, especially in the fractions 0.22 (80 %) and 0.10 μm (64 %), which indicates a possible affinity to larger colloids. S was only found in the smallest fraction, and in a much lower concentration than in the other two size fractions, which reached 25 % and 40 % in EN 12457–2 and TCLP-2 eluates.

Acid dissolution may have affected certain phases by converting elements to dissolved states or combining them with smaller colloidal forms, leading to differences in the distribution and mobility of elements in the different fractions and under different leaching protocols. Nonetheless, the relationship between elements and a particular particle size is site- and CCR-specific, precluding broader estimates of their size-dependent mobility based on matrix type alone.

5. Conclusions

This study demonstrates that early pedogenesis has a measurable and systematic impact on oxyanion mobility in coal-combustion residues. Total element concentrations at both landfills deviate from global Clarke values, reflecting differences in coal sources and combustion conditions. Elemental contrasts between bare and vegetated materials were more pronounced at the Štrmac landfill, where vegetation has already induced substantial mineralogical transformation.

Across all leaching tests, Plaški samples released higher concentrations and higher relative mass leached (RML) than Štrmac samples, with several oxyanions (Mo, S, Se) showing up to an order of magnitude greater release. This behaviour is consistent with the finer texture, higher specific surface area, higher CEC and lower abundance of buffering Ca-bearing phases in Plaški CCR. In Štrmac bare material, gypsum, portlandite and ettringite played a dominant role in controlling the release of S, Mo and Se, whereas the leaching of As, V, U and P was governed by dissolution of minor phases and surface-controlled processes.

EPA 1313 tests demonstrated that pedogenesis alters the pH-dependent leaching mechanisms: in vegetated Štrmac samples, concentrations of As, V and P remained low from pH 2 to ~ 10.5 and then increased sharply at higher pH, consistent with the loss of Ca-S-Al buffering phases and greater reliance on Fe/Al-surface desorption. In contrast, Ca-rich bare samples exhibited only minor concentration changes across the same pH range. EPA 1316 tests further showed that pedogenesis shifted the release of several oxyanions (As, V, P) from content-limited to solubility-limited behaviour at higher L/S ratios, confirming that weathering modifies both retention mechanisms and leaching pathways.

Together, these findings demonstrate that natural weathering and vegetation-driven pedogenesis substantially modify oxyanion mobility in CCR within decades. Incorporating the effects of such mineralogical evolution into long-term monitoring and management strategies is essential for accurately predicting the environmental behaviour of CCR landfills.

CRedit authorship contribution statement

Marija Petrović: Writing – review & editing, Writing – original draft, Visualization, Methodology, Formal analysis. **Antonela Ninčević Grassino:** Validation, Investigation, Data curation. **Jasmina Lapić:** Validation, Investigation, Data curation. **Senka Djaković:** Validation, Investigation, Data curation. **Martina Furdek Turk:** Methodology, Investigation, Formal analysis. **Gordana Medunić:** . **Željka Fiket:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2026.115450>.

Data availability

Data will be made available on request.

References

- Bp, 2020. Statistical Review of World Energy 2020 [WWW Document]. accessed 12.4.23. <https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html>.
- Brandt, J.E., Bernhardt, E.S., Dwyer, G.S., Di Giulio, R.T., 2017. Selenium Ecotoxicology in Freshwater Lakes Receiving Coal Combustion Residual Effluents: a North Carolina example. *Environ. Sci. Technol.* 51, 2418–2426. <https://doi.org/10.1021/acs.est.6b05353>.
- CEN, 2002. Characterization of waste–Leaching–Compliance test for leaching of granular waste material and sludge. Part 2: One stage batch test at a liquid to solid ratio of 10 L/kg with article size below 4 mm (without or with size reduction). EN 12457–2. Brussels.
- Chu, L.M., 2008. Natural revegetation of coal fly ash in a highly saline disposal lagoon in Hong Kong. *Appl. Veg. Sci.* 11, 297–306. <https://doi.org/10.3170/2008-7-18427>.
- Deonarine, A., Kolker, A., Doughten, M.W., Holland, J.T., Bailoo, J.D., 2021. Mobilization of arsenic from coal fly ash in the presence of dissolved organic matter. *Appl. Geochemistry* 128, 104950. <https://doi.org/10.1016/j.apgeochem.2021.104950>.
- Dick, D.P., Knicker, H., Ávila, L.G., Inda, A.V., Giasson, E., Bissani, C.A., 2006. Organic matter in constructed soils from a coal mining area in southern Brazil. *Org. Geochem.* 37, 1537–1545. <https://doi.org/10.1016/j.orggeochem.2006.06.017>.
- Harris, D., Heidrich, C., Feuerborn, J., 2019. Global aspects on Coal Combustion Products. *VGB Power Tech* 10, 25–33.
- Hassett, D.J., Pflughoeft-Hassett, D.F., Heebink, L.V., 2005. Leaching of CCBs: Observations from over 25 years of research. *Fuel* 84, 1378–1383. <https://doi.org/10.1016/j.fuel.2004.10.016>.

- Horgnies, M., Chen, J.J., Bouillon, C., 2013. Overview about the use of fourier transform infrared spectroscopy to study cementitious materials. *WIT Trans. Eng. Sci.* 77, 251–262. <https://doi.org/10.2495/MC130221>.
- Izquierdo, M., Querol, X., 2012. Leaching behaviour of elements from coal combustion fly ash: an overview. *Int. J. Coal Geol.* 94, 54–66. <https://doi.org/10.1016/j.coal.2011.10.006>.
- Ketris, M.P., Yudovich, Y.E., 2009. Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. *Int. J. Coal Geol.* 78, 135–148. <https://doi.org/10.1016/j.coal.2009.01.002>.
- Kosson, D.S., Garrabrants, A.C., Thorne, S.A., Fagnant, D., Helms, G., Connolly, K., Rodgers, M., 2019. Leaching Environmental Assessment Framework (LEAF) How-to Guide [WWW Document]. U.S. EPA <https://www.epa.gov/hw-sw846/how-guide-leaching-environmental-assessment-framework>.
- Kostić, O., Jarić, S., Gajić, G., Pavlović, D., Pavlović, M., Mitrović, M., Pavlović, P., 2018. Pedological properties and ecological implications of substrates derived 3 and 11 years after the revegetation of lignite fly ash disposal sites in Serbia. *Catena* 163, 78–88. <https://doi.org/10.1016/j.catena.2017.12.010>.
- Kruger, R.A., 2017. In: Introduction to the Utilization of Coal Combustion Products. Characteristics, Utilization and Beneficiation. Elsevier Ltd., Coal Combustion Products (CCPs) <https://doi.org/10.1016/B978-0-08-100945-1.00004-6>.
- Lemly, A.D., 2018. Selenium poisoning of fish by coal ash wastewater in Herrington Lake, Kentucky. *Ecotoxicol. Environ. Saf.* 150, 49–53. <https://doi.org/10.1016/j.ecoenv.2017.12.013>.
- Lewńska, K., Karczewska, A., Sienkiewicz, M., Galka, B., 2018. The release of antimony from mine dump soils in the presence and absence of forest litter. *Int. J. Environ. Res. Public Health* 15. <https://doi.org/10.3390/ijerph15122631>.
- Medunić, G., Kuharić, Ž., Krivohlavek, A., Đuroković, M., Dropučić, K., Radenović, A., Oberiter, B.L., Krizmanić, A., Bajramović, M., 2018. Selenium, sulphur, trace metal, and BTEX levels in soil, water, and lettuce from the croatian raša bay contaminated by superhigh-organic-sulphur coal. *Geosci.* 8. <https://doi.org/10.3390/geosciences8110408>.
- Medunić, G., Kuharić, Ž., Krivohlavek, A., Fiket, Ž., Radenović, A., Gödel, K., Kampic, Š., Kniewald, G., 2018. Geochemistry of Croatian superhigh-organic-sulphur Raša coal, imported low-S coal and bottom ash: their se and trace metal fingerprints in seawater, clover, foliage and mushroom specimens copyright. *Int. J. Oil, Gas Coal Technol.* 18, 3–24. <https://doi.org/10.1504/IJOGCT.2018.091517>.
- Medunić, G., Radenović, A., Bajramović, M., Švec, M., Tomac, M., 2016. Once grand, now forgotten: what do we know about the superhigh-organic-sulphur Raša coal? *Rud. Geol. Naft. Zb.* 31, 27–45. <https://doi.org/10.17794/rgn.2016.3.3>.
- Mohebbi, M., Rajabipour, F., Madadian, E., 2022. A framework for identifying the host phases in Coal-derived fly ash. *Fuel* 314, 122806. <https://doi.org/10.1016/j.fuel.2021.122806>.
- Palansooriya, K.N., Shaheen, S.M., Chen, S.S., Tsang, D.C.W., Hashimoto, Y., Hou, D., Bolan, N.S., Rinklebe, J., Ok, Y.S., 2020. Soil amendments for immobilization of potentially toxic elements in contaminated soils: a critical review. *Environ. Int.* 134, 105046. <https://doi.org/10.1016/j.envint.2019.105046>.
- Petrović, M., Fiket, Ž., 2022. Environmental damage caused by coal combustion residue disposal: a critical review of risk assessment methodologies. *Chemosphere* 299, 134410. <https://doi.org/10.1016/j.chemosphere.2022.134410>.
- Petrović, M., Fiket, Ž., Medunić, G., Chakravarty, S., 2022. Mobility of metals and metalloids from SHOS coal ash and slag deposit: mineralogical and geochemical constraints. *Environ. Sci. Pollut. Res.* 29, 46916–46928. <https://doi.org/10.1007/s11356-022-19074-5>.
- Petrović, M., Ivanić, M., Vdović, N., Dolenec, M., Čermelj, B., Šket, P., Medunić, G., Fiket, Ž., 2023. Physicochemical and mineral characteristics of soil materials developed naturally on two ~ 50 years old coal combustion residue disposal sites in Croatia. *Catena* 231. <https://doi.org/10.1016/j.catena.2023.107338>.
- Ruhl, L., Vengosh, A., Dwyer, G.S., Hsu-Kim, H., Schwartz, G., Romanski, A., Smith, S.D., 2012. The impact of coal combustion residue effluent on water resources: a north carolina example. *Environ. Sci. Technol.* 46, 12226–12233. <https://doi.org/10.1021/es303263x>.
- USEPA, 2017a. Validated Test Method 1313: Liquid-Solid Partitioning as a Function of Extract pH using a Parallel batch Extraction Procedure [WWW Document] accessed 10.1.22 <https://www.epa.gov/sites/default/files/2015-12/documents/1313.pdf>.
- USEPA, 2017b. Validated Test Method 1316: Liquid-Solid Partitioning as a Function of Liquid-to-Solid Ratio in Solid Materials using a Parallel batch Procedure accessed 10.1.22 [WWW Document]. https://www.epa.gov/sites/default/files/2017-10/documents/method_1316_-_final_8-3-17.pdf.
- Usepa, 2015. SW-846 Test Method 1311: Toxicity Characteristic Leaching Procedure. accessed 10.1.22 [WWW Document]. <https://www.epa.gov/sites/default/files/2015-12/documents/1313.pdf>.
- Uzarowicz, Ł., Skiba, M., Leue, M., Zagórski, Z., Gasiński, A., Trzcinski, J., 2018. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part II. Mineral Transformations and Soil Evolution. *Catena* 162, 255–269. <https://doi.org/10.1016/j.catena.2017.11.005>.
- Uzarowicz, Ł., Zagórski, Z., Mendak, E., Bartmiński, P., Szara, E., Kondras, M., Oktaba, L., Turek, A., Rogoziński, R., 2017. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part I. Properties, classification, and indicators of early pedogenesis. *Catena* 157, 75–89. <https://doi.org/10.1016/j.catena.2017.05.010>.
- Vejahati, F., Xu, Z., Gupta, R., 2010. Trace elements in coal: Associations with coal and minerals and their behavior during coal utilization - a review. *Fuel* 89, 904–911. <https://doi.org/10.1016/j.fuel.2009.06.013>.
- Wang, T., 2007. The leaching behavior of arsenic, selenium and other trace elements in coal fly ash. University of Missouri-Rolla.
- Wang, X., Garrabrants, A.C., van der Sloot, H.A., Chen, Z., Brown, K.G., Hensel, B., Kosson, D.S., 2023. Leaching and geochemical evaluation of oxyanion partitioning within an active coal ash management unit. *Chem. Eng. J.* 454, 140406. <https://doi.org/10.1016/j.cej.2022.140406>.
- Wang, X., van der Sloot, H.A., Brown, K.G., Garrabrants, A.C., Chen, Z., Hensel, B., Kosson, D.S., 2022. Application and uncertainty of a geochemical speciation model for predicting oxyanion leaching from coal fly ash under different controlling mechanisms. *J. Hazard. Mater.* 438. <https://doi.org/10.1016/j.jhazmat.2022.129518>.
- Weber, J., Straczyńska, S., Kocowicz, A., Gilewska, M., Bogacz, A., Gwizdz, M., Debicka, M., 2015. Properties of soil materials derived from fly ash 11 years after revegetation of post-mining excavation. *Catena* 133, 250–254. <https://doi.org/10.1016/j.catena.2015.05.016>.
- Yin, Y., Yin, H., Wu, Z., Qi, C., Tian, H., Zhang, W., Hu, Z., Feng, L., 2019. Characterization of coals and coal ashes with high Si content using combined second-derivative infrared spectroscopy and Raman spectroscopy. *Crystals* 9. <https://doi.org/10.3390/cryst9100513>.
- Zhang, S., Dai, S., Finkelman, R.B., Graham, I.T., French, D., Hower, J.C., Li, X., 2019. Leaching characteristics of alkaline coal combustion by-products: a case study from a coal-fired power plant, Hebei Province, China. *Fuel* 255, 115710. <https://doi.org/10.1016/j.fuel.2019.115710>.
- Zhao, L., Dai, S., Finkelman, R.B., French, D., Graham, I.T., Yang, Y., Li, J., Yang, P., 2020. Leaching behavior of trace elements from fly ashes of five chinese coal power plants. *Int. J. Coal Geol.* 219, 103381. <https://doi.org/10.1016/j.coal.2019.103381>.
- Zikeli, S., Jahn, R., Kastler, M., 2002. Initial soil development in lignite ash landfills and settling ponds in Saxony-Anhalt, Germany. *J. Plant Nutr. Soil Sci.* 165, 530–536. [https://doi.org/10.1002/1522-2624\(200208\)165:4530::AID-JPLN5303.0.CO;2-J](https://doi.org/10.1002/1522-2624(200208)165:4530::AID-JPLN5303.0.CO;2-J).

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Toxicity assessment of coal ash after 50 years of weathering: the integration of multielement analysis and biological endpoints

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Coal ash disposal poses a significant environmental risk due to the potential leaching of toxic elements into surrounding ecosystems. Here, we analysed the phytotoxic effect of two coal ash disposal sites after 50 years of weathering to evaluate whether coal ash remains toxic after long-term disposal and whether vegetated areas are less toxic than bare ones. To analyse that, a combination of multielement analysis of coal ash and eluates and two bioassays—seed germination and *Allium* test—was used. Multielement analysis revealed that some samples exceed the World Health Organization's drinking water thresholds; however, biological responses did not consistently align with the total element concentrations. Seed germination was inhibited in 7 out of 12 samples, most strongly in soil and bare ash eluates from both sites. The *Allium*-based cytogenetic assay showed high mitotic inhibition and genotoxicity in most eluates. Correlation analyses linked Al, As, and V with increased chromosomal aberrations. However, the potential for synergistic or antagonistic interactions among elements complicates the straightforward predictions of toxicity based on concentration alone. Overall, these results advocate for the integration of biological endpoints with chemical data and highlight the persistent toxicity of coal ash even after 50 years of weathering.

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Environmental significance

Coal combustion residues (CCR) are one of the world's largest industrial waste streams, yet their long-term environmental risks remain poorly understood. This study provides one of the first systematic evaluations of phytotoxicity and genotoxicity from ~50-year-old weathered coal ash deposits. By combining chemical analysis with bioassays, we show that coal ash remains toxic decades after disposal, despite partial natural attenuation through vegetation and pedogenesis. Correlation analyses, supported by mechanistic evidence from the literature, suggest that aluminum, arsenic, and vanadium are likely contributors to the observed chromosomal damage. Biological responses did not consistently align with measured elemental concentrations, highlighting the limitations of relying solely on concentration-based thresholds and emphasize the need for integrated chemical–biological approaches in the management of legacy CCR disposal sites.

1. Introduction

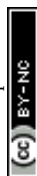
Coal combustion residues (CCRs) refer to four materials (fly ash, bottom ash, slag, and flue gas desulfurization by-products) generated as by-products during coal combustion. Approximately 1.1 billion tons of CCRs are produced annually worldwide, out of which 60% is utilized, and the rest is disposed of in surface impoundments.¹ CCRs, excluding the flue-gas desulfurization by-products, consist of non-combustible inorganic materials with varying percentages of unburned coal particles (organic matter) and are enriched in organic pollutants (PAHs) and trace elements.^{2,3}

Among these trace elements are naturally occurring radionuclides (e.g., ²³⁸U, ²³²Th, and ²²⁶Ra) and potentially hazardous metal(loid)s (e.g., As, Pb, Cd, Cr, Hg, Se, B, and Mo) that exist at 2–10 times higher concentrations than that in the parent coal.⁴ When CCR is disposed of in landfills or impoundments, contaminants may leach into surrounding soils and waters, while fine ash particles can get transported over long distances as they are airborne, creating multiple exposure pathways.^{5,6}

The toxic effects of CCR both in the field and laboratory settings are well documented. In aquatic and terrestrial systems, coal ash has reduced the swimming speed of toads, leading to higher predation risk;⁷ caused oral and spinal deformities in amphibians and fish;^{8,9} and contributed to mercury poisoning in cattle that are grazing near coal power plants.¹⁰ Epidemiological investigations have reported associations between proximity to CCR disposal sites and increased respiratory symptoms, developmental concerns and

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neurobehavioral problems in children.^{11–13} Laboratory bioassays across a wide range of model systems, including plants, invertebrates, microbes, and human cells, have demonstrated that CCR can impair growth, reproduction, and genetic integrity, with dose-dependent effects.^{14–19} Collectively, these findings demonstrate that the impacts of CCR extend from microorganisms to higher organisms. These responses are commonly associated with oxidative stress, inflammation, and DNA damage, resulting from the release and bioavailability of enriched metal(loid)s, such as As, Cd, Cr, Pb, Hg, and Se.^{15,20–22} However, trace elements, PAHs, radionuclides, and high salinity may act alone or synergistically, making it difficult to pinpoint the mechanisms of toxicity.^{23,24}

Moreover, the magnitude of the toxic effects depends strongly on the ash composition, which can differ significantly even among ashes from the same power plant.⁵ Because the ash composition governs toxicity, understanding how it changes under environmental conditions is essential.

Over time, CCR does not remain chemically static. After disposal, decade-long weathering processes alter its physicochemical properties. Reported changes include a decline in pH (from ~12 to <9), secondary mineral precipitation (*e.g.*, calcite), and an increase in organic matter.^{25,26} These transformations affect pollutant release²⁷ and, consequently, toxicity. Yet, most CCR are assessed before disposal, even though landfills worldwide are now several decades old and continue to evolve. Understanding the toxicity of weathered CCR is therefore essential for long-term risk assessment.

To date, few studies have addressed the toxicity of weathered CCR. For example, Bandarra *et al.*²⁸ tested weathered CCR eluates on five organisms (the plant *Lepidium sativum*, the bacteria *Alivibrio fischeri*, the microalgae *Raphidocelis subcapitata*, the macrophyte *Lemna minor* and the microcrustacean *Daphnia magna*) and found overall low impairment, with *Daphnia magna* being the most sensitive. Toxicity was reduced after pH adjustment, underscoring the influence of weathering. Still, systematic evaluations of weathered CCR remain rare, despite the global prevalence of old CCR disposal sites.²⁹

Both landfills investigated in this study are Croatian CCR disposal sites, each comprising a mosaic of bare ash deposits and vegetated areas that have undergone differing degrees of weathering and early pedogenesis.²⁶ Vegetated zones exhibit lower pH levels, greater secondary mineral formation, and higher organic matter content compared to adjacent bare or cemented deposits, which retain properties resembling fresh ash. In our previous work, we demonstrated that this pronounced spatial heterogeneity results from cementation processes and early soil formation developing over the past ~50 years.²⁶ These contrasting conditions within each landfill provide a natural framework for comparing the toxicity of differently weathered CCR materials exposed to the same climate and deposition history.

In this study, we investigated two legacy Croatian CCR landfills using two phytotoxicity assays: the seed germination test and the *Allium* test, following established procedures widely used in environmental monitoring.^{30–32} The seed germination assay evaluates phytotoxicity by measuring the

inhibition of germination and early root elongation, providing a sensitive indicator of plant-level stress caused by CCR exposure. Because germination and early root growth represent the first stages of plant establishment, this assay is particularly relevant for assessing how vegetated and bare areas differ in their ability to support plant growth. The *Allium* test assesses cytotoxic and genotoxic effects in actively dividing root meristem cells through mitotic index and chromosomal aberration endpoints. This allows the evaluation of whether CCR exposure disrupts normal cell division and induces chromosomal damage.

Therefore, we aim to (1) assess the toxicity of ~50-year-old weathered CCR, (2) test whether vegetated areas are less toxic than bare deposits, and (3) evaluate statistical associations between toxicity endpoints and trace element concentrations using correlation analyses to identify which elements are most likely contributing to toxicity. Because experimental testing of individual chemical species in isolation was beyond the scope of this study, these correlations serve as an informative first step toward identifying potential toxic contributors. By addressing these aims, we provide new insight into the long-term evolution of CCR toxicity and its implications for the management and rehabilitation of legacy disposal sites.

2. Materials and methods

2.1. Study area

This study focuses on two unlined CCR landfills located in Štrmac and Plaški villages in Croatia (Europe) (Fig. 1).

The first landfill (LŠ) is situated in Štrmac, a village on the Istrian peninsula, western Croatia (Fig. 1b). It covers ~17 000 m² and consists of coal bottom ash and slag disposed of by a local foundry in the 1960s. The nearest residents live only ~12 m away. The top of the landfill is planted with conifers, while the slopes remain largely bare, with patches of grass and other pioneer species. The ash was produced by burning local Raša coal, a super-high-organic-sulfur coal enriched in S, Se, Mo, U, V, and Re.^{33,34} A detailed description of the geological and geochemical characteristics of Raša coal can be found elsewhere (Medunić *et al.*, 2018; Medunić *et al.*, 2016), as well as environmental pollution caused by its combustion.^{22,35,36}

The second landfill (LP) is situated in Plaški, a village in the Lika Region (Fig. 1c). The landfill consists of 70 000 m³ of fly and bottom ash disposed of by the former sulfate pulp factory operating from 1965 to 1991. The height of the landfill varies from 3.5 to ~13 m.³⁷ The top of the landfill is covered with naturally growing grass, while the slopes are bare, with patches of pioneer plant species (Fig. 1c). Slopes are cemented, which is often found in such landfills.³⁸ The type of coal burned in the factory is publicly unknown.

A detailed characterization of the physicochemical and mineralogical properties of the samples from these two landfills, including granulometric characteristics, distribution of mineral phases, cation exchange capacity, and particle surface area, can be found in the study by Petrović *et al.*²⁶ According to this study, the bare section of the Štrmac landfill is primarily influenced by abiotic processes (the second stage of landfill



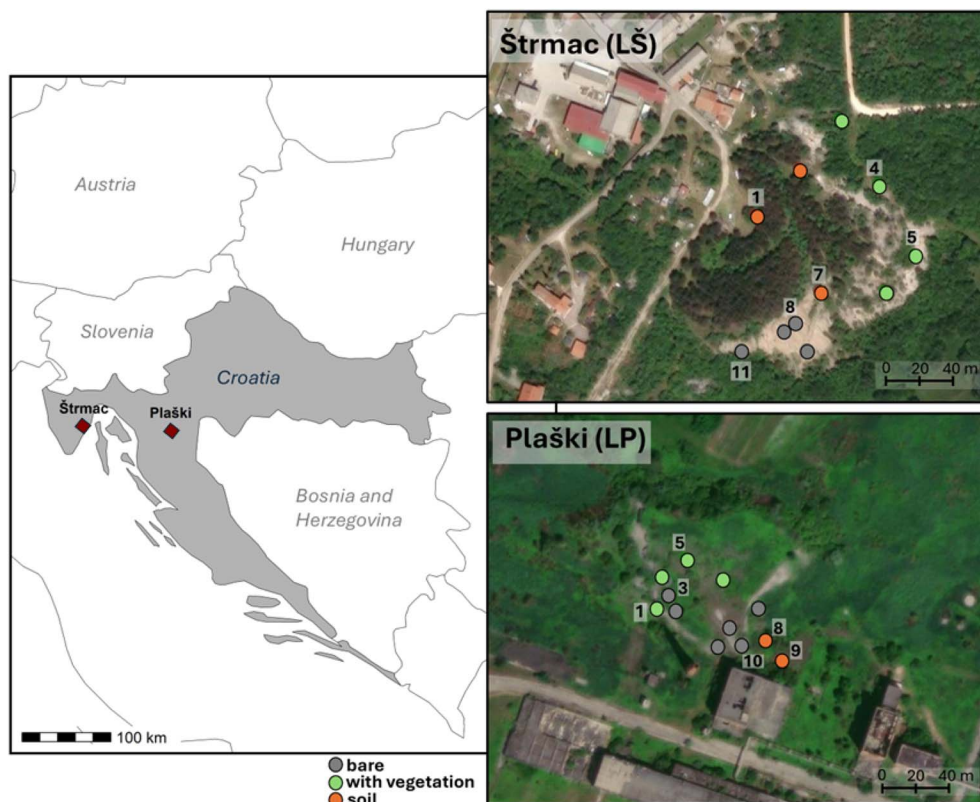


Fig. 1 Study area adapted from Petrović *et al.*²⁶ showing the locations of the two landfills in Croatia and the sampling sites at Štrmac (LŠ) and Plaški (LP) landfills. At each location, several samples with varying depths were taken, and the ones with visible numbers were used for the phytotoxicity study. The physicochemical and mineralogical characteristics of all collected samples are presented in Petrović *et al.*²⁶ Note: an LP1 sample is an intermediate sample. Chemically, it resembles a bare sample, and the grass did not fully cover it like it did the rest of the samples 'with vegetation'. However, that area had patches of vegetation growing on it; thus, in this study, it was classified as a sample with vegetation.

evolution), while the vegetated areas exhibit early signs of pedogenesis (the third stage). In contrast, both the bare and vegetated samples of the Plaški landfill show signs of early pedogenesis (3rd stage).

2.2. Sampling and sample preparation

The sampling campaign was conducted in July 2020 (LŠ) and May 2021 (LP) with a total of 69 samples collected. The sampling details and sample preparation can be found in Petrović *et al.*²⁶ For the total element analysis, all samples were analyzed. For phytotoxicity testing, 12 samples were chosen (6 from both landfills), including soil samples (LŠ1, LŠ7, LP8, LP9), naturally vegetated samples (LŠ5, LŠ4, LP5, LP1) and bare samples (LŠ8, LŠ11, LP3, LP10). In addition, an Allium test was performed on two "fresh" ash samples (fly ash, FA and bottom ash, BA) generated, collected, and properly stored in the 1970s from the Plomin Thermal Power Plant, which used the same Raša coal as the foundry in Štrmac.

2.2.1. Sample preparation for the total element analysis. For the total element analysis, sub-samples (0.05 g), previously homogenized in an agate mill, were subjected to a total digestion in the microwave oven (Multiwave 3000, Anton Paar, Graz, Austria) in a two-step procedure. The latter involved digestion

with a mixture of 4 mL of nitric acid (HNO_3 , 65%, pro analysi, Kemika, Zagreb, Croatia), 1 mL of hydrochloric acid (HCl), and 1 mL of hydrofluoric acid (HF, 48%, pro analysi, Kemika, Zagreb, Croatia), followed by the addition of 6 mL of boric acid (H_3BO_3 , Fluka, Steinheim, Switzerland). Prior to analysis, digests were 10-fold diluted, acidified with 2% (v/v) HNO_3 (65%, supra pur, Fluka, Steinheim, Switzerland), and In ($1 \mu\text{g L}^{-1}$) was added as the internal standard.

2.2.2. Eluate preparation. A standardized European leaching batch test (EN-12457-2) at a liquid to solid ratio of 10 : 1 was used for eluate preparation.³⁹ The prepared suspensions were shaken for 24 h using the mechanical shaker at 320 rpm, centrifuged, and filtered using a $0.45 \mu\text{m}$ filter. Since some samples have very high pH (>11), the pH of the eluates was adjusted to 6–7 with 1 M, 0.5 M, and 0.1 M HCl to remove pH as a toxic parameter and focus on ash constituents (Table S1).

2.3. Multielement analysis

Elemental concentrations were determined by inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ, 8900 Agilent, USA). A total of 30 elements were analysed: Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, U, V, and Zn.



Analytical quality control included procedural blanks, instrument blanks, and repeated analysis ($n = 6$) of certified reference materials (CRMs). Three CRMs were used to verify the analytical performance across different matrices: NCS DC 77302 (China National Analysis Centre for Iron and Steel, Beijing, China) for soil samples, NCS FC 28145 (China National Analysis Centre for Iron and Steel, Beijing, China) as a certified coal ash reference material, and SLRS-4 (National Research Council Canada) for aqueous eluate analyses.

Recoveries for all elements ranged between 90% and 110% of certified values. The relative standard deviations (RSD) for the CRM replicate analyses were generally below 5%. Instrument blanks were consistently below the detection limits for all measured elements. The limits of detection (LOD) were calculated as three times the standard deviation of repeated procedural blank measurements and are reported in the Tables S4 and S6.

The results of total analysis for As, Cr, Mo, Se, U, and V were reported previously for the interpretation of leaching tests.²⁷ The total concentration for the rest of the elements and the eluate concentrations have not been previously published. The results of the eluates were compared to the EU non-hazardous landfill leachate limits⁴⁰ and the more rigid WHO/EU drinking water thresholds.⁴¹

2.4. Ecotoxicity testing

2.4.1. Seed germination test. The germination test was performed according to the procedures described in Fritz *et al.*⁴² (2007) and Luo *et al.*³² (2018) with certain modifications. Two layers of sterile filter paper and 5 mL of the sample or 5 mL of pure water (Milli-Q), which we used as a negative control, were added to sterile plastic Petri dishes with a diameter of 9 cm. 20 lettuce seeds (*Lactuca sativa* L., a variety of Dalmatian ice lettuce) were placed in each bowl. Four replicates for each sample investigated were left in the dark at a temperature of 22 ± 1 °C. For four days (96 h), we recorded the number of germinated seeds. To maintain humidity, on the third day of the experiment (after 72 h), we added another 2.5 mL of the sample, or Milli-Q water (control), to the Petri dishes. At the end of the fourth day of the experiment (96 h), we measured two toxicity endpoints: seed germination and radicle length.⁴²

We expressed the results as follows:

(a) Seed germination (SG): the percentage of germinated seeds in a certain period of time:

$$SG(\%) = \frac{\text{no. of germinated seeds}}{\text{no. of total seeds}} \times 100$$

(b) Relative seed germination (RSG): the percentage of germinated seeds in the treatment compared to the control (used only to calculate the Germination index):

$$RSG(\%) = \frac{\text{no. of germinated seeds}(\text{sample})}{\text{no. of total seeds}(\text{control})} \times 100$$

(c) Relative radicle growth (RRG): the length of the radicle after the treatment compared to the length in the control:

$$RRG(\%) = \frac{\text{radicle length in treatment}}{\text{radicle length in control}} \times 100$$

(d) Germination index (GI):

$$GI = \frac{RSG \times RRG}{100}$$

2.4.2. Allium test. Onion bulbs (*Allium ascalonicum* L.), with ~2 cm diameter, were prepared by removing the dry outer scales and gently cleaning the base of each bulb without damaging the root primordia. The bulbs were placed on the top of glass flasks filled with reverse osmosis-purified tap water (pH 6.5), and roots were allowed to grow for 48 hours, with daily water changes. Once the roots reached ~1.5 cm, the bulbs were exposed for 24 hours to sample eluates, with five biological replicates per treatment. Tap water was used as the negative control, and a $5 \mu\text{mol L}^{-1}$ copper sulfate solution ($\text{CuSO}_4 \times 5 \text{H}_2\text{O}$) was used as the positive control.

After treatment, some roots were fixed immediately in ethanol-acetic acid (3 : 1), while others were placed in fresh tap water for a 24-hour recovery before fixation. All procedures were carried out at 22 ± 1 °C and shielded from light. It should also be noted that the tap water used during root growth, the recovery period, and as a negative control was left at room temperature for 24 hours and aerated for at least 5 minutes before use in the experiment. During the experiment, the water was changed every 24 hours.

Fixed roots were hydrolyzed in 1 M HCl (Lach-Ner s.r.o.) at 60 °C for 10 minutes and stained with Schiff's reagent⁴³ for 1.5 hours. The roots were then prepared for microscopy by immersing the meristem region in a drop of 45% (v/v) glacial acetic acid. The meristem region was then cut off, and the tissue of the root tip was crushed with a glass rod, covered with a coverslip and pressed with the thumb ("squash" technique). At least five microscope slides were prepared per treatment, and a minimum of 4000 cells were analyzed per condition using a Primo Star Zeiss light microscope under 40× or 100× magnification. The following parameters were determined:

(a) Mitotic index (MI): the percentage of dividing cells in the total number of observed cells:

$$MI(\%) = \frac{\text{no. of dividing cells}}{\text{no. of total cells}} \times 100$$

(b) Chromosomal aberrations (CA): the percentage of cells with chromosomal or mitotic aberrations in the total number of cells in division:

$$CA(\%) = \frac{\text{no. of cells with aberrations}}{\text{no. of cells in division}} \times 100$$

In addition, the types of chromosomal aberrations were recorded.



2.5. Statistical analyses

All values are obtained from four replicates. Unless otherwise stated, descriptive values in the text refer to sample means. Boxplots in all figures display medians and interquartile ranges. Statistical analyses were performed in MATLAB R2023b.

Differences among treatments were evaluated separately for each landfill (Štrmac and Plaški). For the seed germination test, one-way ANOVA, followed by Tukey's *post hoc* test, was performed, including all eluate treatments and the corresponding negative control within each site. For the Allium test, separate one-way ANOVAs were conducted for the mitotic index (MI) and chromosomal aberrations (CA), including all exposure treatments and controls within each site. Recovery-phase data were analyzed independently using the same approach. The significance level was set at $p < 0.05$.

Spearman correlation coefficients were calculated for biological endpoints and eluate concentrations, and the results were visualized as heatmaps.

3. Results and discussion

3.1. Geochemical characterization of weathered coal ash samples

The geochemical composition of major oxides in CCR samples was assessed using concentration coefficients (CC), defined as the ratio between measured oxide concentrations and the average composition of European coal ash. This approach highlights the relative enrichment (CC > 1) or depletion (CC < 1) of elements compared to the typical European CCR.⁴⁴

The results revealed the high enrichment of sulfur and calcium and the depletion of other oxides (Al_2O_3 , Fe_2O_3 , K_2O , MgO , MnO , Na_2O , P_2O_5 , and TiO_2) (Fig. 2). A high sulfur enrichment in Štrmac CCR reflects their origin from Raša coal, a unique coal type with exceptionally high organic sulfur content.^{33,45,46} Similarly, CaO enrichment and the depletion of Al_2O_3 and Fe_2O_3 were expected, given the abundance of Ca-bearing minerals, such as calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), portlandite (Ca(OH)_2), and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) in these ashes.^{26,46}

These oxide patterns have important implications for ash reactivity, as they classify both ashes as Ca-rich ash (class C).⁴⁷ Ca-rich ashes typically have high buffering capacity, alkaline pH, and a tendency to leach oxyanion-forming elements, such as As, Cr, Mo, P, S, Se, Sb, U, and V.⁴⁶

The CC of the trace elements in the coal ash samples, normalized to world coal ash averages,⁴⁸ revealed clear patterns of enrichment and depletion across the two landfill sites and material types (Fig. 3). At Plaški, high enrichment was observed for Ni, Cr, and U, with moderate enrichment of V, Mo, and Cs. At Štrmac, similarly high values were recorded for Mo and U, along with relatively greater enrichment of Se compared to the case at Plaški. In contrast, unweathered ash samples (FA and BA) showed enrichment in Rb (6.4) and Mo (3.1), together with consistently higher CCs for several alkali metals compared to weathered landfill materials (Table S5).

When comparing different sample types (bare and with vegetation), the Plaški samples displayed a more uniform distribution, with bare ash consistently enriched in most trace elements. At

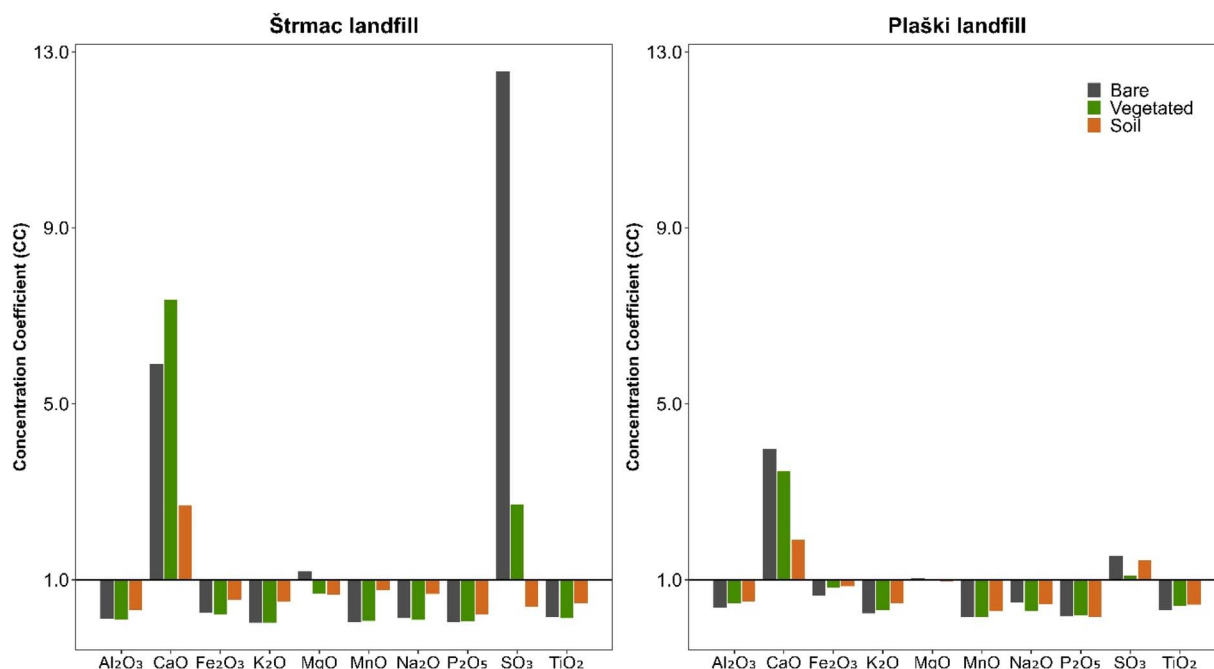


Fig. 2 Median concentration coefficients (CC) of major oxides in the samples from the Štrmac and Plaški coal combustion residue (CCR) landfills. CC was calculated as the ratio of the oxide concentration in each sample type to the average oxide concentration in European coal ash.⁴⁴ Values above 1 indicate enrichment, while values below 1 indicate depletion. Total oxide concentrations for each sample are reported in the SI (Tables S2 and S3).



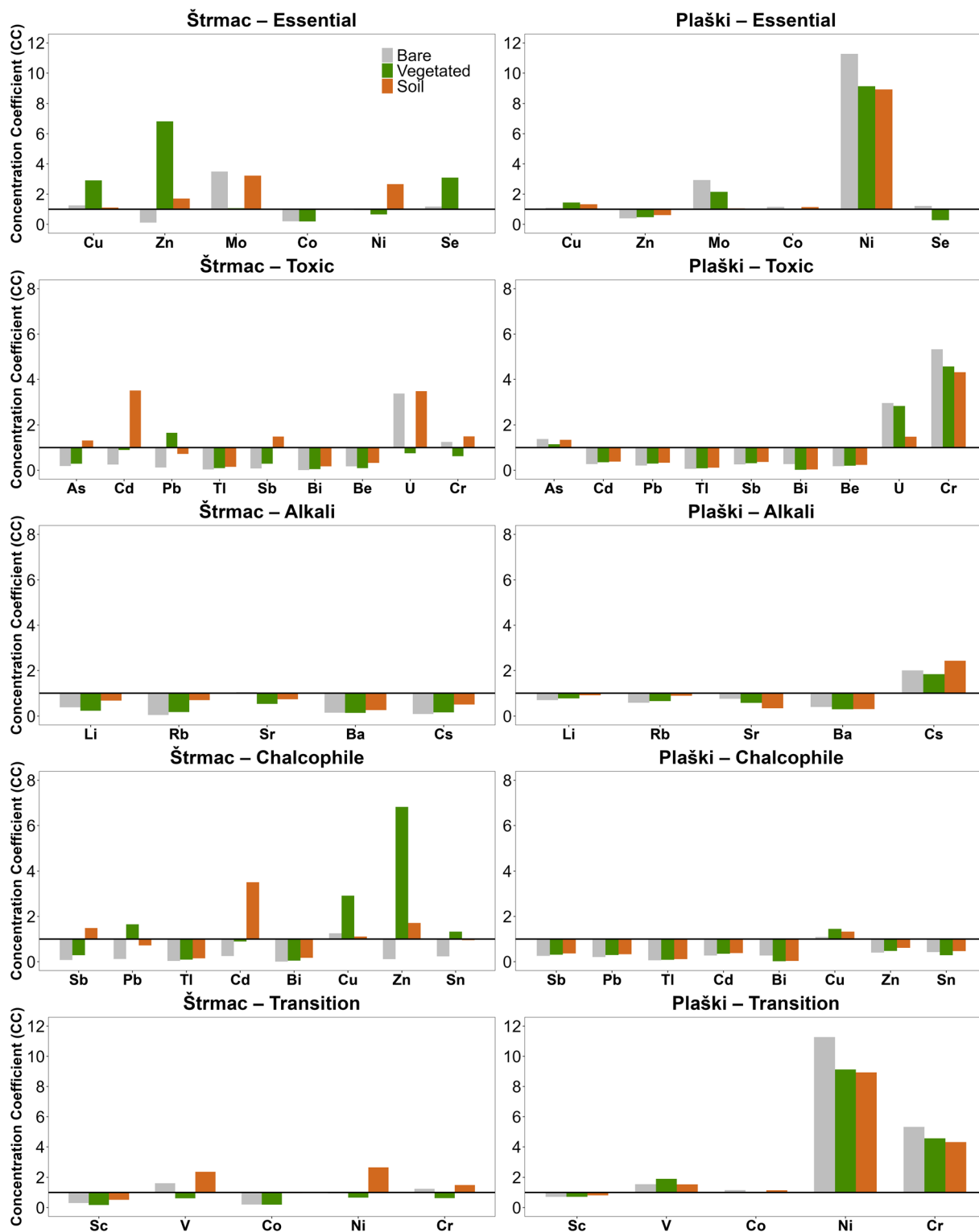


Fig. 3 Average concentration coefficients (CC) of trace elements in the Štrmac and Plaški samples. CC was calculated as the ratio of the sample element concentration to the global coal ash average.⁴⁸ Elements were grouped by plant relevance (essential vs. toxic) and geochemical behaviour (alkali, transition and chalcophile) to highlight mobility and uptake pathways.^{49,50} Categories are not mutually exclusive; hence, some elements appear in more than one group. Full concentrations are in the SI (Tables S4 and S5).

Štrmac, the distribution was less uniform, where ash with vegetation showed higher enrichment in Cu, Zn, and Se, and soil materials in Ni and Cd, compared to the bare ash samples.

3.2. Geochemical characterization of ash leachates

Although the analyzed samples were enriched in several major and trace elements compared to the European and global



averages, the total concentration alone does not reflect the toxic capacity of coal ashes. To better assess the environmental risk, the relative mass leached (RML, %) and water-soluble concentrations were determined.

Most major and trace elements showed low mobility (RML < 1%), indicating strong retention in the solid phase. However, several elements exhibited much higher release, depending on the sample type and site conditions. Among major elements, Na, K, and Ca were the most mobile. Na reached 22.6% in LP3 and 16.1% in BA, with elevated values also in FA (7.9%), LŠ1 (5.5%), and LŠ11 (6.4%). K peaked in LŠ4 (27.4%) and LŠ8 (13.5%), while Ca was highly soluble in BA (24.0%). Mg was generally stable, except in LP3 (5.6%) (Table S7). These values are consistent with the dissolution of soluble salts and Ca-bearing phases, such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), portlandite ($\text{Ca}(\text{OH})_2$), and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), which are typical of high-Ca ashes.^{26,46,51,52}

Among trace elements, the highest mobilities were observed for Cd, Mo, Pb, Zn, Sr, and Se (Fig. 4 and Table S7). Cd was highly mobile in LP3 (21.6%) and BA (24.0%). Mo reached 22.6% in LP3 and was also elevated in LŠ1 (5.5%) and LŠ11 (6.4%). Pb showed moderate release in LP3 (5.1%). Zn reached 11.5% in LŠ11 and 8.9% in BA. Sr was especially mobile in FA (9.5%), while Se was enriched in BA (15.2%) and FA (6.4%). In contrast, Ni remained consistently low (<0.5%) in all samples, despite its enrichment in Plaški ashes.

Clear differences were observed between sample types. Bare ashes (LP3, LŠ11) and unweathered ashes (FA, BA) consistently showed the highest leaching fractions, reflecting the dominance of soluble phases, typical of the early abiotic stage of landfill evolution.²⁶ Within this group, individual samples, such as LP3 and LŠ11, showed especially high leaching fractions. This variability between the same sample type may be linked to localized cementation, which could have reduced infiltration and promoted the accumulation of soluble salts in parts of the landfill, similar to cementation zones described in mine tailings.⁵³

In contrast, vegetated or soil samples (LP1, LP5, LŠ7, LŠ5) generally showed lower RML values than bare samples. Lower RML values in vegetated samples are likely a result of more advanced pedogenesis in those samples.²⁶ A decrease in pH to a more neutral value, a higher organic matter content, and the precipitation of more stable secondary minerals (calcite, clays) may all have caused the reduction in element release.⁵⁴ However, some excepted results were observed, including more mobile As in the vegetated Plaški sample (LP5) and U, As, and V in the vegetated Štrmac samples. Unlike cationic elements (*e.g.*, Pb, Zn, and Ni), which are strongly retained by clays, oxides, and organic matter, these elements occur mainly as oxyanions (arsenate, uranyl-carbonate, vanadate). The shift from hyper-alkaline conditions in bare ash to neutral-alkaline conditions in vegetated samples²⁶ may have promoted higher release of the mentioned oxyanion species. This has been observed in modelling studies of the leaching of oxyanion species from coal ash⁵⁵ and our previous leaching study, which showed that pedogenesis changes how As and V are released.²⁷ Thus, while vegetation and soil development generally reduce trace element

release, they may simultaneously promote the mobility of certain oxyanion-forming elements.

Site-specific differences were also evident. Plaški samples were more prone to releasing oxyanion-forming elements (As, V) and alkali metals (Li, Rb). In contrast, Štrmac samples released more Ba, Ca, Sr, Cr, and Cu, likely reflecting the Raša coal origin and the abundance of soluble Ca-S phases that favor co-leaching of alkaline earths and redox-sensitive trace metals under strongly alkaline conditions.^{36,45}

Overall, element mobility appears to be governed by both the stage of pedogenesis and site-specific mineralogy, with cementation and salt accumulation offering explanations for localized hotspots, such as LP3. Bare and unweathered ashes (LP3, LŠ11, FA, BA) exhibited the highest leaching, while soil and vegetated samples were more stable, with exceptions in certain oxyanion-forming species. These findings highlight the role of landfill evolution, cementation, and coal origin in determining which elements remain environmentally relevant during long-term weathering of CCR.

3.2.1. Comparison with environmental standards. To further assess the risk and describe the samples' composition, elemental concentrations were compared to two regulatory thresholds commonly used for comparison in leaching studies.

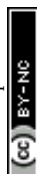
When compared to the EU non-hazardous landfill leachate limits,⁴⁰ most eluate concentrations were below regulatory thresholds. Only Mo in one sample (LP3, bare) exceeded the EU limits for non-hazardous waste leachate. No other sample exceeded these limits; therefore, from a waste classification perspective, almost all samples would be considered acceptable for disposal at non-hazardous waste facilities.

When applying the more stringent drinking water standards,⁴¹ multiple exceedances were observed (Table 1). The As concentrations exceeded the $10 \mu\text{g L}^{-1}$ threshold in four Plaški samples (LP1, LP3, LP5, LP8), while Cd was above the $3 \mu\text{g L}^{-1}$ guideline in LP3. The Cr and Pb levels surpassed their respective drinking water limits ($50 \mu\text{g L}^{-1}$ and $10 \mu\text{g L}^{-1}$) in LP3 and LP5, and Pb also exceeded the limit in Štrmac samples LŠ4 and LŠ11. Mo exceeded the $70 \mu\text{g L}^{-1}$ limit only in LP3, which also had the highest concentrations of multiple other metals, including U, Sb, and Ba. The U concentrations were also above the drinking water limit ($30 \mu\text{g L}^{-1}$) in LŠ7, and the barium levels exceeded the $700 \mu\text{g L}^{-1}$ limit in LŠ11.

Despite the relatively low total concentrations for many metals, these findings highlight that several eluates (LP3, LP5, LŠ7, LŠ11, LŠ4) contain trace elements at levels that exceed safe drinking water standards. This suggests potential environmental risks if such eluates were to enter groundwater systems or surface water bodies, especially in scenarios of long-term leaching. This is particularly important because both landfills are unlined.

3.3. Phytotoxicity of weathered coal ash

3.3.1. Influence of weathered coal ash on seed germination and radicle growth. The potential toxic effects of weathered coal ash eluates and associated soils were evaluated based on three



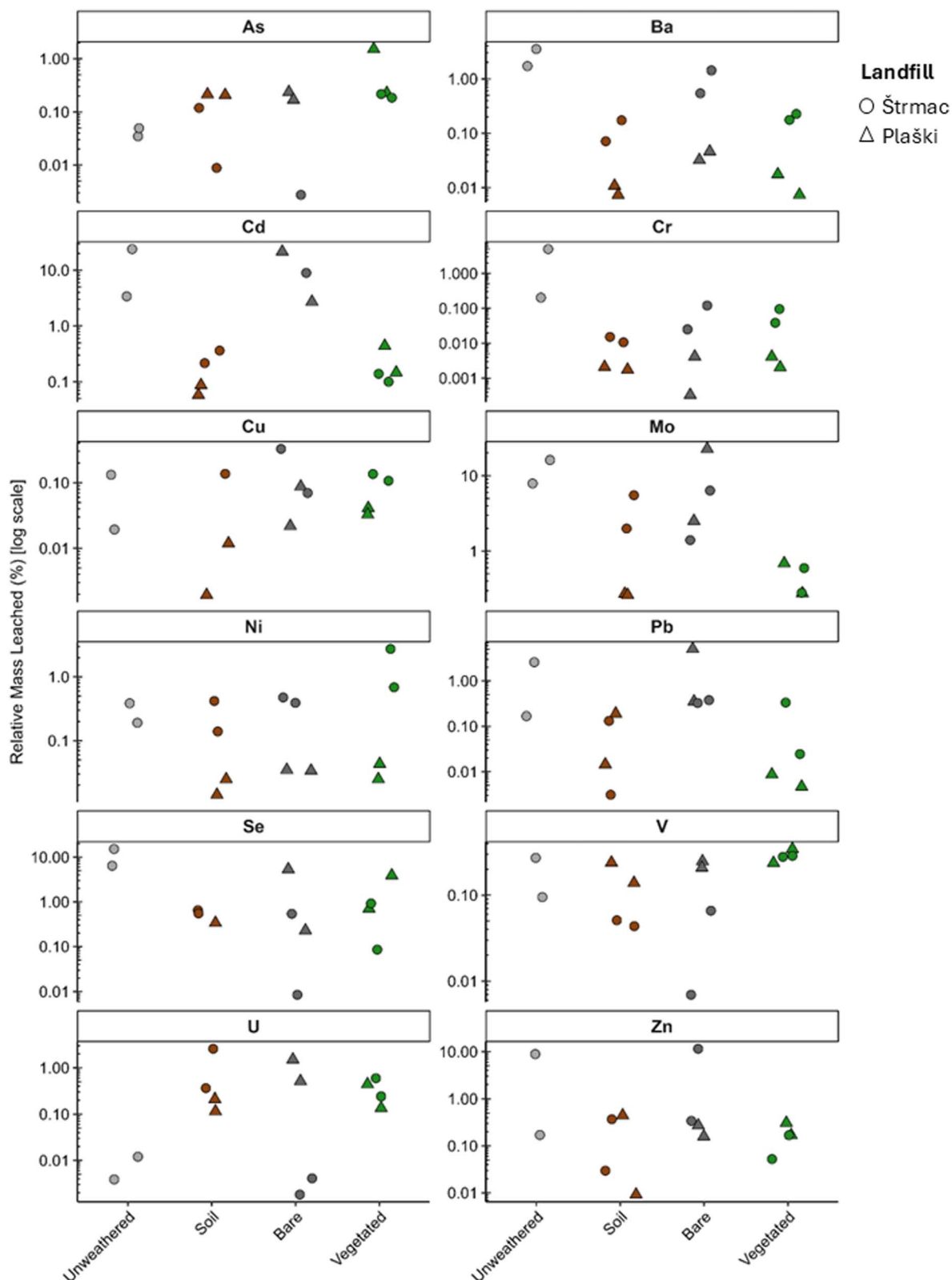


Fig. 4 Relative mass leached (%) of selected trace elements (As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Se, V, U, and Zn) from coal ash samples in different sample types (unweathered, soil, bare, and vegetated). Values are shown on a logarithmic scale to account for the variation across orders of magnitude. Symbols: Plaški landfill, triangles; Štrmac landfill, circles. Measured concentrations and calculated relative mass leached (RML) values for every element and sample are in the SI (Tables S6 and S7).



Table 1 Comparison of the measured element concentrations in eluates to two different regulatory thresholds: the EU non-hazardous landfill leachate limits at a liquid-to-solid ratio (L/S) of 10 L kg⁻¹ (ref. 40) and more rigid WHO drinking water thresholds.⁴¹

	EU non-hazardous waste leachate limit (μg L ⁻¹)	WHO drinking water limit (μg L ⁻¹)	Minimum (μg L ⁻¹)	Maximum (μg L ⁻¹)	Above limit?	Samples exceeding the limit
As	200	10	0.13	62.5	Yes (4)	LP1, LP3, LP5, LP8
Ba	10 000	1300	5.37	8260	Yes (1)	LŠ11
Cd	100	3	0.01	9.83	Yes (1)	LP3
Cr	1000	50	1.5	98.0	Yes (2)	LP5, LP3
Cu	5000	2000	0.58	132	No	—
Mo	1000	70	0.24	1235	Yes (1)	LP3
Ni	1000	70	11.4	133	Yes (1)	LŠ4
Pb	1000	10	0.06	73.8	Yes (3)	LP3, LŠ4, LŠ11
Sb	70	5	0.03	0.99	No	—
Se	50	40	0.03	6.28	No	—
U	—	30	0.13	276	Yes (2)	LP3, LŠ7
Zn	5000	—	0.25	54.9	No	—

indicators: seed germination, relative radicle growth, and germination index.

Seed germination (SG) of seeds treated with eluates from the Štrmac locality (LŠ1, LŠ4, LŠ5, LŠ7, LŠ8, LŠ11) ranged from 35% to 91%, while for the Plaški samples (LP1, LP3, LP5, LP8, LP9, LP10), it ranged from 20% to 90% (Fig. 5). In comparison, the control seeds germinated at 95%.

Based on ANOVA followed by Tukey's *post hoc* test (Table S8 and Fig. 5), seven of the tested samples showed significant inhibition of germination compared to the control. Among the

Štrmac coal ash samples, inhibition was observed for two bare ash eluates (LŠ8, LŠ11) and one vegetated ash eluate (LŠ5). Among the Plaški coal ash samples, inhibition was observed for two bare ash eluates (LP3, LP10). No significant differences were found between the vegetated and bare ash samples within the Štrmac locality. In Plaški, however, the vegetated ash samples (LP1, LP5) exhibited significantly higher SG than the bare ash samples (LP3, LP10), suggesting early pedogenic effects that mitigate toxicity.

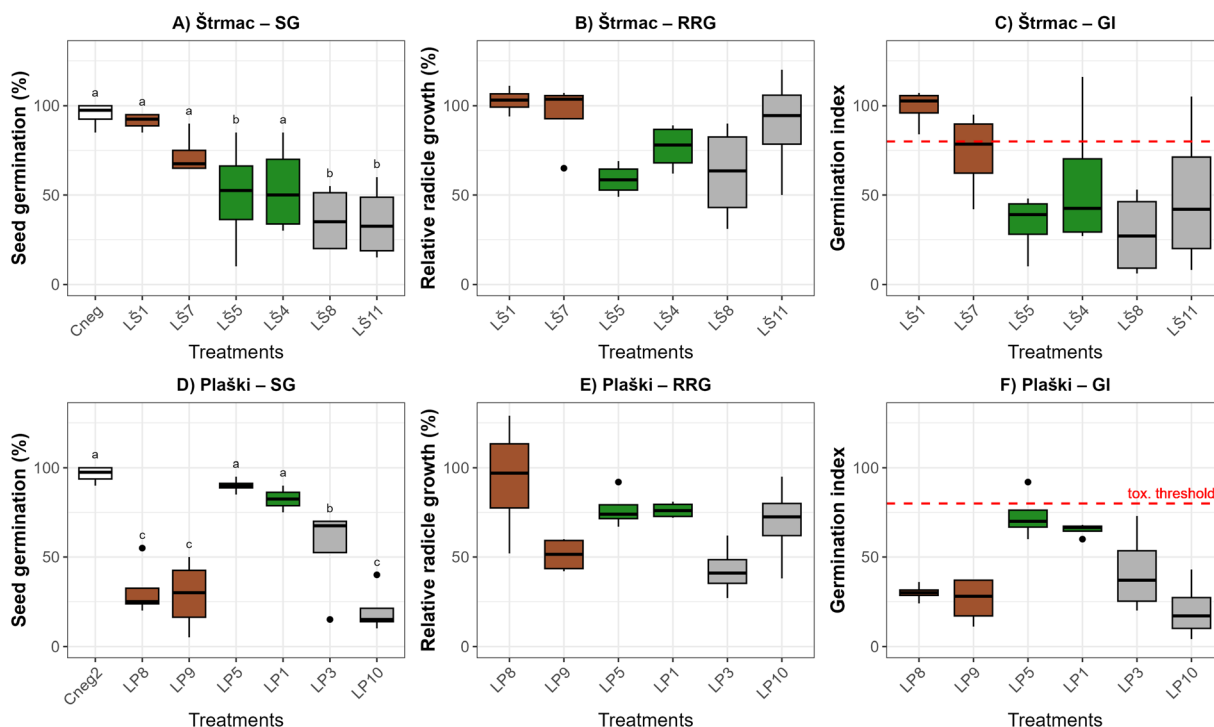


Fig. 5 Seed germination (%; (A) and (D)), relative radicle growth (%; (B) and (E)), and germination index (C and F) of seeds treated with eluates from the Štrmac (A–C) and Plaški (D–F) localities. Colors denote sample types: negative control (white), soil samples around the landfill (brown), samples with vegetation (green), and bare ash samples (grey). Different lowercase letters above boxplots indicate statistically significant differences between treatments based on one-way ANOVA, followed by Tukey's *post hoc* test ($p < 0.05$). Black dots represent outliers. Based on the literature, a value of 80 was taken as the toxicity threshold (red dashed line) for the germination index.³²



For soil eluates, significant inhibition was observed in both Plaški soil samples (LP8, LP9), whereas none of the Štrmac soil samples (LŠ1, LŠ7) showed inhibition. The contrasting toxicity patterns most likely stem from differences in sampling locations. Štrmac soils were collected on top of the landfill, whereas Plaški soils were collected downslope beneath the ash body, where leachate accumulation is expected to be greater.

Because radicle growth is a more sensitive indicator of stress,^{56,57} it is commonly evaluated for samples that do not significantly inhibit seed germination. The relative radicle growth (RRG) incorporates negative control into its calculation; therefore, values below 100% reflect reduced radicle growth.

Among the Štrmac samples without significant effects on SG (LŠ1, LŠ7, LŠ4), the RRG values varied considerably. Soil samples LŠ1 and LŠ7 showed radicle growth close to the reference level (100%), whereas the vegetated LŠ4 sample exhibited a noticeable reduction. A similar pattern was observed for Plaški. Although vegetated samples LP5 and LP1 did not significantly inhibit SG, both displayed reduced RRG.

These findings demonstrate that germination alone may underestimate toxicity, as radicle growth can be impaired even when seeds germinate successfully. This highlights radicle growth as an important complementary indicator for identifying sublethal effects that may disturb seedling growth and development.

It is worth noting that the samples that inhibited seed germination had a relative radicle growth similar to or even higher than the samples that did not inhibit seed germination, which seems contradictory. For example, two bare samples from both localities, LŠ11 and LP10, had the lowest seed germination of all samples at their respective location, but their radicles were among the longest. Although it could be that some ash constituents only affect seed germination and not radicle growth, it is more likely that the cause is stress-induced growth,⁵⁸ particularly because the radicles were visually more twisted and thinner than radicles from the control group. This may be an adaptive mechanism of the plant to explore a larger soil volume to find less toxic zones or more nutrients, or it may be caused by some other effect (e.g., alteration of hormonal balance in the radicles),⁵⁹ which future studies should address.

To integrate both germination and radicle growth effects, the germination index (GI) was calculated as it comprehensively reflects the toxicity of the sample.^{32,60} For seeds treated with the Štrmac samples, the germination index ranged from 28 to 99, and for the seeds treated with the Plaški samples, the values ranged from 20 to 73 (Fig. 5). Seeds treated with LP10 (20), LŠ8 (28) and LP8 (30) had the lowest indices, and those treated with samples LŠ1 (99), LŠ7 (73), and LP5 (73) had the highest germination indices, showing that toxicity varied among samples.

A GI value of 80 is commonly used as a toxicity threshold; therefore, values above 80 indicate non-toxic conditions, and lower values reflect phytotoxicity.^{32,56} Thus, based on this criterion, nine out of twelve samples were classified as toxic. In the Štrmac locality, two bare samples (LŠ8 and LŠ11) and two vegetated (LŠ4 and LŠ5) were classified as toxic, while the soil samples were the least affected. All Plaški samples exhibited GI

< 80, with vegetated samples LP5 (73) and LP1 (65) showing milder toxicity than bare ash eluates LP3 (42) and LP10 (20).

Although most samples showed phytotoxic effects, the severity of toxicity varied between sample types and localities. At Štrmac, the vegetated and bare ash eluates exhibited similar toxicity levels, while at Plaški, the vegetated samples displayed substantially higher GI values, indicating that early pedogenesis has already moderated toxicity in certain parts of the landfill.

Taken together, these results show that early pedogenesis can measurably reduce phytotoxicity, not only through geochemical changes, such as pH buffering, reduced salinity, and secondary mineral formation (see Section 3.2), but also by lessening biological impacts on germination and early root growth (higher GI, higher RRG where SG is unaffected). In other words, pedogenesis at Plaški is already translating into reduced biological stress, even though exceptions remain (e.g., oxyanion-forming elements discussed above). This highlights that landfill evolution influences both geochemical properties and ecological outcomes for the resident biota.

3.4. Influence of weathered coal ash on the cell division and chromosomes of *Allium ascalonicum* root tips

The *Allium ascalonicum* root-tip assay revealed that exposure to weathered coal ash caused notable suppression of cell division and induced a spectrum of chromosomal abnormalities in the root meristems. These effects varied by sample type and site of origin, and clear differences were observed before vs. after a recovery period in clean water. The results are detailed below, along with a discussion of their implications and mechanisms.

3.4.1. Cytotoxicity of weathered coal ash. Microscopic observations of the *A. ascalonicum* meristematic root tip cells revealed differences in cell division between the negative control and roots treated with the ash (Fig. 6 and Table S8). 11 out of 14 samples significantly lowered cell division compared to the negative control, with the average mitotic index ranging from 1.94% to 4.53%. The highest inhibition of cell division was caused by the vegetated LP1 sample (MI = 1.94%), followed by two unweathered fly (FA) and bottom (BA) ash samples (2.36 and 2.56%, respectively). Soil LŠ1, vegetated LŠ4, and bare LP10 samples did not cause a significant difference in cell division compared to the negative control. For comparison, the mitotic indices of the bulbs treated with the negative and positive controls were 6.03% and 0.35%, respectively (Fig. 6).

A decrease in MI is a well-established indicator of cytotoxicity, reflecting cell-cycle arrest or prolongation of specific phases due to toxic stress. Reduced MI indicates that fewer cells are able to progress into mitosis under chemical exposure.⁶¹ Comparable responses have been reported for fresh coal fly ash. Jana *et al.*¹⁵ documented a >50% reduction in MI in onion roots exposed to concentrated ash leachates, while Chakraborty *et al.*¹⁴ observed complete growth arrest and severe inhibition of mitotic activity at high ash concentrations. These findings support the interpretation that the reduced MI in our samples reflects inhibition of normal cell-cycle progression. Mechanistically, toxicants commonly present in ash, such as certain metals and metalloids, can delay the G₂/M transition, disrupt



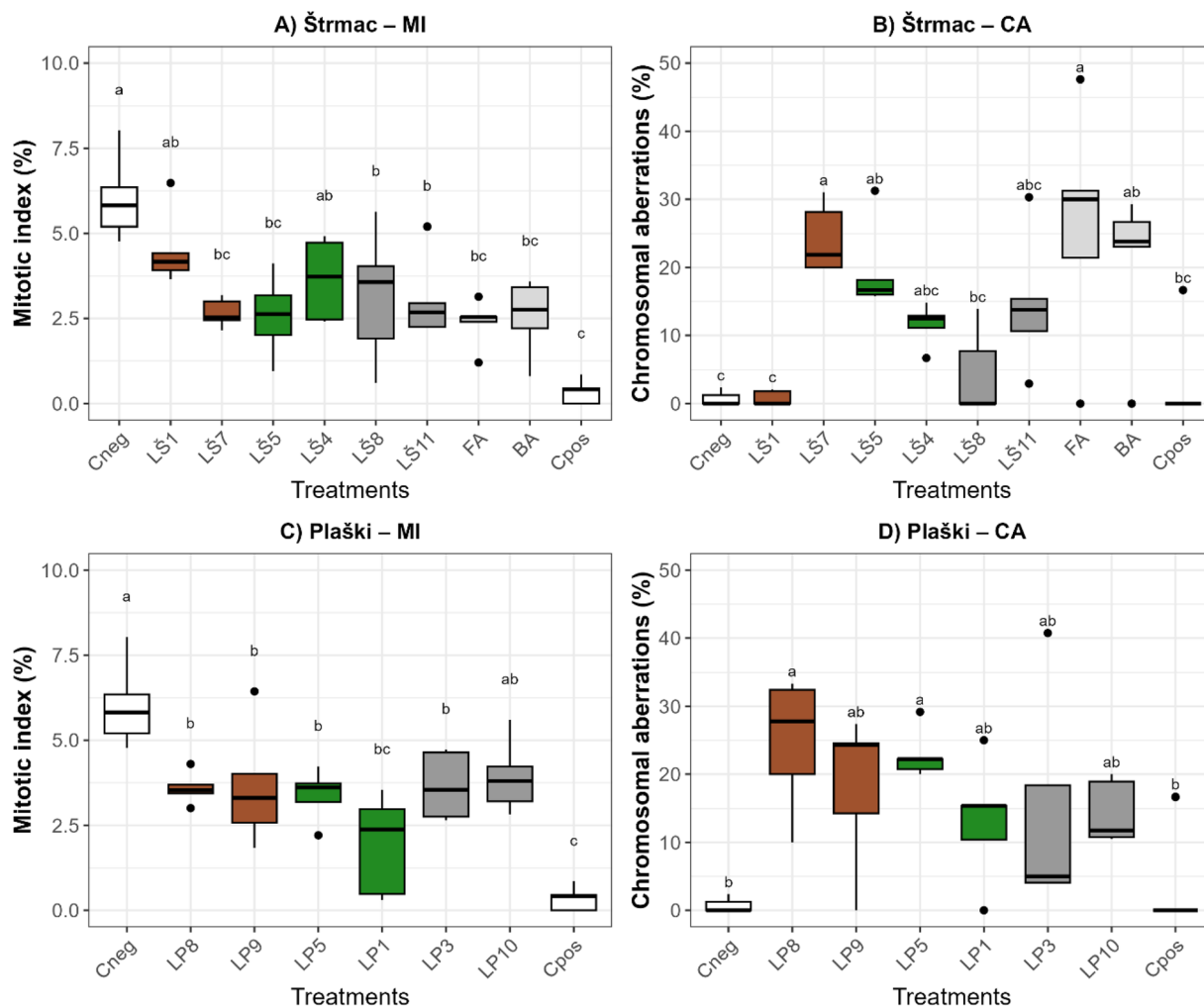


Fig. 6 Mitotic index (%) and chromosomal aberrations (%) in *Allium ascalonicum* root tips exposed to eluates from Štrmac (A and B) and Plaški (C and D). Panels A and C show mitotic index, and B and D chromosomal aberrations. Colors denote different samples: control (no color), soil samples around the landfill (brown), samples with vegetation (green), and bare samples (grey). Different lowercase letters above boxplots indicate statistically significant differences between treatments based on one-way ANOVA, followed by Tukey's *post hoc* test ($p < 0.05$). Black dots represent outliers.

spindle formation, or activate DNA-damage checkpoints, resulting in fewer cells entering mitosis at any given time.^{15,62}

In our study, unweathered FA and BA induced the strongest mitotic suppression, consistent with the higher availability of contaminants in unweathered ash. Weathered samples exhibited a broader range of MI responses, which likely reflects differences in their eluate composition. These relationships are examined in more detail in Section 3.3.

After 24 hours of recovery, which included placing roots in control water and allowing cells to divide under no influence of the leachate sample, cell division increased in all analyzed root tips, with the mitotic index ranging from 2.46% to 5.44%. In comparison, the mitotic indices of the negative and positive controls were 5.36 and 2.97% after recovery, respectively (Fig. 7). All samples, except LP1, LP5, and the positive control, showed an increased MI after recovery compared to their exposure values, indicating that the mitotic inhibition caused by many treatments was at least partially reversible. The reversibility of

MI suppression is commonly interpreted as evidence of acute, non-permanent cell-cycle inhibition rather than irreversible cytotoxic damage, as plants can repair sublethal injuries once the toxicant is removed.⁶³

However, not all treatments achieved full recovery. FA remained below the MI of the negative control even after recovery, and LP8 showed a decrease in MI following recovery, suggesting persistent or delayed toxicity. Such patterns may arise when contaminants remain bound within root tissues and continue to affect cell physiology through mechanisms such as oxidative stress or enzyme inhibition, even after external exposure ends.¹⁵

Overall, the evaluated MI revealed that both unweathered and weathered coal ash eluates can suppress mitotic activity, with varying degrees of reversibility. These data distinguish samples that exert predominantly acute effects from those with more lasting cytotoxic influence.



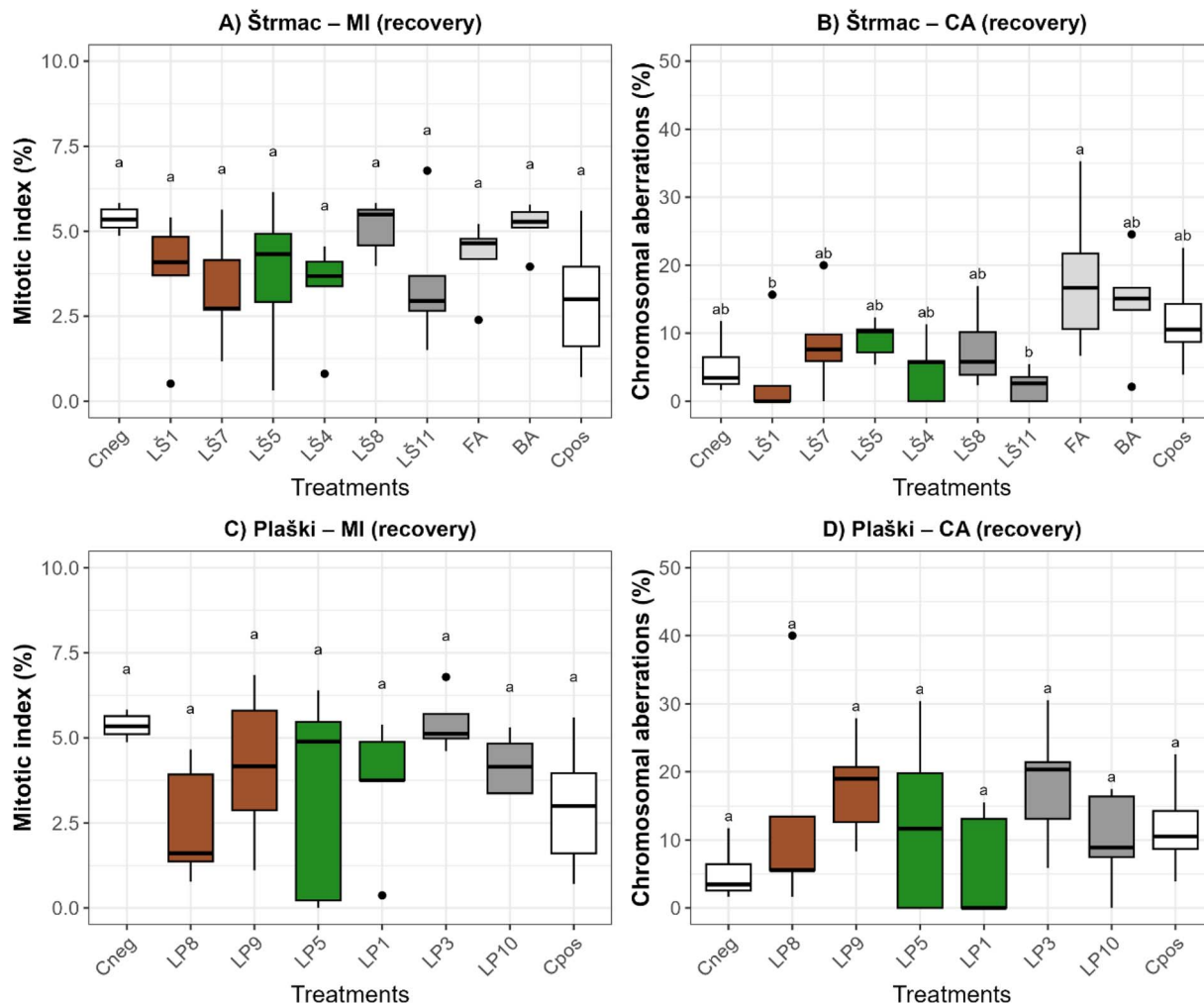


Fig. 7 Mitotic index (%) (A and C) and chromosomal aberrations (%) (B and D) in *Allium ascalonicum* root tips after the 24-h recovery period in water for Štrmac samples (A and B) and Plaški samples (C and D). Boxplots show medians and interquartile ranges; black dots represent outliers. Different lowercase letters above boxplots indicate statistically significant differences among treatments based on one-way ANOVA, followed by Tukey's *post hoc* test ($p < 0.05$). Colors denote sample categories: negative and positive controls (white), soil-derived eluates (brown), ash with vegetation (green), bare weathered ash (grey), and unweathered fly and bottom ash (light grey).

3.4.2. Genotoxicity of weathered coal ash. Alongside mitotic inhibition, coal ash exposure induced a variety of chromosomal aberrations in the dividing cells of the root tips. Microscopic observations of chromosomal aberrations revealed that 9 out of 14 samples had significantly higher percentages of cells with chromosomal aberrations, compared to the negative control, with the average chromosomal aberrations (CA) ranging from 0.73% to 26.1%. In comparison, the CA of bulbs treated with the negative and positive controls were 0.72% and 3.34%, respectively (Fig. 6). The highest CA was caused by unweathered fly ash (FA, 26.1%), LP8 (soil, 24.7%), and LŠ7 (soil, 24.2%), while the LŠ1 (soil), LŠ8 (bare), and LP3 (bare) samples did not cause a significant difference in CA.

The spectrum of aberrations included multipolar anaphases, disturbed prophase, lagging and vagrant chromosomes, C-metaphases, anaphase bridges, and chromosomal stickiness (Tables S9, S10 and Fig. 8). This combination of lesion types is consistent with both clastogenic (chromosome-breaking) and

aneugenic (spindle-disrupting) mechanisms.⁶² Bridges, fragments and micronuclei are typical of agents that induce DNA strand breaks and misrepair, whereas laggards, C-mitoses and multipolar spindles indicate interference with the mitotic spindle and chromosome segregation.^{15,31} Chromosome stickiness, observed in the most affected treatments (especially FA and the most toxic weathered samples), is considered an irreversible alteration of chromatin structure and is frequently associated with cell death.³¹ Together, these aberration types indicate that coal ash eluates can both damage the genetic material and disrupt the mitotic apparatus.

After a 24-hour recovery period in clean water, the frequency of chromosomal aberrations decreased in most samples, with values ranging from 2.32% to 18.2% (Fig. 7). Notable reductions were observed in LŠ7 (from 24% to 9%), LP5 (23% to 12%), and LP8 (25% to 13%), indicating partial damage repair and regeneration by healthier dividing cells. However, recovery was incomplete for several treatments. The unweathered fly ash (FA)



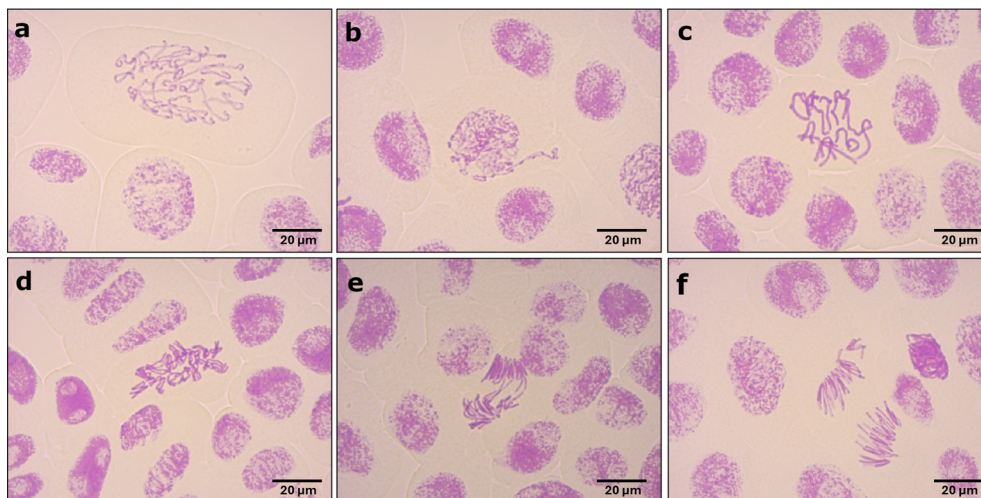


Fig. 8 Some of the observed chromosomal aberrations: (a) disturbed prophase, (b) chromatin erosion, (c) prolonged prophase, (d) spindle disturbance at the metaphase, (e) anaphase bridge and irregular position of the anaphase groups, and (f) chromosomes isolated from the anaphase group.

retained a high aberration rate ($\sim 18\%$), while two bare ash samples (LŠ8 and LP3), as well as the positive control, showed no improvement or even slight increases in CA, suggesting persistent genotoxic effects or delayed manifestation of earlier DNA damage.

Overall, the CA data confirm that both unweathered and weathered coal ash eluates are genotoxic, with the vegetated and soil samples often being more damaging than bare ash at both sites. Because some treatments produced relatively modest MI suppression but strong CA responses (e.g., LP8), while others showed the opposite pattern, chromosomal aberrations should be interpreted jointly with the mitotic index. Taken together, MI and CA reveal that coal ash can induce both acute and residual cytogenetic damage in root meristems, even after a recovery period in clean water.

Data from both mitotic index and percentage of chromosomal aberrations underscore that weathering and revegetation do not universally diminish cytotoxicity and genotoxicity. Even after ~ 50 years of weathering, many ash samples from both sites retain the capacity to impair cell division and induce genetic damage in plant roots. This finding contrasts with observations by Bandarra *et al.*,²⁸ who reported relatively low toxicity of decade-old fly ash leachates in several bioassays (with only slight effects on most test organisms). In our case, even ash that had weathered ~ 50 years, including material from vegetated zones, still contained enough contaminants to significantly impair cell division. This highlights that site-specific factors (such as the original ash composition, coal type, and mode of weathering) can greatly influence the persistence of CCR toxicity.

3.5. Linking elemental composition to toxic effects

To identify potential drivers of toxicity in coal ash eluates, correlation analyses were performed separately for Plaški and Štrmac landfills (Fig. 9) to evaluate the potential site-specific

relationship between elemental concentrations (33 detected elements) and biological endpoints: seed germination (SG), relative radicle growth (RRG), mitotic index (MI), and chromosomal aberrations (CA).

In the Plaški eluates, seed germination (SG) decreased with higher levels of Be ($r = -0.64$) and Rb ($r = -0.42$), while Zn ($r = 0.62$) and Ba ($r = 0.60$) showed positive associations. Radicle growth (RG) was negatively associated with Sb (-0.68), Li (-0.61), and Cs (-0.61), but positively linked to Zn (0.72) and Cu (0.48). Mitotic index (MI) was reduced with higher Al (-0.67), Cr (-0.61), and Ni (-0.57), and chromosomal aberrations (CA) increased with V (0.81), As (0.66), and Be (0.60).

Correlation trends in the Štrmac eluates showed both parallels and contrasts. SG correlated positively with Mg (0.81), Co (0.85), and Mn (0.63) but negatively with Cs (-0.57) and Cr (-0.60). RG had strong positive associations with Be (0.90), Na (0.89), and Mg (0.52) and negative ones with As (-0.81) and Fe (-0.43). MI decreased with increasing Al (-0.60), Ti (-0.67), and V (-0.63) while showing a slight positive correlation with Cu (0.42). CA was mostly associated with Ti (0.79), V (0.85), and Ca (0.74).

Despite site-specific differences, several elements showed consistent correlations with toxicity endpoints across the Plaški and Štrmac eluates. Al was negatively associated with MI in Plaški ($r = -0.67$) and Štrmac ($r = -0.60$), suggesting mitotic inhibition. As and V showed consistent positive correlations with AI (Plaški: V = 0.81 , As = 0.66 ; Štrmac: V = 0.85 , As = 0.43). These recurring patterns point toward a potential role of these elements in driving genotoxic responses.

Correlation alone cannot prove causation; however, the types of chromosomal abnormalities observed in this study (multi-polar anaphases, bridges, laggards, stickiness) are consistent with previously described effects of Al, As, and V in root meristems. Al has been shown to interfere with microtubule polymerization and spindle formation, which reduces the mitotic index and produces C-mitosis, sticky chromosomes, and



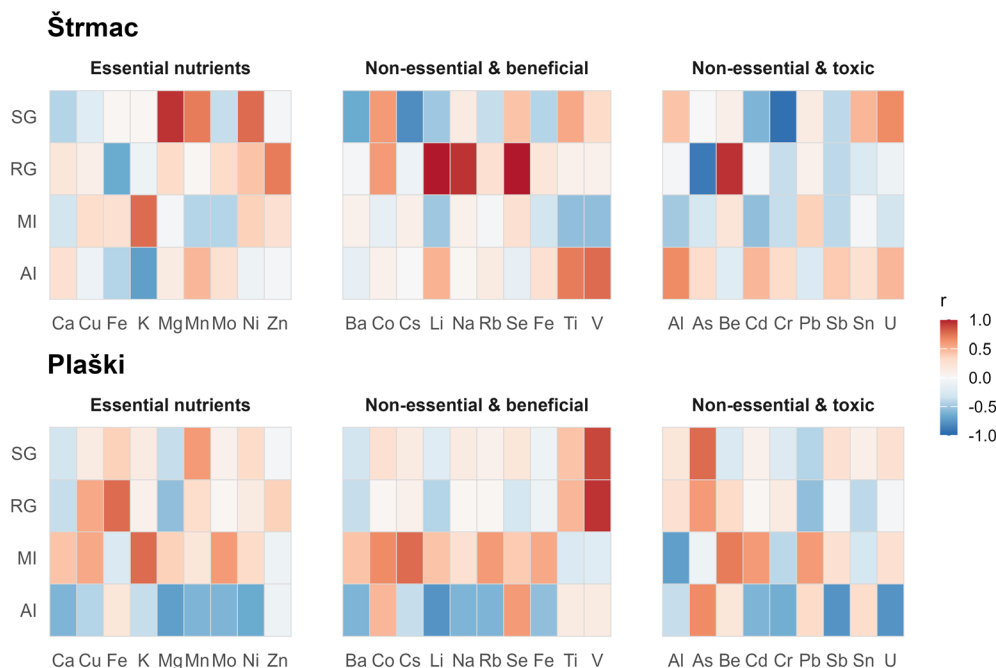


Fig. 9 Correlation heatmap showing relationships between elemental concentrations and bioassay responses—seed germination (SG), radicle growth (RG), mitotic index (MI), and aberration index (AI)—in eluates from weathered coal ash in Štrmac and Plaški. Warm colours (red shade) indicate positive correlations, while cool colours (blue shade) represent negative correlations.

lagging figures.⁶⁴ Arsenic primarily exerts genotoxicity through the generation of reactive oxygen species and the disruption of spindle assembly, leading to DNA damage, micronuclei formation, and segregation errors.^{65,66} Vanadium, often present as vanadate (V^{5+}), can substitute for phosphate in enzymatic processes and disrupt the phosphorylation-dependent steps of mitosis. In addition, it induces oxidative stress, resulting in spindle defects, chromosomal stickiness, and lagging chromosomes.^{67,68} Published thresholds for vanadium toxicity in *Allium* roots begin at approximately $25\text{--}100\text{ }\mu\text{g L}^{-1}$,^{67,68} which overlaps with the concentrations detected in our eluates.

Importantly, previous leaching experiments conducted on the same CCR materials²⁷ demonstrated that pedogenetic changes modify the mobility of oxyanion-forming elements, particularly As and V, under the prevailing alkaline to near-neutral pH conditions. These elements exhibit pH-dependent release behaviour, meaning that localized shifts in buffering capacity can enhance their availability in eluates even when total concentrations remain moderate. Thus, the cytogenetic responses observed here are consistent not only with the known cellular mechanisms of Al, As, and V toxicity, but also with their demonstrated mobility in weathered CCR systems. While direct causality cannot be established, the combined geochemical and biological evidence supports their likely contribution to the observed genotoxicity.

Taken together, these mechanisms provide a plausible explanation for the observed cytogenetic effects and support the conclusion that Al, As, and V are among the main contributors to the persistent genotoxicity of weathered CCR eluates.

However, it has to be noted that many elements in coal ash eluates likely act synergistically or antagonistically, which complicates the attribution of specific toxic effects to individual elements.⁵

This is evident in the discrepancy between the elemental concentrations in eluates and the toxic effect of the sample. For example, seven out of twelve eluates significantly inhibited seed germination, including both the soil and bare ash samples from the Plaški (LP3, LP8, LP9, LP10) and Štrmac (LŠ5, LŠ8, LŠ11) landfills. Meanwhile, eluates such as LP3, LP5, LŠ7, LŠ11, and LŠ4 contained trace element concentrations exceeding WHO drinking water thresholds, but not all induced equally strong biological effects. This discrepancy is especially evident in the *Allium* test results: LP1 (vegetated), with moderate elemental content, caused the highest inhibition of cell division ($MI = 1.94\%$), whereas LŠ4 (vegetated) showed no significant impact on mitosis despite exceeding the WHO limit. Similarly, chromosomal aberrations were highest in eluates from fly ash (FA, 26.06%), LP8 (soil, 24.7%), and LŠ7 (soil, 24.2%), while other samples with comparable or higher elemental content, such as LŠ1, LŠ8, and LP3, did not cause significant genotoxicity.

Coal ash is an inherently complex material, often containing various organic and inorganic compounds, as well as dozens of elements across wide concentration ranges and in various chemical forms. The interactions between elements, their competitive uptake by plants, and their speciation in aqueous media can dramatically influence toxicity outcomes. The observed, sometimes contradictory, correlations highlight the need for more detailed chemical characterization in the future, such as speciation modeling or bioavailability assays, to fully



understand the mechanisms of coal ash toxicity. In addition, relying solely on elemental concentrations for coal ash assessment may overlook relevant biological risks, underscoring the value of integrated bioassay approaches. These observations emphasize both the importance and the inherent challenges of assessing CCR toxicity.

3.6. Study scope and future perspectives

The present study provides novel insight into the long-term toxicity of approximately 50-year-old weathered CCR under field conditions. However, as with any complex environmental system, certain aspects remain beyond the scope of the current investigation.

The correlation analyses identify statistically robust associations between elemental concentrations and biological endpoints, but they do not allow definitive attribution of toxicity to single elements, as CCR represents a chemically heterogeneous mixture in which multiple components may interact.

In addition, toxicity was evaluated using aqueous eluates and two established plant-based bioassays, which effectively capture early phytotoxic and cytogenetic responses but do not encompass all possible ecological exposure pathways or long-term field effects.

Future research integrating element-specific experimental designs, multi-species testing, and extended field monitoring would further refine our understanding of the mechanisms controlling weathered CCR toxicity. Nevertheless, the combined geochemical and biological approach applied here provides a robust framework for assessing the environmental relevance of legacy coal ash deposits.

4. Conclusions

This study demonstrated that weathered coal ash remained phytotoxic even after ~50 years of natural exposure. Both seed germination and *Allium* tests revealed the significant inhibition of growth and cytogenetic damage in eluates from two Croatian landfills, despite evidence of pedogenesis and partial vegetation cover.

Our results show that

(1) Pedogenesis mitigates, but does not eliminate, effects. Vegetated samples generally released fewer trace elements and exhibited weaker toxicity, yet exceptions occurred, particularly for oxyanion-forming elements (As, V, U).

(2) Coal ash continues to impair germination, radicle growth, and cell division, confirming its relevance as a legacy waste.

(3) Correlation analyses identified Al, As, and V as consistent drivers of mitotic inhibition and chromosomal aberrations, supported by known mechanistic pathways. Importantly, the vanadium concentrations in our eluates fall within published toxicological thresholds for *Allium* roots.

(4) Elemental exceedances did not always correspond to the strongest biological responses, reflecting interactions among elements, speciation effects, and bioavailability constraints.

Together, these findings underscore the need to integrate biological endpoints with chemical characterization when assessing the environmental risks of coal ash disposal sites. For effective management and rehabilitation of legacy landfills, monitoring frameworks should move beyond concentration-based thresholds and incorporate bioassays to capture the full spectrum of potential ecological impacts. Such an approach may also be relevant for other waste systems, including mine waste facilities and contaminated soils associated with industrial activities, where complex mixtures can limit the interpretability of chemical data alone, highlighting the value of integrating bioassays in characterisation workflows.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting the findings of this study are available in the supplementary information (SI) accompanying this article. Supplementary information: analytical quality-control parameters (limits of detection and control measurements), pH data, total and leachable elemental concentrations, relative mass leached values, seed germination and radicle growth results, *Allium* cytogenetic assay data (mitotic index, chromosomal aberrations, and aberration types), recovery-phase results, and statistical outputs (ANOVA and *post hoc* analyses). See DOI: <https://doi.org/10.1039/d5em01010a>.

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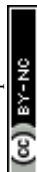
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References

- 1 R. A. Kruger, *Introduction to the Utilization of Coal Combustion Products*, Elsevier Ltd, 2017.
- 2 X. Zhang, Management of coal combustion wastes, https://usea.org/sites/default/files/012014_Managementofcoalcombustionwastes_ccc231.pdf, accessed 4 March 2026.
- 3 J. Ribeiro, T. F. Silva, J. G. Mendonça Filho and D. Flores, Fly ash from coal combustion - An environmental source of organic compounds, *Appl. Geochem.*, 2014, **44**, 103–110.
- 4 G. Akar, M. Polat, G. Galecki and U. Ipekoglu, Leaching behavior of selected trace elements in coal fly ash samples from Yenikoy coal-fired power plants, *Fuel Process. Technol.*, 2012, **104**, 50–56.
- 5 M. Petrović and Ž. Fiket, Environmental damage caused by coal combustion residue disposal: A critical review of risk assessment methodologies, *Chemosphere*, 2022, **299**, 134410.
- 6 Y. Chen, Y. Fan, Y. Huang, X. Liao, W. Xu, T. Zhang and F. Ash, A comprehensive review of toxicity of coal fly ash



- and its leachate in the ecosystem, *Ecotoxicol. Environ. Saf.*, 2024, **269**, 115905.
- 7 S. M. Raimondo, C. L. Rowe and J. D. Congdon, Exposure to Coal Ash Impacts Swimming Performance and Predator Avoidance in Larval Bullfrogs, *J. Herpetol.*, 1998, **32**, 289–292.
 - 8 C. L. Rowe, O. M. Kinney, A. P. Fiori and J. D. Congdon, Oral deformities in tadpoles (*Rana catesbeiana*) associated with coal ash deposition: Effects on grazing ability and growth, *Freshwater Biol.*, 1996, **36**, 723–730.
 - 9 A. D. Lemly, Selenium poisoning of fish by coal ash wastewater in Herrington Lake, Kentucky, *Ecotoxicol. Environ. Saf.*, 2018, **150**, 49–53.
 - 10 V. E. Mahajan, R. R. Yadav, N. P. Dakshinkar, V. M. Dhoot, G. R. Bhojane, M. K. Naik, P. Shrivastava, P. K. Naoghare and K. Krishnamurthi, Influence of mercury from fly ash on cattle reared nearby thermal power plant, *Environ. Monit. Assess.*, 2012, **184**, 7365–7372.
 - 11 C. H. Zhang, L. Sears, J. V. Myers, G. N. Brock, C. G. Sears and K. M. Zierold, Proximity to coal-fired power plants and neurobehavioral symptoms in children, *J. Exposure Sci. Environ. Epidemiol.*, 2022, **32**, 124–134.
 - 12 R. Kamath, S. E. Udayar, G. Jagadish, P. Prabhakaran, K. K. Madhipatla and Research Team, Assessment of Health Status and Impact of Pollution from Thermal Power Plant on Health of Population and Environment Around the Plant in Udupi District, Karnataka, *Indian J. Public Health.*, 2022, 91–97.
 - 13 M. Karavuş, A. Aker, D. Cebeci, M. Taşdemir, N. Bayram and Ş. Çali, Respiratory Complaints and Spirometric Parameters of the Villagers Living around the Seyitomer Coal-Fired Thermal Power Plant in Kütahya, Turkey, *Ecotoxicol. Environ. Saf.*, 2002, **52**, 214–220.
 - 14 R. Chakraborty, A. K. Mukherjee and A. Mukherjee, Evaluation of genotoxicity of coal fly ash in *Allium cepa* root cells by combining comet assay with the Allium test, *Environ. Monit. Assess.*, 2009, **153**, 351–357.
 - 15 A. Jana, M. Ghosh, S. Sinha, M. Jothiramajayam, A. Nag and A. Mukherjee, Hazard identification of coal fly ash leachate using a battery of cyto-genotoxic and biochemical tests in *Allium cepa*, *Arch. Agron. Soil Sci.*, 2017, **63**, 1443–1453.
 - 16 R. Chakraborty and A. Mukherjee, Mutagenicity and genotoxicity of coal fly ash water leachate, *Ecotoxicol. Environ. Saf.*, 2009, **72**, 838–842.
 - 17 V. L. Markad, K. M. Kodam and V. S. Ghole, Effect of fly ash on biochemical responses and DNA damage in earthworm, *Dichogaster curgensis*, *J. Hazard. Mater.*, 2012, **215–216**, 191–198.
 - 18 B. Sambandam, T. Devasena, V. I. Hairul Islam and B. M. Prakhya, Characterization of coal fly ash nanoparticles and their induced in vitro cellular toxicity and oxidative DNA damage in different cell lines, *Indian J. Exp. Biol.*, 2015, **53**, 585–593.
 - 19 P. K. Singh, P. Tripathi, S. Dwivedi, S. Awasthi, M. Shri, D. Chakrabarty and R. D. Tripathi, Fly-ash augmented soil enhances heavy metal accumulation and phytotoxicity in rice (*Oryza sativa* L.); A concern for fly-ash amendments in agriculture sector, *Plant Growth Regul.*, 2016, **78**, 21–30.
 - 20 V. L. Markad, S. S. Adav, V. S. Ghole, S. K. Sze and K. M. Kodam, Proteomics study revealed altered proteome of *Dichogaster curgensis* upon exposure to fly ash, *Chemosphere*, 2016, **160**, 104–113.
 - 21 A. P. Crnić, D. Damijanić, N. Bilandžić, M. Sedak and G. Medunić, Enhanced levels of hazardous trace elements (Cd, Cu, Pb, Se, Zn) in bird tissues in the context of environmental pollution by Raša coal, *Rud.-Geol.-Naftni Zb.*, 2022, **37**, 19–30.
 - 22 S. Radić, G. Medunić, Ž. Kuharić, V. Roje, K. Maldini, V. Vujčić and A. Krivohavek, The effect of hazardous pollutants from coal combustion activity: Phytotoxicity assessment of aqueous soil extracts, *Chemosphere*, 2018, **199**, 191–200.
 - 23 Y. Cui, Y. G. Zhu, R. Zhai, Y. Huang, Y. Qiu and J. Liang, Exposure to metal mixtures and human health impacts in a contaminated area in Nanning, China, *Environ. Int.*, 2005, **31**, 784–790.
 - 24 S. Mortazavi, G. Mortazavi and M. Paknahad, Levels of arsenic, mercury, cadmium, copper, lead, zinc, and manganese in serum and whole blood of resident adults from mining and non-mining communities in Ghana, *Environ. Sci. Pollut. Res.*, 2016, **23**, 22220–22221.
 - 25 Ł. Uzarowicz, Z. Zagórski, E. Mendak, P. Bartmiński, E. Szara, M. Kondras, L. Oktaba, A. Turek and R. Rogoziński, Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part I. Properties, classification, and indicators of early pedogenesis, *Catena*, 2017, **157**, 75–89.
 - 26 M. Petrović, M. Ivanić, N. Vdović, M. Dolenc, B. Čermelj, P. Šket, G. Medunić and Ž. Fiket, Physicochemical and mineral characteristics of soil materials developed naturally on two ~ 50 years old coal combustion residue disposal sites in Croatia, *Catena*, 2023, **231**, 107338.
 - 27 M. Petrović, A. Ninčević Grassino, J. Lapić, S. Djaković, M. Furdek Turk, G. Medunić and Ž. Fiket, Changes in the mobility of oxyanions from coal combustion residues after 50 years of natural weathering, *Waste Manage.*, 2026, **216**, 115450.
 - 28 B. S. Bandarra, L. A. Gomes, J. L. Pereira, F. J. M. Gonçalves, R. C. Martins and M. J. Quina, Assessment of hazardous property HP 14 using ecotoxicological tests: a case study of weathered coal fly ash, *Environ. Sci. Pollut. Res.*, 2020, **27**, 20972–20983.
 - 29 R. J. Haynes, Reclamation and revegetation of fly ash disposal sites - Challenges and research needs, *J. Environ. Manage.*, 2009, **90**, 43–53.
 - 30 G. Fiskesjö, in *Environmental Toxicology and Risk Assessment: 2nd Volume, American Society for Testing and Materials*, ed. J. W. Gorsuch, F. J. Dwyer, C. G. Ingersoll and T. W. La Point, STP 1216, Philadelphia, 1993, pp. 331–345.
 - 31 G. Fiskesjö, The Allium test as a standard in environmental monitoring, *Hereditas*, 1985, **102**, 99–112.
 - 32 Y. Luo, J. Liang, G. Zeng, M. Chen, D. Mo, G. Li and D. Zhang, Seed germination test for toxicity evaluation of



- compost: Its roles, problems and prospects, *Waste Manage.*, 2018, **71**, 109–114.
- 33 G. Medunić, A. Radenović, M. Bajramović, M. Švec and M. Tomac, Once grand, now forgotten: What do we know about the superhigh-organic-sulphur Raša coal?, *Rud.-Geol.-Naftni Zb.*, 2016, **31**, 27–45.
 - 34 G. Medunic, Ž. Kuharic, A. Krivohlavek, Ž. Fiket, A. Radenovic, K. Gödel, Š. Kampic and G. Kniewald, Geochemistry of Croatian superhigh-organic-sulphur Raša coal, imported low-S coal and bottom ash: Their se and trace metal fingerprints in seawater, clover, foliage and mushroom specimens copyright, *Int. J. Oil, Gas Coal Technol.*, 2018, **18**, 3–24.
 - 35 Ž. Fiket, G. Medunić, Ž. Vidaković-Cifrek, P. Jezidžić and P. Cvjetko, Effect of coal mining activities and related industry on composition, cytotoxicity and genotoxicity of surrounding soils, *Environ. Sci. Pollut. Res.*, 2020, **27**, 6613–6627.
 - 36 G. Medunić, M. Ahel, I. B. Mihalić, V. G. Srček, N. Kopjar, Ž. Fiket, T. Bituh and I. Mikac, Toxic airborne S, PAH, and trace element legacy of the superhigh-organic-sulphur Raša coal combustion: Cytotoxicity and genotoxicity assessment of soil and ash, *Sci. Total Environ.*, 2016, **566–567**, 306–319.
 - 37 V. Oreščanin, R. Kollar, K. Buben, I. L. Mikelic, K. Kollar, M. Kollar and G. Medunic, Chemical and radiological characterization of fly and bottom ash landfill of the former sulfate pulp factory Plaški and its surroundings, *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.*, 2012, **47**, 1592–1606.
 - 38 J. Weber, S. Straczyńska, A. Kocowicz, M. Gilewska, A. Bogacz, M. Gwizdz and M. Debicka, Properties of soil materials derived from fly ash 11years after revegetation of post-mining excavation, *Catena*, 2015, **133**, 250–254.
 - 39 CEN, Characterization of waste–Leaching–Compliance test for leaching of granular waste material and sludge. Part 2: One stage batch test at a liquid to solid ratio of 10 L/kg with article size below 4 mm (without or with size reduction). EN 12457–2, Brussels, 2002.
 - 40 European Commission, Council Decision 2003/33/EC of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 and Annex II of Directive 1999/31/EC, <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32003D0033%0A%0A>.
 - 41 World Health Organization, *Guidelines for Drinking-Water Quality*, World Health Organization, Geneva, 4th edn, 2022.
 - 42 D. Fritz, A. P. Bernardi, J. S. Haas, B. M. Ascoli, S. A. L. De Bordignon and G. Von Poser, Germination and growth inhibitory effects of *Hypericum myrianthum* and *H. polyanthemum* extracts on *Lactuca sativa* L, *Rev. Bras. Farmacogn.*, 2007, **17**, 44–48.
 - 43 A. K. Sharma and A. Sharma, *Chromosome Techniques: Theory and Practice*, Butterworths & Co Ltd, London, 2nd edn, 1972.
 - 44 N. Moreno, X. Querol, J. M. Andrés, K. Stanton, M. Towler, H. Nugteren, M. Janssen-Jurkovicová and R. Jones, Physico-chemical characteristics of European pulverized coal combustion fly ashes, *Fuel*, 2005, **84**, 1351–1363.
 - 45 N. R. Lieberman, M. Izquierdo, C. Muñoz-Quirós, H. Cohen and S. R. Chenery, Geochemical signature of superhigh organic sulphur Raša coals and the mobility of toxic trace elements from combustion products and polluted soils near the Plomin coal-fired power station in Croatia, *Appl. Geochem.*, 2020, **114**, 104472.
 - 46 M. Petrović, Ž. Fiket, G. Medunić and S. Chakravarty, Mobility of metals and metalloids from SHOS coal ash and slag deposit: mineralogical and geochemical constraints, *Environ. Sci. Pollut. Res.*, 2022, **29**, 46916–46928.
 - 47 P. Suraneni, L. Burris, C. R. Shearer and R. D. Hooton, ASTM C618 fly ash specification: Comparison with other specifications, shortcomings, and solutions, *ACI Mater. J.*, 2021, **118**, 157–167.
 - 48 M. P. Ketris and Y. E. Yudovich, Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals, *Int. J. Coal Geol.*, 2009, **78**, 135–148.
 - 49 G. Faure, *Principles and Applications of Geochemistry: a Comprehensive Textbook for Geology Students*, Prentice-Hall, Inc., 2nd edn, 1998.
 - 50 P. Marschner, *Marschner's Mineral Nutrition of Higher Plants*, 2012.
 - 51 M. Izquierdo and X. Querol, Leaching behaviour of elements from coal combustion fly ash: An overview, *Int. J. Coal Geol.*, 2012, **94**, 54–66.
 - 52 S. Zhao, Z. Chen, J. Shen, J. Kang, J. Zhang and Y. Shen, Leaching mechanisms of constituents from fly ash under the influence of humic acid, *J. Hazard. Mater.*, 2017, **321**, 647–660.
 - 53 B. Dold and L. Fontboté, A mineralogical and geochemical study of element mobility in sulfide mine tailings of Fe oxide Cu-Au deposits from the Punta del Cobre belt, northern Chile, *Chem. Geol.*, 2002, **189**, 135–163.
 - 54 O. Kostić, S. Jarić, G. Gajić, D. Pavlović, M. Pavlović, M. Mitrović and P. Pavlović, Pedological properties and ecological implications of substrates derived 3 and 11 years after the revegetation of lignite fly ash disposal sites in Serbia, *Catena*, 2018, **163**, 78–88.
 - 55 X. Wang, H. A. van der Sloot, K. G. Brown, A. C. Garrabrants, Z. Chen, B. Hensel and D. S. Kosson, Application and uncertainty of a geochemical speciation model for predicting oxyanion leaching from coal fly ash under different controlling mechanisms, *J. Hazard. Mater.*, 2022, **438**, 129518.
 - 56 S. M. Tiquia, N. F. Y. Tam and I. J. Hodgkiss, Effects of composting on phytotoxicity of spent pig-manure sawdust litter, *Environ. Pollut.*, 1996, **93**, 249–256.
 - 57 A. Fuentes, M. Lloréns, J. Sáez, M. I. Aguilar, J. F. Ortuño and V. F. Meseguer, Phytotoxicity and heavy metals speciation of stabilised sewage sludges, *J. Hazard. Mater.*, 2004, **108**, 161–169.
 - 58 R. Karlova, D. Boer, S. Hayes and C. Testerink, Root plasticity under abiotic stress, *Plant Physiol.*, 2021, **187**, 1057–1070.
 - 59 H. Q. Wang, X. Y. Zhao, W. Xuan, P. Wang and F. J. Zhao, Rice roots avoid asymmetric heavy metal and salinity



- stress via an RBOH-ROS-auxin signaling cascade, *Mol. Plant*, 2023, **16**, 1678–1694.
- 60 E. R. Emmino and P. R. Warman, Biological Assay for Compost Quality, *Compost Sci. Util.*, 2004, **12**, 342–348.
- 61 D. M. Leme and M. A. Marin-Morales, *Allium cepa* test in environmental monitoring : A review on its application, *Mutat. Res., Rev. Mutat. Res.*, 2009, **682**, 71–81.
- 62 D. M. Leme and M. A. Marin-Morales, *Allium cepa* test in environmental monitoring : A review on its application, *Mutat. Res., Rev. Mutat. Res.*, 2009, **682**, 71–81.
- 63 S. Gantayat, S. Mania, C. Pradhan and A. B. Das, Ionic Stress Induced Cytotoxic Effect of Cadmium and Nickel Ions on Roots of *Allium cepa* L, *Cytologia*, 2018, **83**, 143–148.
- 64 D. Liu, W. Jiang and D. Li, Effects of aluminium ion on root growth, cell division, and nucleoli of garlic (*Allium sativum* L.), *Environ. Pollut.*, 1993, **82**, 295–299.
- 65 L. Wu, H. Yi and M. Yi, Assessment of arsenic toxicity using *Allium/Vicia* root tip micronucleus assays, *J. Hazard. Mater.*, 2010, **176**, 952–956.
- 66 H. Yi, L. Wu and L. Jiang, Genotoxicity of arsenic evaluated by *Allium-root* micronucleus assay, *Sci. Total Environ.*, 2007, **383**, 232–236.
- 67 L. Marcano, I. Carruyo, Y. Fernández, X. Montiel and Z. Torrealba, Determination of vanadium accumulation in onion root cells (*Allium cepa* L.) and its correlation with toxicity, *Biocell*, 2006, **30**, 259–267.
- 68 M. Kaya, K. Çavuşoğlu, E. Yalçın and A. Acar, DNA fragmentation and multifaceted toxicity induced by high-dose vanadium exposure determined by the bioindicator *Allium* test, *Sci. Rep.*, 2023, **13**, 1–11.



Coal ash fingerprints in surface waters: integrating geochemical and isotopic signatures in an understudied European coal region

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Abstract

Coal combustion residues (CCR) can release contaminants to aquatic systems, but source attribution is difficult in industrial regions with overlapping anthropogenic inputs. This study evaluated the geochemical and isotopic fingerprinting potential of CCR in Southeast Europe by analyzing coal, coal ash, standardized ash leachates, and surface waters near three coal-fired power plants in Bosnia and Herzegovina (Tuzla, Stanari, and Gacko).

CCR showed strong geochemical heterogeneity, while leaching experiments demonstrated selective mobility, with preferential release of sulfate, Sr, Ba, B, Mo, and Se. Surface waters exhibited site-specific rather than universal coal-related signatures. Gacko showed sulfate-dominated downstream enrichment, Tuzla reflected mixed anthropogenic influence, and Stanari displayed clearer isotopic than hydrochemical differentiation. Post-mining lakes retained persistent dissolved signatures linked to legacy coal basin influence. Strontium isotopes proved the most effective tracer, while boron isotopes provided complementary evidence.

These results show that coal-related aquatic impacts are governed by selective transfer of dissolved constituents rather than bulk ash composition, and that integrated geochemical and isotopic fingerprinting improves source attribution in complex industrial settings.

1. INTRODUCTION

Coal combustion residuals (CCRs), including fly ash, bottom ash, and boiler slag, are among the largest industrial solid waste streams generated worldwide. Global production exceeds one billion tonnes annually, with a substantial proportion still disposed of in landfills, lagoons, and surface impoundments despite increasing rates of beneficial reuse (Kruger, 2017). Because coal combustion concentrates non-combustible mineral phases, CCRs are frequently enriched in trace elements, naturally occurring radioactive materials (NORM), and residual organic constituents

relative to the parent coal (Ribeiro et al., 2014; Zhang, 2014). As a result, CCR disposal sites can remain chemically reactive long after deposition, acting as persistent secondary sources of environmental contamination through leaching, atmospheric dust dispersion, and biological uptake (Petrović et al., 2022, 2026b).

The environmental impacts of CCR disposal have been extensively documented, particularly in North America, where contamination of groundwater and receiving surface waters near coal ash impoundments has been associated with elevated concentrations of boron, arsenic, selenium, molybdenum, strontium, uranium, and other ash-derived constituents (Harkness et al., 2016; Vengosh et al., 2019). Ecotoxicological studies further demonstrate that CCR leachates may adversely affect aquatic and terrestrial organisms, highlighting that environmental risk extends beyond simple exceedance of regulatory concentration thresholds (Petrović et al., 2026a). However, while contamination associated with CCR disposal is well established, identifying coal as the definitive source becomes more challenging in regions where multiple industrial activities, mining operations, and heterogeneous geological backgrounds may produce overlapping geochemical signatures.

In contrast to North America, the environmental impacts of coal ash in Europe, particularly in Southeast Europe, remain comparatively poorly characterized, despite increasing evidence of environmental contamination associated with historical and active coal combustion sites. Coal-fired power plants have operated across the region for decades, generating large quantities of CCRs that have often been disposed of in unlined or poorly engineered landfills and impoundments, increasing the risk of contaminant release to surrounding ecosystems.

This challenge is particularly relevant in Southeast Europe, where coal combustion has played a central role in regional energy production for decades, yet the environmental behavior and fingerprinting characteristics of coal combustion residues remain comparatively underexplored. In Bosnia and Herzegovina, several coal-fired power plants continue to operate, often in close proximity to rivers, lakes, agricultural land, and residential areas. Previous studies from the region have reported elevated concentrations of trace elements in surrounding soils, waters, and biota, as well as evidence of airborne dust dispersion and localized radiological impacts. However, direct source attribution remains insufficiently characterized.

Isotopic tracers offer a powerful approach for resolving this ambiguity. Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) have been successfully used to trace coal ash-derived contamination in aquatic systems and biological receptors, particularly in North America (Campbell et al., 2008; Harkness et al., 2016; Vengosh et al., 2019). Because coal ash inherits isotopic characteristics from the parent fuel and associated mineral phases while simultaneously concentrating strontium during combustion, distinct $^{87}\text{Sr}/^{86}\text{Sr}$ signatures may provide robust source fingerprints. Boron represents a complementary tracer due to its high mobility and frequent enrichment in CCR leachates (Harkness et al., 2016; Ruhl et al., 2014; Vengosh et al., 1994). In addition to concentration-based evidence, boron isotopic compositions ($\delta^{11}\text{B}$) may further strengthen source attribution by distinguishing CCR-derived inputs from natural waters or other anthropogenic sources (Harkness et al., 2017; Vengosh et al., 2016).

Beyond their trace element content, coal combustion residues typically contain elevated activities of naturally occurring radioactive materials (NORM), as combustion concentrates radionuclides associated with uranium and thorium decay series in the residual ash (Lauer et al., 2017, 2015). Therefore, radionuclides such as ^{226}Ra , ^{228}Ra , ^{210}Pb , and ^{238}U represent an additional dimension of potential environmental risk linked to CCR disposal.

This study addresses that gap by combining source characterization with environmental application. Specifically, we (1) characterize the geochemical, isotopic, and radionuclide fingerprints of coals and coal combustion residues from Croatia and Bosnia and Herzegovina; (2) evaluate the applicability of strontium and boron isotopes as tracers of CCR-derived contamination; and (3) assess coal ash influences on rivers, streams, and mine-associated lakes near three coal-fired power plants in Bosnia and Herzegovina using an integrated geochemical fingerprinting approach. By linking source materials to impacted aquatic systems, this study provides one of the first comprehensive assessments of coal combustion residue tracing in Southeast Europe and demonstrates a transferable framework for identifying CCR-derived contamination in complex industrial landscapes.

2. MATERIALS AND METHODS

2.1. Study area

Coal, coal ash, and surface water samples were collected from coal-fired power plant sites in Southeast Europe, including Croatia and Bosnia and Herzegovina (BiH) (Figure 1).

Coal and coal ash samples were obtained from three legacy CCR landfills in Croatia ($n = 3$) which physiochemical properties have been described previously (Petrović et al., 2023), and from active three thermal power plants in Bosnia and Herzegovina ($n = 4$). The Croatian samples represent historical disposal sites containing approximately 50-year-old weathered coal combustion residues derived from coal-fired energy production, providing insight into long-term post-depositional alteration of CCRs under natural weathering conditions.

The Bosnian sites represent three major coal-fired power generation centres exploiting distinct coal basins and coal types. Tuzla Thermal Power Plant, located in northeastern Bosnia and Herzegovina, is one of the country's largest and oldest coal-fired power stations and primarily burns lignite sourced from the Kreka coal basin, where industrial mining began in the late 19th century. The basin includes several major open-pit and underground mines and has been intensively exploited for over a century (Smajic et al., 2009). Stanari Thermal Power Plant, located in northern Bosnia and Herzegovina, has operated since 2016 and burns lignite from the nearby Stanari coal basin, a historically exploited brown coal deposit (Bušatlić et al., 2025). Gacko Thermal Power Plant, situated in southeastern Bosnia and Herzegovina, burns lignite from the Gacko basin, a major Neogene lignite deposit in the Dinaric region that has supported power generation since the 1980s (Savić et al., 2018).

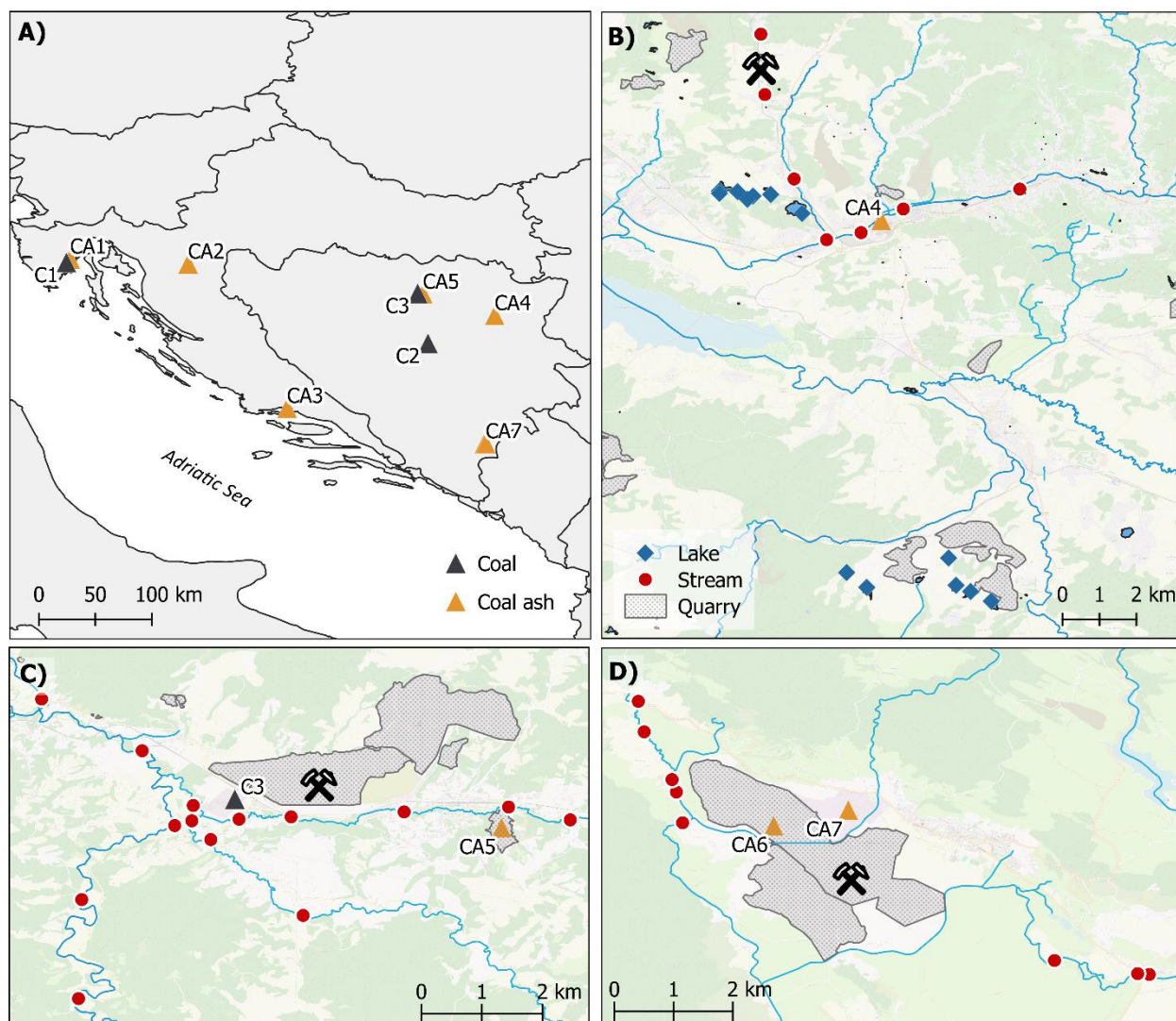


Figure 1. Locations of the investigated thermal power plants (TPPs) in Bosnia and Herzegovina (Tuzla, Stanari, and Gacko) and associated water sampling sites. (A) Coal and coal combustion residue (CCR) samples from Croatia and Bosnia and Herzegovina used for radiological and isotope analyses. Locations of coal, ash, and natural water sampling at (B) Tuzla, (C) Stanari, and (D) Gacko thermal power plants.

Surface water samples ($n = 42$) were collected in the vicinity of the Tuzla, Stanari, and Gacko thermal power plants to capture a range of hydrological settings potentially influenced by coal combustion residue disposal. Sampling included both lotic (rivers and streams) and lentic (lakes) systems located upstream and downstream of ash disposal areas.

At the Tuzla site, sampling targeted both flowing waters and standing waters associated with the broader Tuzla lignite region. River and stream samples were collected from the Jala River and

Mramor Stream. Standing waters included lakes distributed across the Kreka and Đurđevik coal basins, formed by flooding former lignite excavations, some of which are now used for recreation (e.g., fishing and tourism) (Smajić et al., 2021). In the Kreka basin, sampled waters included Kop Lake, Bistarac Lake, Bistarac Groundwater, Lake near Bistarac, Ribarsko Lake, Lukavac Lake, and Odlagač Lake. In the Đurđevik basin, sampled standing waters included Hadžija Lake, Požar Lake, Šahić Lake, Panjik Lake, Suhodanj Lake, and Brestovica Lake.

At the Stanari site, sampling was conducted within the Ukrina River catchment, including the Mala Ukrina, Radnja and Ostružnja tributaries. At the Gacko site, samples were collected from the Mušnica River and its tributary, the Trnovac Stream, both hydrologically connected to the Gacko lignite mining and combustion complex.

2.2. Solid sample collection and preparation

Coal and coal ash samples (fly ash and bottom ash) were collected directly from ash disposal sites. All sampled power plants in Bosnia and Herzegovina were in active operation at the time of sampling, whereas Croatian samples were collected from abandoned coal ash disposal sites.

All solid samples were air-dried, powdered, and homogenized prior to analysis. Coal samples were combusted in a muffle furnace at 500 °C for 4 h to remove organic matter, after which loss on ignition (LOI, wt%) was determined. Both combusted coal samples and coal ash samples were subsequently used for elemental and isotopic analyses.

In addition, coal ash samples were subjected to batch leaching using Milli-Q water as the eluate at a liquid-to-solid ratio of 10:1, following the standardized leaching procedure EN 12457-2 (CEN, 2023). Resulting eluates were filtered through 0.45 µm membrane filters and used for multi-element and strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) analyses.

2.3. Surface water sampling and field measurements

Surface water samples were collected in July and August 2023 during low-flow hydrological conditions using a grab sampling approach, following U.S. Geological Survey (USGS) sampling protocols (Wilde, 2010). Samples were filtered in the field through 0.45 µm syringe filters and stored in pre-cleaned polyethylene bottles. Each water sample was split into two aliquots: (1) an acidified aliquot (1% ultrapure HNO_3) for trace element and strontium isotope analyses, and (2) a

non-acidified aliquot for anion and boron isotope analyses. In situ physicochemical parameters, including pH, oxidation-reduction potential (ORP), electrical conductivity (EC), total dissolved solids (TDS), and turbidity, were measured at each site using a calibrated Hanna multiparameter meter (HI9829). Instrument calibration was performed at the beginning of each sampling day.

2.4. Anion analysis

Major anions (Cl^- , SO_4^{2-} , PO_4^{3-} , and NO_3^-) were measured in non-acidified water samples by ion chromatography using a Dionex DX-2100 ion chromatograph. Analytical quality control was ensured through repeated measurements of calibration standards at varying concentrations, procedural blanks, and check standards analyzed before, during, and after sample runs.

2.5. Multi-element analysis by ICP-MS

52 element concentrations (Li, Be, B, Na, Mg, Al, P, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Nb, Mo, Rh, Ag, Cd, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Ta, Tl, Pb, Th, U) in solid, leachate, and water samples were determined by a Thermo Fisher X-Series II inductively coupled plasma mass spectrometer (ICP-MS).

Solid samples were digested overnight using acid digestion protocol in a hydrofluoric acid (HF) and nitric acid (HNO_3) mixture (v/v = 2 mL: 1 mL; optima grade) at 90-100 °C, whereas acidified water samples and leachate were analyzed directly following appropriate dilution.

The ICP-MS was calibrated using NIST SRM 1643e (Trace Elements in Water), which was analyzed at multiple concentrations throughout each analytical session. Internal standards (In, Th, and Bi) were added to all samples prior to analysis to correct for instrumental drift and matrix effects. Detection limits for each element were calculated as three times the standard deviation of repeated blank measurements divided by the slope of the calibration curve. Certified reference materials, including NIST SRM 1633c (coal fly ash) and NIST SRM 1632e (bituminous coal), were analyzed alongside samples to assess analytical accuracy.

2.6. Strontium and boron isotope analysis

Strontium and boron isotope ratios were measured by thermal ionization mass spectrometry (TIMS) using a ThermoFisher Triton instrument at the Duke University TIMS laboratory.

For boron isotope analysis, coal ash leachates were oxidized using 10% Optima-grade hydrogen peroxide to remove organic interferences prior to chemical separation. Boron was analyzed in negative ion mode as BO_2^- , and $^{11}\text{B}/^{10}\text{B}$ ratios were normalized to NIST SRM-951 and reported in $\delta^{11}\text{B}$ notation. Long-term replicate measurements of the SRM-951 standard ($n = 60$) yielded an analytical precision of $\pm 0.6\text{‰}$.

For strontium isotope analysis, Sr was measured in coal ash samples, CCR eluates, and natural waters. Water and eluate samples were preconcentrated by evaporation in a HEPA-filtered clean hood and redissolved in 0.6 mL of 3.5 N Optima-grade HNO_3 . Strontium was separated using Eichrom Sr-specific ion-exchange resin. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured in positive ion mode, and external reproducibility was monitored using NIST SRM-987 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710265 \pm 0.000006$).

2.7. Radionuclide analysis

Radionuclide activities in coal and coal ash samples were determined by high-resolution gamma spectrometry. Powdered samples were packed into Petri-style containers (6.5 cm diameter, 2 cm height), sealed with electrical tape, and coated with wax to prevent the escape of ^{222}Rn ($t_{1/2} = 3.8$ days). Samples were stored for at least 21 days before analysis to allow radioactive equilibrium between ^{226}Ra and its short-lived progeny. Gamma-ray measurements were conducted for 48 h using a Canberra Broad Energy Germanium (BEGe) detector housed within a 10 cm lead shield at Duke University. Activities of radionuclides from the U and Th decay series were quantified using established photopeaks and corrected for background, detector efficiency, and sample geometry.

2.8. Statistical analysis

Data processing, statistical summaries, and visualization were performed in RStudio (R version 2024.09.0). Relationships among elemental concentrations, isotope ratios, and radionuclide activities were explored using descriptive statistics, cross-plots, and comparative graphical analysis. Selected elemental ratios, isotope ratios, enrichment factors, and radionuclide activity ratios were calculated to facilitate interpretation of source signatures and comparison with published datasets and global reference values.

3. RESULTS & DISCUSSION

3.1. Geochemical characterization of coal combustion residues

Coal combustion residues (CCR) are commonly classified as either Ca-rich or Al-Si-rich, reflecting the mineral composition of the parent coal and combustion conditions (Gamage et al., 2013). Because SiO₂ data were not available, major oxide composition was evaluated using CaO dominance relative to alumina and iron ($\text{CaO}/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$) together with CaO/TiO₂, where TiO₂ serves as a proxy for the relatively immobile aluminosilicate fraction.

The investigated CCR clearly separate into two compositional groups. The $\text{CaO}/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ ratio ranges from 0.27 to 8.8 (Table S1), clearly separating the investigated CCR into two compositional groups. Štrmac, Plaški, Stanari, and Gacko-Ca are classified as Ca-rich (calcareous) CCR, whereas Kaštel, Tuzla, and Gacko-cassette are aluminosilicate-dominated. This distinction is further supported by CaO/TiO₂ ratios ranging from 3.7 to 300.

The compositional separation is also evident in the ratio of major-oxide elements in CCR against the upper continental crust (UCC) and reported values for European coal ash (Figure 2) (Blissett and Rowson, 2012; Rudnick and Gao, 2014). Relative to European coal ash averages, CaO concentrations are elevated by approximately 3-6 times in Štrmac, Plaški, and Gacko-Ca, with Štrmac and Gacko-Ca exceeding the reported upper European range (28.9 wt.%) (Figure 2) (Blissett and Rowson, 2012). In contrast, most other major oxides (Al₂O₃, Fe₂O₃, MgO, Na₂O, P₂O₅, MnO) occur at lower concentrations than the European mean, with only occasional enrichment in TiO₂ and MgO (Fig. 2B).

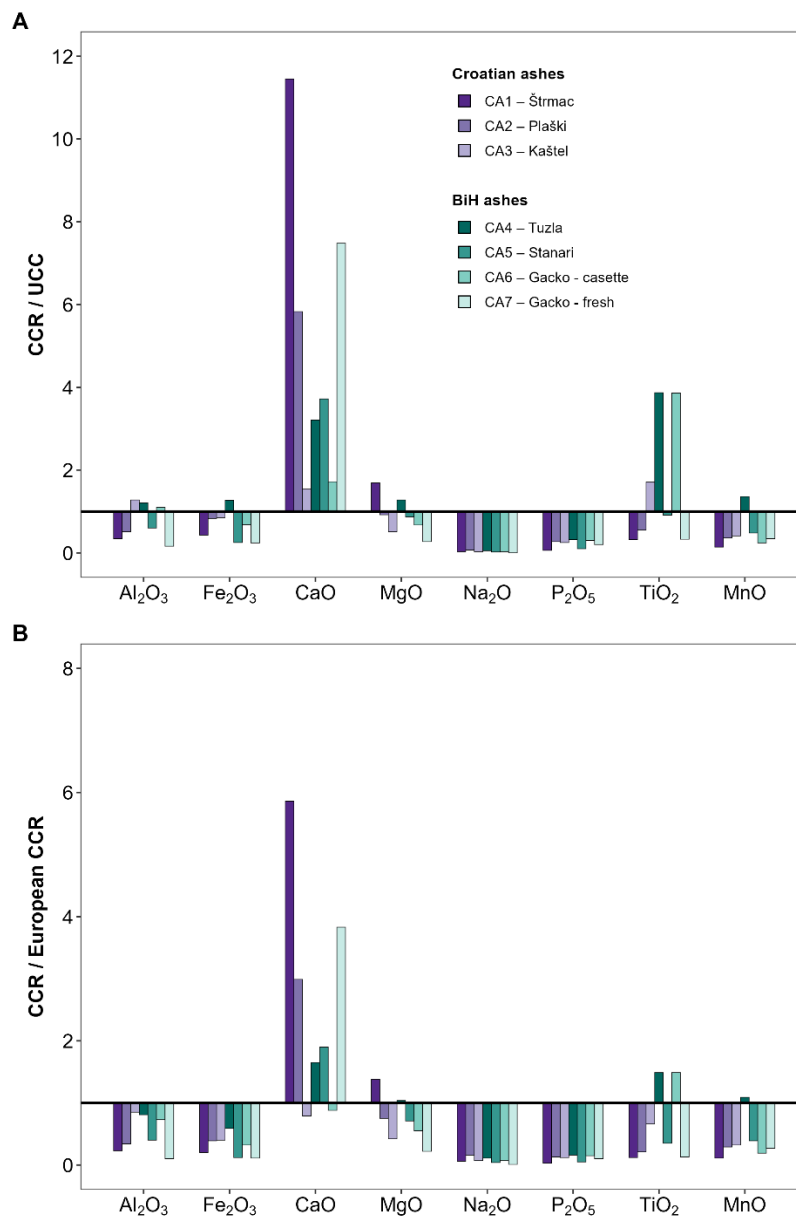


Figure 2. Major oxide composition of investigated coal combustion residues (CCR) from Croatia and Bosnia and Herzegovina normalized to (A) upper continental crust (UCC) (Rudnick and Gao, 2014) and (B) average European coal ash composition (Blissett and Rowson, 2012).

Trace element distributions broadly follow the major-element classification. Most Ca-rich CCR, except Stanari, contain comparatively low concentrations of trace elements. This pattern is consistent with previous studies showing that lignite-derived Ca-rich ashes are commonly diluted by abundant calcic phases, including free lime, anhydrite, and secondary carbonates, whereas aluminosilicate-rich ashes tend to retain higher trace element and rare earth concentrations within

silicate and glassy phases (Blissett and Rowson, 2012; Izquierdo and Querol, 2012; Vejehati et al., 2010). However, several important deviations indicate that parent coal composition remains a critical control beyond bulk ash mineralogy.

Among the Ca-rich CCR, Štrmac exhibits relatively low overall concentrations for most trace elements but shows distinct enrichment in V, Cu, Se, Sr, Mo, and U. This geochemical signature is consistent with the documented trace element enrichment of Raša coal, from which this ash was derived (Lieberman et al., 2020; Medunić et al., 2016). Plaški shows moderate trace element concentrations overall but is distinguished by elevated B (1276 mg/kg), together with increased As and U, suggesting selective retention or enrichment of environmentally relevant oxyanion-forming elements. In contrast, Gacko-Ca contains the lowest overall trace element concentrations of all investigated CCR, with only Sr and Ba occurring at moderate levels, a pattern typical of strongly Ca-dominated ash systems (Harkness et al., 2016).

The remaining CCR show intermediate to high trace element abundances with distinct compositional signatures. Gacko-cassette is characterized by relatively uniform, moderate trace element concentrations without pronounced enrichment in specific elemental groups. Tuzla shows elevated concentrations of transition metals, particularly Ni, Cr, and V, consistent with stronger retention in aluminosilicate phases. The most trace-element-rich samples are Stanari and Kaštel, although with contrasting geochemical signatures. Stanari, despite its classification as Ca-rich, exhibits exceptionally strong transition-metal enrichment, with Ni (2251 mg/kg), Cr (994 mg/kg), Co (133 mg/kg), and Zn (382 mg/kg), indicating that parent coal composition can override the expected dilution effect of Ca-rich mineral matrices. Similar departures from bulk compositional expectations have been reported where trace element partitioning reflects specific coal mineralogy rather than general ash type, particularly for transition metals associated with sulfides, clay minerals, or organometallic associations in the parent coal (Vassilev and Vassileva, 1996). In contrast, Kaštel is distinguished by elevated lithophile and radioactive elements, including V (410 mg/kg), Pb (32.6 mg/kg), Th (17.5 mg/kg), and U (76.9 mg/kg) (Table S2), likely reflecting the heterogeneous fuel history of the former Adriavil thermoelectric facility, which utilized coal from multiple geological sources, including uranium-enriched Raša anthracite and lignites from Bosnia and Herzegovina (Oreščanin et al., 2006).

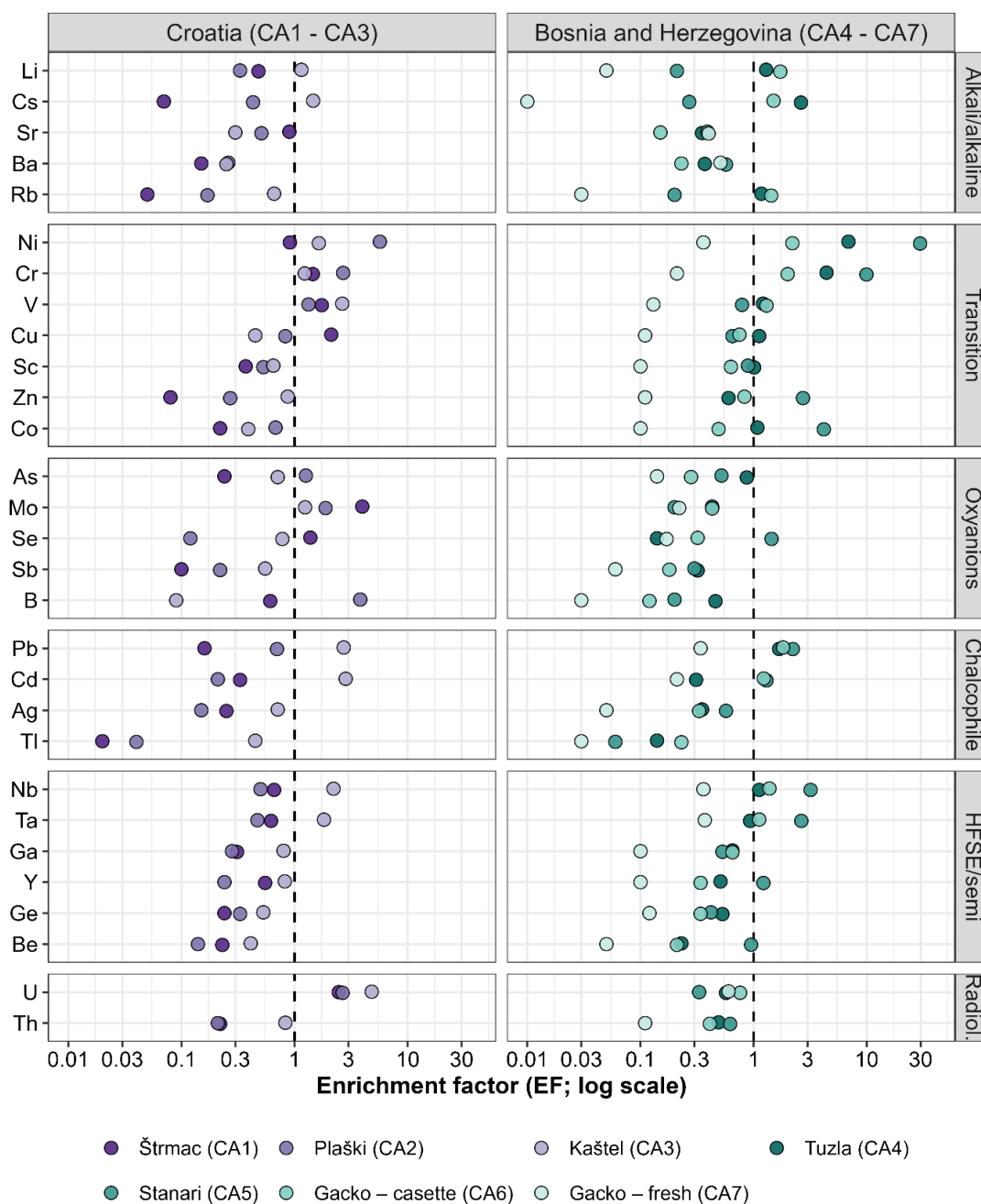


Figure 3. Enrichment factors (EF; log scale) of selected trace elements in coal combustion residues (CCR) from Croatia (CA1-CA3) and Bosnia and Herzegovina (CA4-CA7), calculated relative to world-average coal ash (Ketris and Yudovich, 2009). Elements are grouped according to geochemical affinity (alkali/alkaline earth, transition, oxyanions, chalcophile, high-field-strength/semi-metals, and radioactive elements). The dashed vertical line indicates EF = 1, corresponding to concentrations equivalent to world-average coal ash; values >1 indicate enrichment and values <1 depletion relative to the reference composition.

Enrichment factor (EF) analysis relative to world-average coal ash (Figure 3) supports these observations. Stanari shows the strongest enrichment overall, particularly for transition metals, with Ni (EF $\approx$ 35), Cr (EF $\approx$ 12), and Co (EF $\approx$ 4). Tuzla exhibits a similar but less pronounced transition-metal signature, with elevated Ni (EF $\approx$ 8) and Cr (EF $\approx$ 6). In contrast, most Ca-rich CCR show EF values close to or below unity, confirming relative depletion compared with global coal ash averages. Localized exceptions include enrichment of Mo and U in Štrmac and elevated B and U in Plaški. These patterns are consistent with previous observations that aluminosilicate-rich ashes more effectively retain trace elements during combustion, whereas Ca-rich systems may exhibit compositional dilution unless source-specific enrichment is substantial.

Rare earth elements and yttrium (REY) show a similar compositional control. Total REY concentrations range from 29.6 mg/kg in Gacko-Ca to 306 mg/kg in Stanari, with elevated concentrations also observed in Kaštel (245 mg/kg) and Tuzla (150 mg/kg). In contrast, Štrmac (88.2 mg/kg), Plaški (58.4 mg/kg), and Gacko-cassette contain lower REY abundances. CI-chondrite-normalized REY patterns (Figure 4A) show broadly similar shapes across all samples, characterized by enrichment of light REY relative to heavy REY, suggesting broadly comparable mineralogical controls despite differences in absolute abundance. When normalized to world-average coal ash (Figure 4B), most samples show REY concentrations below the global average, particularly the Ca-rich ashes, whereas Stanari and Kaštel approach average coal ash values for several elements. This pattern further supports the interpretation that REY abundance is primarily governed by the relative contribution of aluminosilicate versus Ca-bearing phases (Blissett and Rowson, 2012).

Overall, the investigated CCR are geochemically heterogeneous, reflecting both parent coal composition and bulk ash mineralogy. Ca-rich residues generally show lower trace element and REY abundances due to dilution by abundant Ca-bearing phases, whereas aluminosilicate-dominated residues retain higher concentrations of trace metals and lithophile elements. However, site-specific deviations, particularly the transition-metal enrichment in Stanari and the distinctive Raša-derived signature in Štrmac, demonstrate that source geology remains an equally important control. Similar complexity has been reported in coal ash systems globally, highlighting that tracer applicability must be evaluated within site-specific geochemical context rather than inferred solely from general ash type.

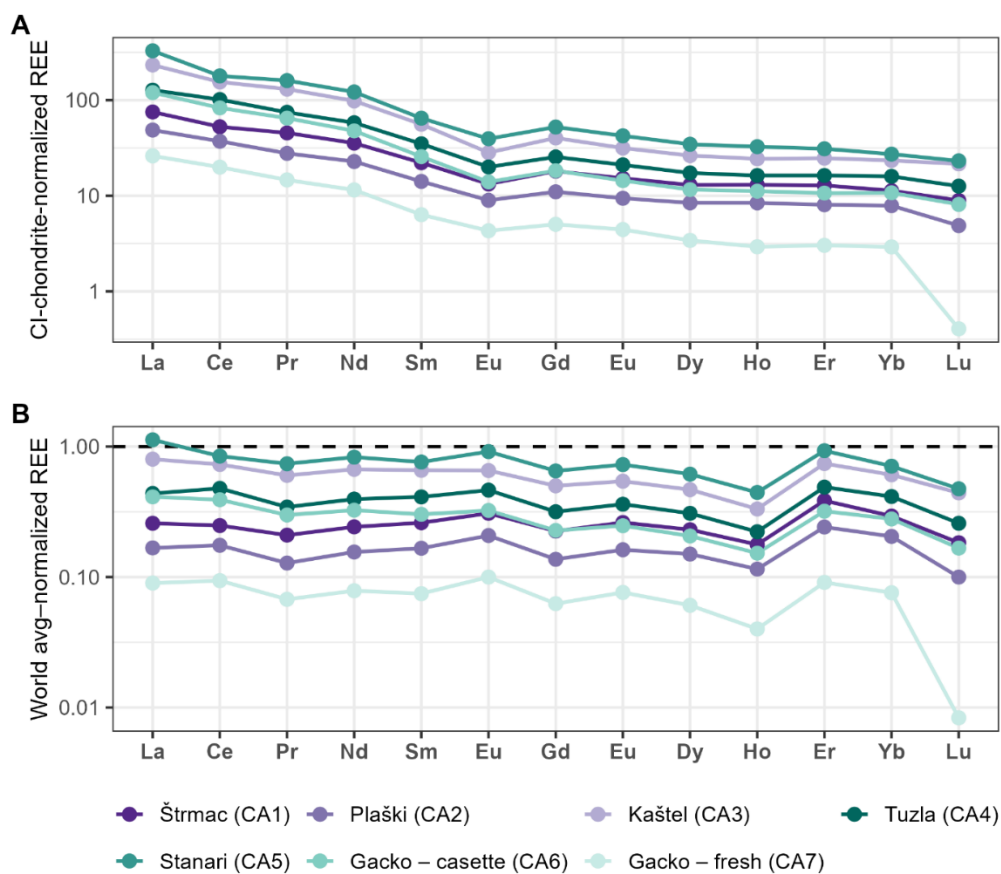


Figure 4. Rare earth element (REE) distribution in coal combustion residues (CCR). (A) CI-chondrite-normalized REE patterns (Sun and McDonough, 1989) and (B) REE concentrations normalized to world-average coal ash (Ketris and Yudovich, 2009) for CCR from Croatia (CA1-3) and Bosnia and Herzegovina (CA4-7).

3.4. Leachate behaviour and mobility of coal combustion residues

To assess the potential environmental release of contaminants from the investigated coal combustion residues (CCR), batch leaching experiments were performed following the standardized EN 12457-2 protocol. A total of 52 elements together with major dissolved anions were quantified in the resulting eluates (Table S3). Leachate composition varied substantially among samples, reflecting differences in bulk geochemistry, mineralogical composition, and element-specific controls on dissolution. Eluate pH ranged from 8.0 to 12.2, indicating predominantly alkaline leaching conditions typical of coal ash systems and expected to strongly influence element mobility (Table S3).

Across all CCR, eluates were dominated by alkaline and alkaline earth elements, particularly Ca, consistent with dissolution of Ca-bearing combustion and secondary weathering phases. Among dissolved anions, sulfate was the dominant species, with concentrations ranging from 0.81 to 1201 mg L⁻¹, whereas chloride, nitrate, bromide, and fluoride occurred at substantially lower concentrations. The predominance of sulfate is consistent with dissolution of sulfate-bearing phases such as gypsum and anhydrite, which commonly form during coal combustion and subsequent ash weathering, particularly in Ca-rich systems (Alhamed and Wohnlich, 2014; Chauhan et al., 2019; Harkness et al., 2016; Wu, 2004).

Trace element release was strongly sample- and element-specific. Plaški exhibited the highest dissolved B concentration (289 mg kg⁻¹) together with elevated Se and Mo, whereas Tuzla showed the highest dissolved Mo concentration (3.5 mg kg⁻¹) and elevated Cr release. Stanari and Gacko-cassette were characterized by comparatively high Sr and Ba concentrations, while Gacko-Ca consistently exhibited low dissolved concentrations across most measured elements. Despite high bulk concentrations in several CCR, transition metals such as Ni, Co, and Cu generally remained at low concentrations in solution, indicating limited aqueous mobility. The limited mobility of cationic trace metals such as Ni, Co, and Cu is consistent with the predominantly alkaline leaching conditions (pH 8.0-12.2), under which these elements exhibit reduced solubility due to precipitation as hydroxides and enhanced sorption onto mineral surfaces (Chandler et al., 1997; Izquierdo and Querol, 2012; Komonweeraket et al., 2015; Sloot et al., 2009).

To evaluate the environmental relevance of these releases, eluate concentrations were compared with EU waste acceptance criteria (WAC) for inert and non-hazardous waste, together with WHO drinking-water guideline values as an environmental context benchmark (Table 1). All investigated CCR complied with thresholds for non-hazardous landfill disposal, indicating that none would be classified as hazardous based on standardized compliance leaching. However, exceedances of inert waste thresholds were observed for several constituents. Chromium exceeded inert WAC in Tuzla, Stanari, and Gacko-cassette, while Mo exceeded inert thresholds in Štrmac, Plaški, Tuzla, and Gacko-cassette. Sulfate exceeded inert waste limits in Plaški.

Table 1. Summary of concentrations for selected elements and anions in coal combustion residues, compared with EU waste acceptance criteria (inert and non-hazardous waste) and WHO drinking-water guideline values (WHO values shown for environmental context only, not as regulatory equivalence). All values are in mg kg⁻¹.

Element	WHO*	EU inert	EU non-haz.	Observed range	Samples exceeding
As	0.01	0.5	2	0.00-0.19	WHO: CA2, CA3, CA4
B	2.4	-	-	bdl-289	WHO: CA2; CA6 slightly
Ba	1.3	20	100	0.09-62.8	WHO: CA4, CA5, CA7; EU inert: CA5, CA7
Cd	0.003	0.04	1	bdl-0.01	WHO: CA2, CA6
Cr (total)	0.05	0.5	10	0.02-2.69	WHO: CA1, CA2, CA4, CA5, CA6; EU inert: CA4, CA5, CA6
Cu	2	2	50	bdl-0.21	-
Mo	0.07	0.5	10	0.16-3.50	WHO: all except CA7; EU inert: CA1, CA2, CA4, CA6
Ni	0.07	0.4	10	bdl-0.06	-
Pb	0.01	0.5	10	bdl-0.01	-
Sb	0.02	0.06	0.7	bdl-0.04	WHO: CA2, CA3, CA6
Se	0.04	0.1	0.5	bdl-0.11	WHO: CA1, CA2, CA4, CA5, CA6; EU inert: CA2, CA5
Zn	-	4	50	0.04-0.06	-
U	0.03	-	-	bdl-0.25	WHO: CA3
Sr	-	-	-	0.76-62.8	-
Cl ⁻	250**	800	15000	bdl-9.88	-
SO ₄ ²⁻	500**	1000	20000	0.81-1201	EU inert: CA2

* WHO drinking-water guideline values are shown as approximate mg/kg equivalents to enable comparison with eluate concentrations (reported at a liquid-to-solid ratio of 10 L/kg); these values are included for environmental context and do not represent regulatory limits for solid waste leachates.

** WHO values for chloride and sulfate are based on drinking-water taste/acceptability considerations rather than health-based limits.

Comparison with the more stringent WHO drinking-water benchmarks provides a different perspective. Several eluates exceeded guideline values for As, Cr, Mo, Se, Ba, and U, despite compliance with waste acceptance criteria. The most widespread exceedances were observed for Mo, which exceeded WHO values in nearly all samples. This discrepancy highlights an important limitation of waste classification frameworks: compliance with landfill acceptance criteria does not necessarily imply low environmental risk if mobilized constituents enter surrounding water

systems. It should be emphasized, however, that WHO guideline values are included here solely as an environmental reference point and do not represent regulatory thresholds for solid waste leachates.

Absolute eluate concentrations alone do not fully describe elemental mobility, as release depends not only on dissolved concentrations but also on the total elemental inventory of the solid residue. To better assess relative mobility, elemental release was expressed as the percentage of total solid-phase content leached during the EN 12457-2 test (Figure 5; Table S4).

Clear differences emerged among geochemical element groups. Alkali and alkaline earth elements generally exhibited the highest relative mobility, particularly Sr and Ba, with maximum release approaching 25% of total content. Among environmentally relevant trace contaminants, oxyanion-forming elements showed the greatest mobility, especially Mo, B, and Se. Molybdenum exhibited the highest relative release, particularly in Tuzla and Gacko-cassette, while Plaški showed elevated mobility of B and Se.

This behaviour is consistent with the known aqueous geochemistry of these elements. Under alkaline leaching conditions (pH 8.0-12.2), oxyanion-forming species such as molybdate, borate, and selenate/selenite remain comparatively soluble and weakly sorbed to mineral surfaces, promoting preferential release. Similar behaviour has been widely reported in coal ash leachates and is one of the primary reasons these elements are considered sensitive indicators of CCR-derived contamination in environmental waters (Izquierdo and Querol, 2012; Harkness et al., 2016; Vengosh et al., 2019).

In contrast, transition metals remained comparatively immobile despite elevated total concentrations in several CCR. This was particularly evident in Stanari, which contains the highest bulk concentrations of Ni, Cr, and Co, yet exhibited minimal leaching of these elements. This demonstrates that total concentration alone is a poor predictor of environmental mobility and suggests strong incorporation of these metals within relatively insoluble mineral phases, such as oxides, aluminosilicates, or combustion-derived spinel-like phases, which suppress dissolution under alkaline conditions.

Similar low mobility was observed for Cu and Zn. Radioactive elements and REE also showed limited release. Thorium remained below detection in all eluates, while uranium showed only

minor release, with slightly elevated mobility in Kaštel, Plaški, and Gacko-cassette. Representative REE (La and Yb) exhibited negligible release across all samples. This limited mobility is consistent with their strong association with refractory mineral phases and low aqueous solubility, making them poor indicators of short-term aqueous CCR contamination despite their abundance in the solid phase.

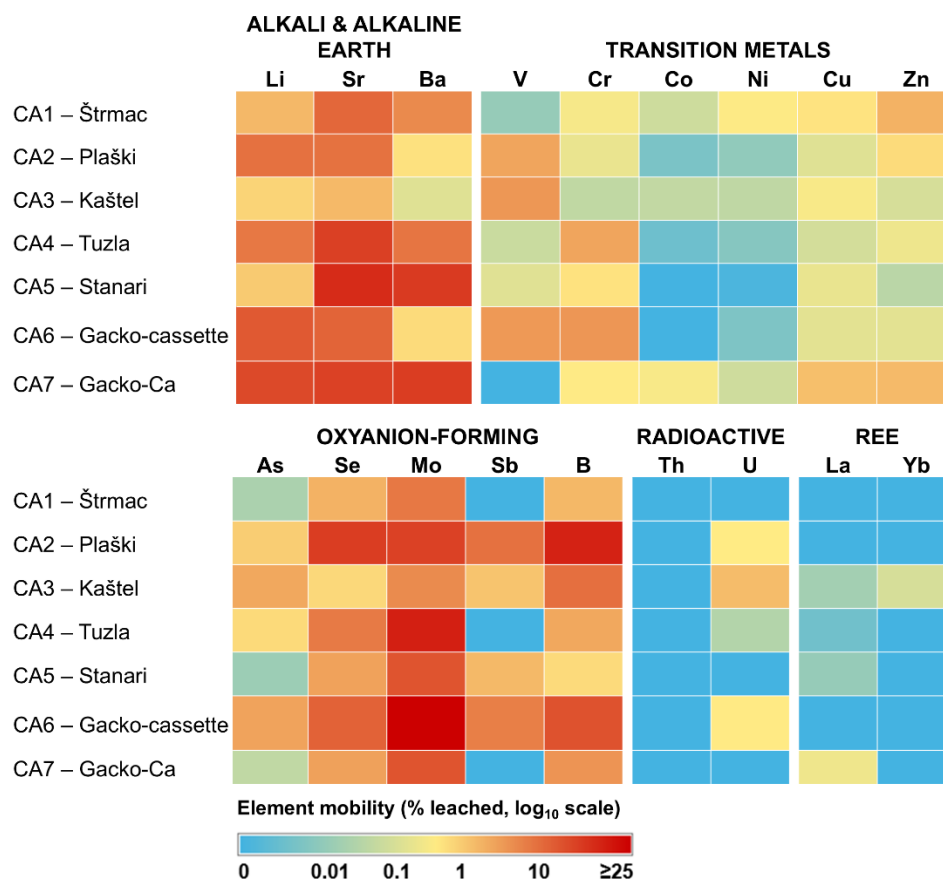


Figure 5. Heatmap showing log₁₀-transformed percentages released after EN 12457-2 leaching of coal combustion residues. Elements are grouped according to geochemical affinity and only selected elements are shown. Data showing exact percentages for all 52 measured elements are in the Supplementary material (Table S5).

Overall, leaching behaviour was controlled less by total elemental abundance than by element speciation, host phase association, and leachate chemistry. The preferential release of oxyanion-forming elements and alkaline earth metals, coupled with strong retention of transition metals,

REE, and thorium, indicates that only a subset of the bulk CCR geochemical signature is environmentally transferable.

3.3 Isotopic and radiological fingerprinting of coal combustion residues

3.3.1 Strontium and boron isotope characteristics

Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) were evaluated as potential tracers of CCR-derived contamination because strontium is both relatively mobile in coal ash leachates and capable of retaining source-specific isotopic signatures linked to parent coal geology and mineral composition. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios show substantial variability across the investigated materials (Table S6; Figure 6), with coal samples ranging from 0.708549-0.710956, CCR solids from 0.707583-0.711661, and CCR leachates from 0.707679-0.710167.

The observed variability reflects the geochemical heterogeneity of the source materials. Ca-rich CCR, particularly the Croatian legacy ashes, show relatively unradiogenic signatures (~0.707583-0.708614) and elevated Sr concentrations, consistent with incorporation of strontium into Ca-bearing phases such as carbonates and sulfates. In contrast, aluminosilicate-dominated ashes generally exhibit lower Sr concentrations and more radiogenic isotope compositions, reflecting stronger silicate control. Similar relationships between ash composition, parent coal provenance, and Sr isotope signatures have been reported previously (Campbell et al., 2008; Hurst et al., 1991; Vengosh et al., 2019).

Comparison between coals, bulk ashes, and corresponding leachates shows that while combustion does not substantially alter the bulk Sr isotopic composition, the dissolved fraction released during leaching may differ from whole-sample values. The clearest example is Gacko-cassette, where bulk ash shows the most radiogenic composition (0.711661), whereas the corresponding leachate is substantially less radiogenic (0.708879). Similar offsets between bulk and water-soluble Sr isotope compositions have been reported for coal fly ash elsewhere (Wang et al., 2020). This likely reflects preferential dissolution of soluble Ca-bearing phases, which release isotopically distinct Sr relative to the residual aluminosilicate matrix. For environmental tracing, this distinction is important because receiving waters reflect the mobile dissolved fraction rather than bulk ash composition.

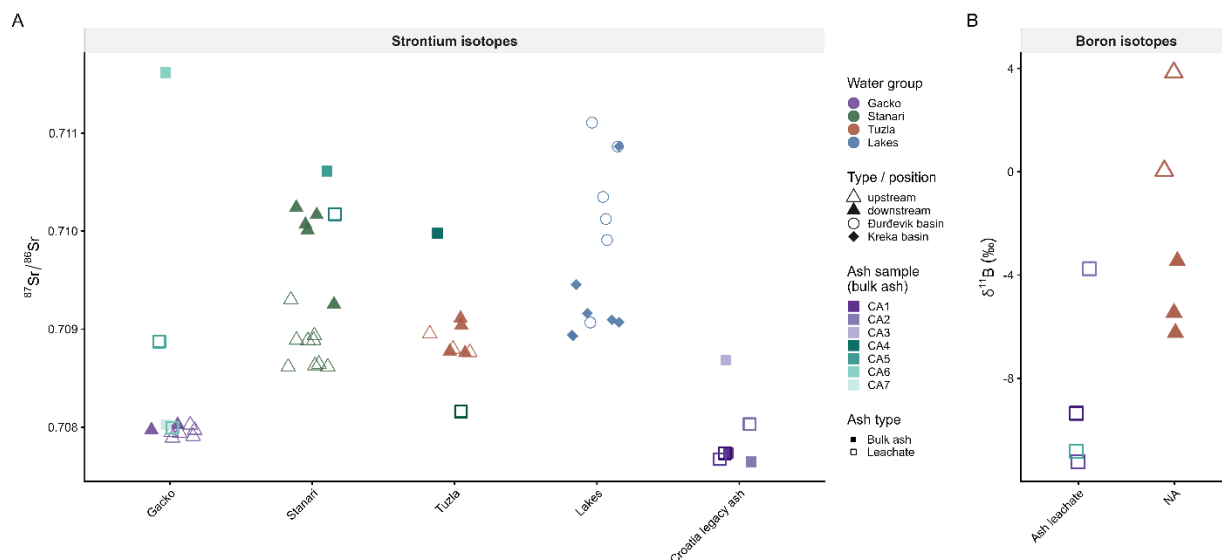


Figure 6. Strontium and boron isotope signatures of coal ash materials and impacted waters. (A) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in coal ash materials, leachates, and regional surface waters. Filled squares represent bulk ash samples, whereas open squares represent corresponding ash leachates. Water samples are grouped by study area (Gacko, Stanari, Tuzla, and Tuzla-associated lakes) and distinguished by hydrological position (upstream, downstream, and lake basin type). (B) $\delta^{11}\text{B}$ values for ash leachates and Tuzla stream waters.

Boron isotope composition ($\delta^{11}\text{B}$) was determined for four representative CCR leachates to characterize the dissolved boron fraction relevant to aqueous transport. Measured values range from -11.2‰ to -3.7‰ , with three samples clustering between -11.2‰ and -9.4‰ and one sample (CA3) showing a less negative composition (-3.7‰). Although limited in number, these values are consistent with previous studies showing that boron isotopes can help distinguish coal ash-derived inputs from other environmental sources (Harkness et al., 2017; Vengosh et al., 2016).

Taken together, Sr isotopes provide the stronger tracer framework in this study due to broader source characterization and direct comparison with environmental waters, whereas $\delta^{11}\text{B}$ serves as a complementary line of evidence.

3.3.2 Naturally occurring radionuclides (NORM)

Activities of naturally occurring radionuclides show substantial variability between coals and corresponding coal combustion residues (CCR) (Table S6; Figure 7), reflecting both source coal

composition and enrichment during combustion. Among CCR, ^{238}U activities range from 90 to 713 Bq kg^{-1} , ^{226}Ra from 80 to 833 Bq kg^{-1} , ^{228}Ra from 51 to 107 Bq kg^{-1} , and ^{210}Pb from 85 to 732 Bq kg^{-1} . The highest activities of uranium-series radionuclides were observed in the Croatian legacy CCR, particularly Kaštel, Plaški, and Štrmac, whereas Bosnian and Herzegovinian samples generally exhibited values typical for coal ash (Lauer et al., 2015).

This contrast likely reflects differences in parent fuel composition. Raša coal, associated with the Štrmac site, is well documented for elevated uranium-series radionuclide content (Medunić et al., 2020, 2016), and the analyzed sample in the present study showed near-equilibrium uranium-series relationships ($^{226}\text{Ra}/^{238}\text{U} = 1.02$; $^{226}\text{Ra}/^{210}\text{Pb} = 0.98$) (Table S6). Elevated activities in Kaštel likely reflect the historical use of mixed industrial fuel sources, including uranium-enriched Raša coal and other regional coals, at the former Adriavini thermoelectric facility (Oreščanin et al., 2006), whereas enrichment in Plaški is consistent with previous reports of elevated radionuclide activities in ash and surrounding soils at the landfill (Oreščanin et al., 2012).

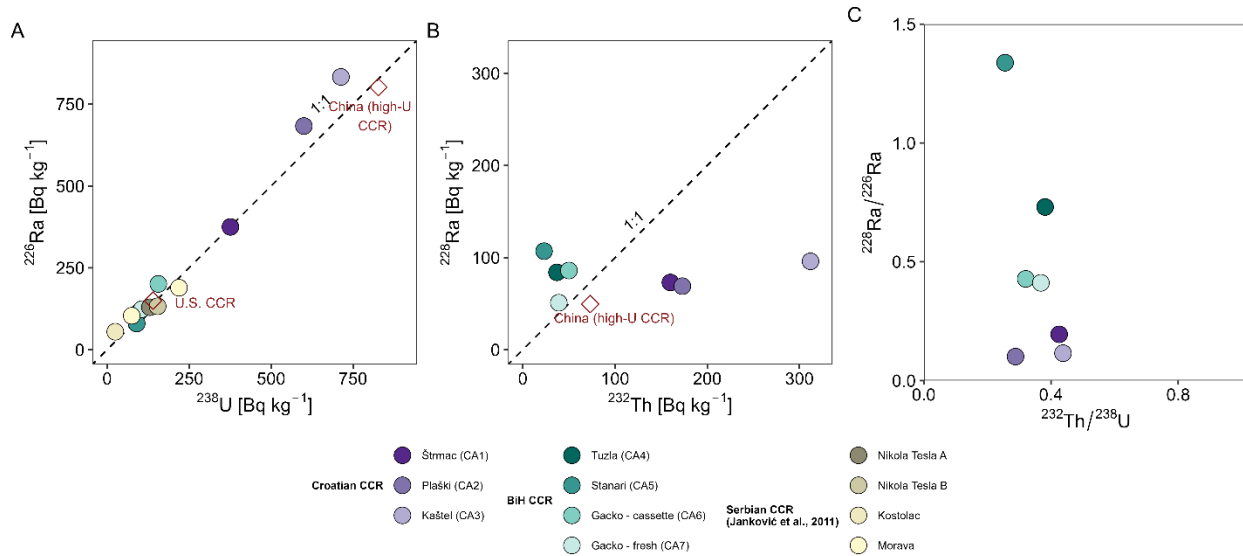


Figure 7. Relationships between radionuclide activities in coal combustion residues (CCR) from Croatia and Bosnia and Herzegovina. (A) ^{226}Ra vs. ^{238}U and (B) ^{228}Ra vs. ^{232}Th , with dashed lines indicating theoretical 1:1 activity equilibrium. Comparative literature values for Serbian CCR (Janković et al., 2011) and uranium-enriched Chinese CCR are shown for context (Lauer et al., 2017). (C) Activity ratio relationship between $^{228}\text{Ra}/^{226}\text{Ra}$ and $^{232}\text{Th}/^{238}\text{U}$.

Activities of ^{226}Ra and ^{238}U show a strong positive relationship and cluster close to the 1:1 equilibrium line (Figure 7A), indicating near-equilibrium behaviour between uranium and radium in most CCR. This suggests limited fractionation between these radionuclides during combustion and subsequent storage, with uranium-series radionuclides largely retained together in the ash matrix. Croatian samples overlap with values reported for uranium-enriched coal combustion residues (Lauer et al., 2017), whereas Bosnian and Herzegovinian samples are more comparable to conventional coal ash datasets (Janković et al., 2011; Lauer et al., 2015).

In contrast, ^{228}Ra does not scale proportionally with ^{232}Th (Figure 7B), indicating decoupling between thorium and radium behaviour. Activity ratio analysis further emphasizes this difference. While $^{226}\text{Ra}/^{238}\text{U}$ ratios remain close to unity (0.90-1.29), consistent with limited uranium-series fractionation, $^{228}\text{Ra}/^{226}\text{Ra}$ ratios vary considerably (0.10-1.34), with the highest value observed in Stanari, indicating substantially greater variability in thorium-series behaviour. Similarly, $^{232}\text{Th}/^{238}\text{U}$ activity ratios are generally low in Croatian CCR (0.03-0.10) but higher in Bosnian samples (0.09-0.59).

This decoupling likely reflects the contrasting geochemical behaviour of uranium- and thorium-associated phases. Uranium and radium may remain relatively closely associated in combustion residues, whereas thorium, which is generally less mobile and more strongly retained in refractory mineral phases, may exhibit different partitioning during combustion and subsequent weathering. In older weathered residues, post-depositional redistribution of more mobile radionuclides such as radium may further modify equilibrium relationships (Bituh et al., 2024).

3.5 Surface water geochemistry and evidence of coal-related influence

Surface waters were characterized using an integrated dataset including physicochemical parameters, major ions, trace elements, rare earth elements, and isotopic tracers ($^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{11}\text{B}$ where available) (Table S7). The full analytical suite included major ions, rare earth elements, and 52 major and trace elements. However, most elements remained consistently low or below detection across the investigated waters, while others showed limited spatial variability. The discussion therefore focuses on constituents that showed clear enrichment, spatial differentiation, or source-diagnostic behavior, particularly SO_4^{2-} , Cl^- , B, Sr, Li, Mo, U, Rb, and isotopic tracers.

3.5.1 Flowing waters: hydrochemical, trace element, and isotopic fingerprints of coal-related influence

Clear hydrochemical differences were observed among the investigated sites, showing that coal-related impacts do not produce a single universal aqueous signature, but site-specific geochemical fingerprints (Figure 8 and 9; Table S7).

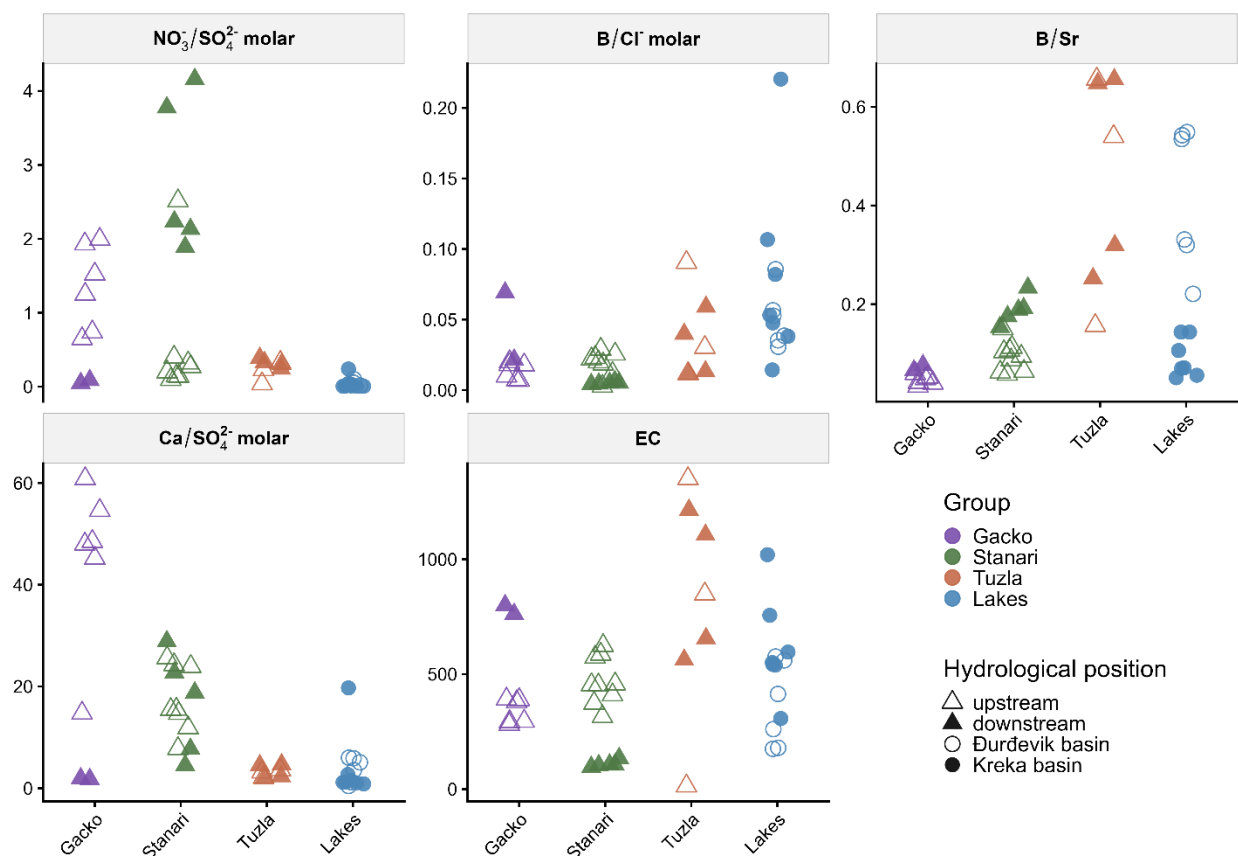


Figure 8. Comparison of selected hydrochemical indicators across investigated surface waters from the Gacko, Stanari, and Tuzla regions, including post-mining lakes used for recreation. Shown parameters include molar $\text{NO}_3^-/\text{SO}_4^{2-}$, B/Cl^- , $\text{Ca}/\text{SO}_4^{2-}$, elemental B/Sr , and electrical conductivity (EC). Symbols indicate hydrological setting (upstream, downstream, Kreka basin lakes, and Đurđevik basin lakes).

A clearer coal-associated gradient was observed in the Mramor stream, which drains directly through the mining area. The upstream reference showed near-pristine conditions ($\text{EC} = 14 \mu\text{S cm}^{-1}$), while downstream waters increased to $563\text{--}656 \mu\text{S cm}^{-1}$, accompanied by higher chloride,

boron, and dissolved trace element concentrations. Boron increased from 90.2 to 131 $\mu\text{g L}^{-1}$, Rb from 1.06 to 4.26 $\mu\text{g L}^{-1}$, and Zn from 8.6 to 18.5 $\mu\text{g L}^{-1}$, whereas Sr, Ca, and U decreased and Mo declined below detection. This indicates a shift in dissolved composition rather than simple downstream accumulation. Isotopic data support a coal-associated source contribution. $^{87}\text{Sr}/^{86}\text{Sr}$ increased from 0.708952 upstream to 0.709041-0.709111 downstream, shifting toward the Tuzla fly ash signature (0.709979). Boron isotopes also shifted from +3.9‰ upstream to negative values in downstream Tuzla waters (down to -5.5‰), consistent with CCR leachate signatures measured in this study (-3.7 to -11.2‰).

The Tuzla region showed the broadest hydrochemical variability and highest overall solute enrichment. Waters in the Jala system exhibited elevated EC (849-1214 $\mu\text{S cm}^{-1}$), sulfate (61.8-104 mg L^{-1}), chloride (37.9-105 mg L^{-1}), boron (350-369 $\mu\text{g L}^{-1}$), and strontium (546-648 $\mu\text{g L}^{-1}$), together with high concentrations of Li (38.7-113 $\mu\text{g L}^{-1}$), Mo (13.4-14.3 $\mu\text{g L}^{-1}$), and Rb (17.0-18.4 $\mu\text{g L}^{-1}$). Hydrochemical ratios further separated Tuzla from the other flowing systems, with elevated B/Cl and B/Sr values indicating enrichment in highly mobile boron-bearing solutes. However, interpretation of the Jala River remains complex because the catchment receives overlapping inputs from thermal power generation, historical ash disposal, other industrial activity, and urban wastewater. Its chemical composition therefore reflects mixed anthropogenic influence rather than a distinct CCR end-member.

The Gacko system exhibited a different hydrochemical fingerprint dominated by sulfate enrichment rather than boron-rich solutes. Upstream Mušnica and Trnovac waters were chemically similar, with low sulfate (2.1-4.2 mg L^{-1}) and moderate EC (281-391 $\mu\text{S cm}^{-1}$). Downstream impacted waters showed abrupt increases in sulfate (162-177 mg L^{-1}), EC (762-800 $\mu\text{S cm}^{-1}$), Ca, and Sr, while B/Sr and B/Cl remained lower than in Tuzla. Trace element enrichment was also pronounced. Relative to upstream waters, boron increased from 5.1-11.2 to 27.2-38.7 $\mu\text{g L}^{-1}$, Sr from 101-272 to 414-506 $\mu\text{g L}^{-1}$, U from 0.13-0.20 to 2.88-3.36 $\mu\text{g L}^{-1}$, Li from 0.98-1.23 to 9.38-10.5 $\mu\text{g L}^{-1}$, and Mo from below detection to 1.87-3.11 $\mu\text{g L}^{-1}$. Unlike Tuzla, this enrichment was accompanied by only a modest isotopic shift, from 0.707890-0.707970 upstream to 0.708023-0.708027 after the CCR discharge. Although numerically small, the shift exceeds analytical uncertainty and trends toward the Gacko ash leachate signatures (0.707994 and 0.708879).

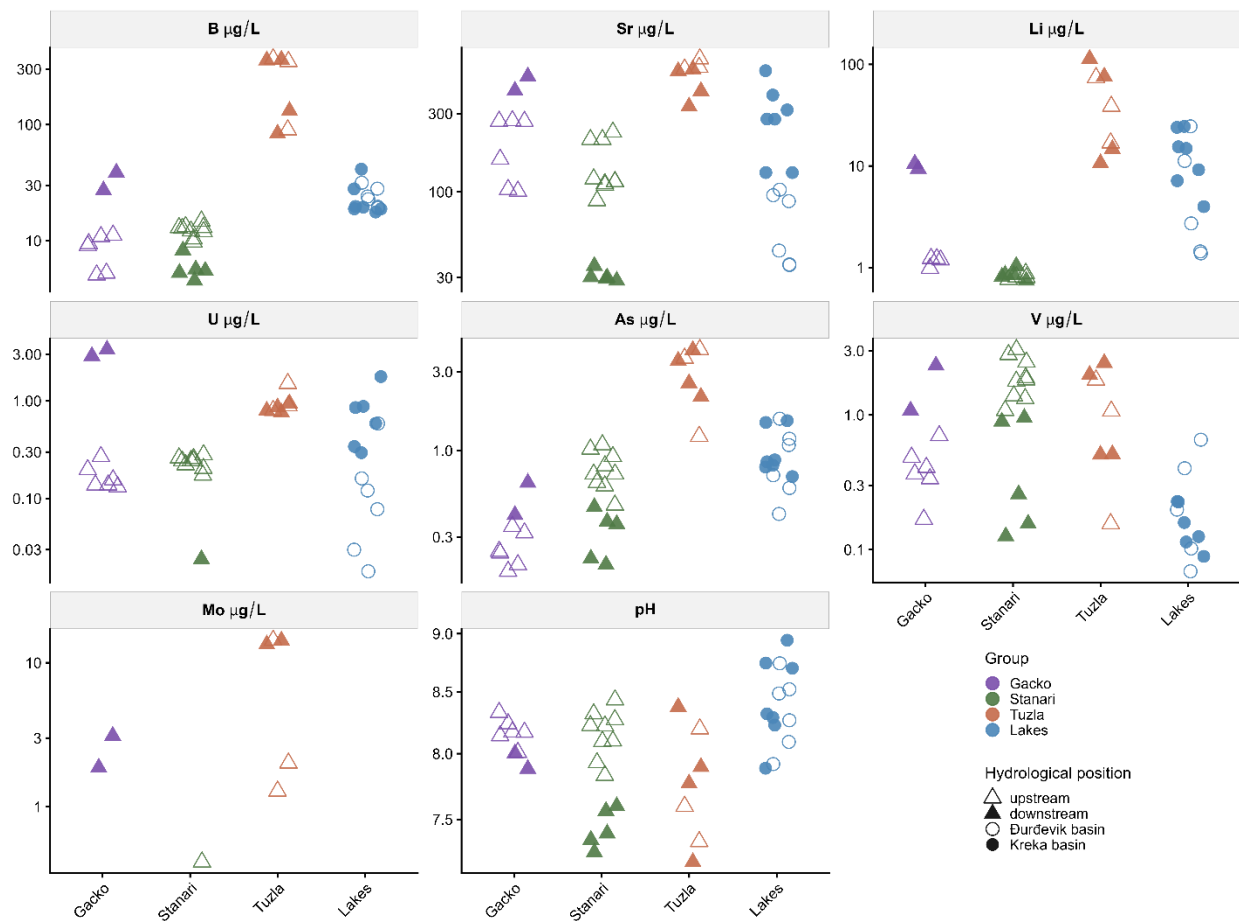


Figure 9. Concentrations of selected dissolved constituents (B, Sr, Li, U, As, V, and Mo) and pH in investigated surface waters from the Gacko, Stanari, and Tuzla regions, including post-mining lakes. Symbols indicate hydrological setting (upstream, downstream, Kreka basin lakes, and Đurđevik basin lakes).

Compared with Tuzla and Gacko, Stanari showed weaker hydrochemical differentiation. EC ranged from 97 to 624 $\mu\text{S cm}^{-1}$, sulfate remained low (1.0–8.4 mg L^{-1}), and hydrochemical ratios showed broader scatter without clear clustering. Trace element contrasts were also weaker, with some constituents showing little change or even decreasing near the expected CCR input zone. In contrast, isotopic separation was clear. Reference waters clustered tightly between 0.708614 and 0.708644, whereas waters from the expected CCR input zone (Ostružnja stream) ranged from 0.710010 to 0.710242, overlapping the Stanari ash leachate signature (0.710167). The weaker concentration-based signal relative to Gacko likely reflects lower contaminant transfer, stronger

dilution, and/or more effective hydrological separation between industrial sources and receiving waters.

Across the flowing systems, sulfate was the most consistently elevated major anion in impacted waters, while trace element enrichment was selective rather than uniform. Many measured elements remained consistently low or below detection, indicating that coal-related aqueous impacts are expressed through mobilization of specific dissolved constituents, particularly SO_4^{2-} , B, Sr, Li, U, Mo, and Rb, rather than generalized enrichment of the full trace element suite.

Comparison with site-specific CCR leachates showed that receiving waters retained selected geochemical fingerprints of source materials rather than reproducing the full leachate composition. The strongest correspondence was observed in Gacko, where sulfate-rich impacted waters matched the ash leachate signature, while Tuzla and Stanari showed clearer isotopic than compositional agreement.

Together, these results show that coal-related impacts do not produce a single aqueous signature, but rather site-specific geochemical fingerprints that reflect differences in source materials, hydrological pathways, and local geochemical processes.

3.5.2 Post-mining and recreational lakes: signatures of legacy coal mining influence

The Tuzla lakes represent flooded mine-pit and post-mining water bodies developed within the broader coal basin. Several are currently used for recreation, fishing, or tourism, making their hydrochemical characterization environmentally relevant beyond source attribution alone.

The lakes separated into two geochemical groups corresponding to the Kreka and Đurđevik coal basins. Kreka basin lakes showed less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.708929-0.709454) and higher dissolved solute loads, whereas Đurđevik basin lakes were more radiogenic (0.709067-0.711106) but generally less mineralized.

The strongest dissolved coal-/mine-associated signature was observed in the Kreka lakes. Odlagač Lake showed the highest sulfate (298 mg L^{-1}), Sr ($548 \text{ } \mu\text{g L}^{-1}$), and elevated U ($1.78 \text{ } \mu\text{g L}^{-1}$). Kop Lake and Ribarsko Lake also showed elevated sulfate (193 and 176 mg L^{-1}) and Sr (390 and $316 \text{ } \mu\text{g L}^{-1}$, respectively). These waters retain a sulfate-Sr-rich signature consistent with prolonged interaction with coal-bearing materials, mine spoil, and potentially ash-affected deposits. Their

isotopic compositions are also closer to the Tuzla ash-related range than the more radiogenic Đurđevik lakes.

In contrast, the Đurđevik lakes showed lower Sr (36-103 $\mu\text{g L}^{-1}$) and U (0.02-0.59 $\mu\text{g L}^{-1}$) despite higher $^{87}\text{Sr}/^{86}\text{Sr}$ values. This indicates that more radiogenic isotopic compositions do not necessarily correspond to stronger coal-associated dissolved loads, but instead reflect basin-specific differences in Sr sources, likely related to coal composition or geological setting. Boron concentrations were moderate across both lake groups (17.7-41.3 $\mu\text{g L}^{-1}$) and did not separate the basins as clearly as sulfate, Sr, or Sr isotopes.

Unlike the flowing waters, where isotopic shifts could often be linked to identifiable upstream-downstream gradients, the lakes represent integrated long-residence systems where evaporation, prolonged water-rock interaction, and historical mine evolution modify aqueous composition. Nevertheless, the elevated sulfate-Sr signature in several Kreka lakes demonstrates that legacy coal-mining influence remains geochemically detectable in standing waters that are now part of the public landscape.

The measured inorganic chemistry does not by itself indicate that these lakes are unsuitable for recreational use. However, the persistence of coal-associated geochemical signatures in publicly accessible post-mining waters highlights the need for continued environmental monitoring.

This integrated dataset shows that coal-related aquatic impacts do not produce a single universal fingerprint. Shared indicators across sites include sulfate enrichment, altered Sr systematics, and selective mobilization of dissolved trace elements, but the dominant expression is site-specific: boron-rich mixed anthropogenic influence in Tuzla, sulfate-dominated trace element mobilization in Gacko, isotopically detectable but chemically muted influence in Stanari, and persistent legacy sulfate-Sr signatures in post-mining lakes.

4. CONCLUSION

This study shows that coal combustion residues do not produce a single universal aquatic fingerprint. Instead, coal-related impacts are expressed through site-specific geochemical and isotopic signatures shaped by source composition, contaminant mobility, and hydrological setting.

Leaching experiments showed that only a subset of the bulk CCR signature is environmentally transferable, with preferential mobilization of sulfate, Sr, Ba, and oxyanion-forming elements such as B and Mo, while many transition metals and REE remained largely immobile. Strontium isotopes proved to be the most effective tracer because they preserved source-specific variability while remaining environmentally relevant in the dissolved phase. Boron isotopes provided complementary evidence but were evaluated more limitedly.

Environmental waters reflected distinct site responses: sulfate-dominated downstream enrichment in Gacko, isotopically detectable but chemically weaker signals in Stanari, mixed anthropogenic influence in Tuzla, and persistent legacy signatures in post-mining lakes. Together, these results demonstrate that integrated geochemical and isotopic fingerprinting is a useful framework for tracing coal-related aquatic contamination in complex industrial environments.

5. REFERENCES

- Alhamed, M., Wohnlich, S., 2014. Environmental impact of the abandoned coal mines on the surface water and the groundwater quality in the south of Bochum, Germany. *Environ. Earth Sci.* 72, 3251-3267. <https://doi.org/10.1007/s12665-014-3230-9>
- Bituh, T., Peco, J., Mihalić, I.B., Gouasmia, S., Grlić, M., Petrinc, B., 2024. Trace element and radiological characterisation of ash and soil at a legacy site in the former Raša coal-mining area. *Arh. Hig. Rada Toksikol.* 75, 245-258. <https://doi.org/10.2478/aiht-2024-75-3897>
- Blissett, R.S., Rowson, N.A., 2012. A review of the multi-component utilisation of coal fly ash. *Fuel* 97, 1-23. <https://doi.org/10.1016/j.fuel.2012.03.024>
- Bušatlić, I., Bušatlić, N., Merdić, N., Haračić, N., Mujezinović, L., 2025. Geopolymers based on fly ash with the addition of granulated blast furnace slag, in: XVI International Mineral Processing and Recycling Conference. Belgrade, pp. 598-604. <https://doi.org/10.5937/imprc25598b>
- Campbell, C.E., Pearson, B.N., Frost, C.D., 2008. Strontium isotopes as indicators of aquifer communication in an area of coal-bed natural gas production, Powder River Basin, Wyoming and Montana. *Rocky Mt. Geol.* 43, 171-197. <https://doi.org/10.2113/gsrocky.43.2.171>

- CEN, 2023. Compliance test for leaching of granular waste materials and sludges: EN 12457-2. Eur. Comm. Stand.
- Chandler, J., Taylor Eighmy, T., Hartlen, J., Hjelm, O., Kosson, D., Sawel, S., van der Sloot, H., Vehlow, J., 1997. Chemical aspects of Leaching. *Stud. Environ. Sci.* 67, 507-578. <https://doi.org/10.12681/eadd/1834>
- Chauhan, R., Awasthi, S., Srivastava, S., Dwivedi, S., Pilon-Smits, E.A.H., Dhankher, O.P., Tripathi, R.D., 2019. Understanding selenium metabolism in plants and its role as a beneficial element. *Crit. Rev. Environ. Sci. Technol.* 49, 1937-1958. <https://doi.org/10.1080/10643389.2019.1598240>
- Gamage, N., Liyanage, K., Fragomeni, S., Setunge, S., 2013. Overview of different types of fly ash and their use as a building and construction material. *Int. Conf. Struct. Eng. Constr. Manag.*
- Harkness, J.S., Darrah, T.H., Moore, M.T., Whyte, C.J., Mathewson, P.D., Cook, T., Vengosh, A., 2017. Naturally Occurring versus Anthropogenic Sources of Elevated Molybdenum in Groundwater: Evidence for Geogenic Contamination from Southeast Wisconsin, United States. *Environ. Sci. Technol.* 51, 12190-12199. <https://doi.org/10.1021/acs.est.7b03716>
- Harkness, J.S., Sulkin, B., Vengosh, A., 2016. Evidence for Coal Ash Ponds Leaking in the Southeastern United States. *Environ. Sci. Technol.* 50, 6583-6592. <https://doi.org/10.1021/acs.est.6b01727>
- Hurst, R.W., Davis, T.E., Elseewi, A.A., 1991. Strontium isotopes as tracers of coal combustion residue in the environment. *Eng. Geol.* 30, 59-77. [https://doi.org/10.1016/0013-7952\(91\)90035-J](https://doi.org/10.1016/0013-7952(91)90035-J)
- Izquierdo, M., Querol, X., 2012. Leaching behaviour of elements from coal combustion fly ash: An overview. *Int. J. Coal Geol.* 94, 54-66. <https://doi.org/10.1016/j.coal.2011.10.006>
- Janković, M.M., Todorović, D.J., Nikolić, J.D., 2011. Analysis of natural radionuclides in coal, slag, and ash in coal-fired power plants in Serbia 47, 149-155. <https://doi.org/10.2298/JMMB110208008J>
- Ketris, M.P., Yudovich, Y.E., 2009. Estimations of Clarkes for Carbonaceous biolithes: World

- averages for trace element contents in black shales and coals. *Int. J. Coal Geol.* 78, 135-148.
<https://doi.org/10.1016/j.coal.2009.01.002>
- Komonweeraket, K., Cetin, B., Aydilek, A.H., Benson, C.H., Edil, T.B., 2015. Effects of pH on the leaching mechanisms of elements from fly ash mixed soils. *Fuel* 140, 788-802.
<https://doi.org/10.1016/j.fuel.2014.09.068>
- Kruger, R.A., 2017. Introduction to the utilization of coal combustion products, *Coal Combustion Products (CCPs): Characteristics, Utilization and Beneficiation*. Elsevier Ltd.
<https://doi.org/10.1016/B978-0-08-100945-1.00004-6>
- Lauer, N., Vengosh, A., Dai, S., 2017. Naturally Occurring Radioactive Materials in Uranium-Rich Coals and Associated Coal Combustion Residues from China. *Environ. Sci. Technol.* 51, 13487-13493. <https://doi.org/10.1021/acs.est.7b03473>
- Lauer, N.E., Hower, J.C., Hsu-Kim, H., Taggart, R.K., Vengosh, A., 2015. Naturally Occurring Radioactive Materials in Coals and Coal Combustion Residuals in the United States. *Environ. Sci. Technol.* 49, 11227-11233. <https://doi.org/10.1021/acs.est.5b01978>
- Lieberman, N.R., Izquierdo, M., Muñoz-Quirós, C., Cohen, H., Chenery, S.R., 2020. Geochemical signature of superhigh organic sulphur Raša coals and the mobility of toxic trace elements from combustion products and polluted soils near the Plomin coal-fired power station in Croatia. *Appl. Geochemistry* 114, 104472.
<https://doi.org/10.1016/j.apgeochem.2019.104472>
- Medunić, G., Bucković, D., Crnić, A.P., Bituh, T., Gaurina Srček, V., Radošević, K., Bajramović, M., Zgorelec, Ž., 2020. Sulfur, metal(Loid)s, radioactivity, and cytotoxicity in abandoned karstic raša coal-mine discharges (the north adriatic sea). *Rud. Geol. Naft. Zb.* 35, 1-16. <https://doi.org/10.17794/rgn.2020.3.1>
- Medunić, G., Rađenović, A., Bajramović, M., Švec, M., Tomac, M., 2016. Once grand, now forgotten: What do we know about the superhigh-organic-sulphur Raša coal? *Rud. Geol. Naft. Zb.* 31, 27-45. <https://doi.org/10.17794/rgn.2016.3.3>
- Oreščanin, V., Kollar, R., Buben, K., Mikelić, I.L., Kollar, K., Kollar, M., Medunic, G., 2012. Chemical and radiological characterization of fly and bottom ash landfill of the former

sulfate pulp factory Plaški and its surroundings. J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng. 47, 1592-1606.
<https://doi.org/10.1080/10934529.2012.680780>

Oreščanin, V., Mikelić, L., Lovrenčić, I., Barišić, D., Mačefat, M.R., Pavlović, G., Lulić, S., 2006. Chemical and Radiological Profile of the Coal Ash Landfill in Kaštel Gomilica. Arch. Ind. Hyg. Toxicol. 57, 9-16.

Petrović, M., Cifrek Vidaković, Ž., Medunić, G., Fiket, Ž., 2026a. Toxicity assessment of coal ash after 50 years of weathering: the integration of multielement analysis and biological endpoints. Environ. Sci. Process. Impacts. <https://doi.org/10.1039/d5em01010a>

Petrović, M., Fiket, Ž., Medunić, G., Chakravarty, S., 2022. Mobility of metals and metalloids from SHOS coal ash and slag deposit: mineralogical and geochemical constraints. Environ. Sci. Pollut. Res. 29, 46916-46928. <https://doi.org/10.1007/s11356-022-19074-5>

Petrović, M., Grassino, A.N., Lapić, J., Djaković, S., Turk, M.F., Medunić, G., Fiket, Ž., 2026b. Changes in the mobility of oxyanions from coal combustion residues after 50 years of natural weathering. Waste Manag. 216, 115450.
<https://doi.org/10.1016/j.wasman.2026.115450>

Petrović, M., Ivanić, M., Vdović, N., Dolenec, M., Čermelj, B., Šket, P., Medunić, G., Fiket, 2023. Physicochemical and mineral characteristics of soil materials developed naturally on two ~ 50 years old coal combustion residue disposal sites in Croatia. Catena 231.
<https://doi.org/10.1016/j.catena.2023.107338>

Ribeiro, J., Silva, T.F., Mendonça Filho, J.G., Flores, D., 2014. Fly ash from coal combustion - An environmental source of organic compounds. Appl. Geochemistry 44, 103-110.
<https://doi.org/10.1016/j.apgeochem.2013.06.014>

Rudnick, R.L., Gao, S., 2014. Composition of the Continental Crust, 2nd ed, Treatise on Geochemistry. Elsevier Ltd. <https://doi.org/10.1016/B978-0-08-095975-7.00301-6>

Ruhl, L.S., Dwyer, G.S., Hsu-Kim, H., Hower, J.C., Vengosh, A., 2014. Boron and strontium isotopic characterization of coal combustion residuals: Validation of new environmental tracers. Environ. Sci. Technol. 48, 14790-14798. <https://doi.org/10.1021/es503746v>

- Savić, D., Nisic, D., Malic, N., Dragosavljevic, Z., Medenica, D., 2018. Research on power plant ash impact on the quality of soil in Kostolac and Gacko coal basins. *Minerals* 8, 1-16.
<https://doi.org/10.3390/min8020054>
- Sloot, H.A. Van Der, Meeussen, J.C.L., Garrabrants, A.C., Kosson, D.S., 2009. Review of the physical and chemical aspects of leaching assessment. *Energy Res. Cent. Netherlands*.
- Smajić, S., Kovačević, M., Pavić, D., 2021. Identification and Geovisualization of Landscape Transformation of Surface Mine Areas in the Đurđevik Coal Basin (Bosnia and Herzegovina). *Geogr. Pannonica* 25, 24-34. <https://doi.org/10.5937/gp25-29151>
- Smajic, S., Kulenovic, S., Pavic, D., 2009. Geographical consequences of the surface exploitation of coal on the area of Tuzla basin, Bosnia and Herzegovina. *Geogr. Pannonica* 13, 32-40. <https://doi.org/10.5937/geopan0902032s>
- Sun, S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geol. Soc. London, Spec. Publ.* 42, 313-345.
- Vassilev, S. V, Vassileva, C.G., 1996. Occurrence , abundance and origin of minerals in coals and coal ashes 48, 85-106.
- Vejahati, F., Xu, Z., Gupta, R., 2010. Trace elements in coal: Associations with coal and minerals and their behavior during coal utilization - A review. *Fuel* 89, 904-911.
<https://doi.org/10.1016/j.fuel.2009.06.013>
- Vengosh, A., Cowan, E.A., Coyte, R.M., Kondash, A.J., Wang, Z., Brandt, J.E., Dwyer, G.S., 2019. Evidence for unmonitored coal ash spills in Sutton Lake, North Carolina: Implications for contamination of lake ecosystems. *Sci. Total Environ.* 686, 1090-1103.
<https://doi.org/10.1016/j.scitotenv.2019.05.188>
- Vengosh, A., Coyte, R., Karr, J., Harkness, J.S., Kondash, A.J., Ruhl, L.S., Merola, R.B., Dywer, G.S., 2016. Origin of Hexavalent Chromium in Drinking Water Wells from the Piedmont Aquifers of North Carolina. *Environ. Sci. Technol. Lett.* 3, 409-414.
<https://doi.org/10.1021/acs.estlett.6b00342>
- Vengosh, A., Heumann, K.G., Juraske, S., Kasher, R., 1994. Boron Isotope Application for

Tracing Sources of Contamination in Groundwater. Environ. Sci. Technol. 28, 1968-1974.
<https://doi.org/10.1021/es00060a030>

Wang, Z., Coyte, R.M., Dwyer, G.S., Ruhl, L.S., Hsu-Kim, H., Hower, J.C., Vengosh, A., 2020. Distinction of strontium isotope ratios between water-soluble and bulk coal fly ash from the United States. Int. J. Coal Geol. 222, 103464. <https://doi.org/10.1016/j.coal.2020.103464>

Wilde, F., 2010. Water-quality sampling by the U.S. Geological Survey-Standard protocols and procedures, Fact Sheet. <https://doi.org/10.3133/fs20103121>

Wu, L., 2004. Review of 15 years of research on ecotoxicology and remediation of land contaminated by agricultural drainage sediment rich in selenium. Ecotoxicol. Environ. Saf. 57, 257-269. [https://doi.org/10.1016/S0147-6513\(03\)00064-2](https://doi.org/10.1016/S0147-6513(03)00064-2)

Zhang, X., 2014. Management of coal combustion wastes [WWW Document]. IEA Clean Coal Cent. URL [https://usea.org/sites/default/files/012014_Management of coal combustion wastes_ccc231.pdf](https://usea.org/sites/default/files/012014_Management%20of%20coal%20combustion%20wastes_ccc231.pdf) (accessed 3.4.26).