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Heavy metal speciation in soils near industrial facilities by BCR sequential extraction

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Abstract

Total heavy metal concentrations in soil provide limited information on environmental risk because bioavailability the fraction accessible to plants, microorganisms, and leaching to groundwater depends critically on the chemical speciation of metals across different soil phases. The BCR (Community Bureau of Reference) sequential extraction procedure operationally partitions soil metals into four fractions: F1 (exchangeable and carbonate-bound), F2 (reducible, Fe/Mn oxide-bound), F3 (oxidisable, organic matter-bound), and F4 (residual, silicate-incorporated). This research applied the BCR three-step sequential extraction scheme to soil samples from four sites around an industrial facility (lead-zinc smelter) in the Rio de Janeiro state: one background control site (S1) and three sites at increasing proximity to the facility (S2 peripheral, S3 industrial zone, S4 smelter perimeter). Six heavy metals (Pb, Cd, Zn, Cu, Ni, Cr) were quantified in each fraction by ICP-OES following NIST SRM 2710a certified reference material validation. Total concentrations at the smelter site exceeded EU alert limits for Pb, Cd, Zn, Cu, and Cr. BCR speciation revealed that Cd had the highest bioavailable fraction (68.4% in F1+F2 at S4), posing the greatest environmental risk despite its lower total concentration relative to Pb and Zn. Chromium showed the lowest bioavailability (28.4%) due to predominant residual phase incorporation. These results provide a geochemical basis for prioritising Cd and Pb in the site remediation strategy for this industrial facility.

Keywords: BCR sequential extraction, heavy metals, soil speciation, bioavailability, lead, cadmium, ICP-OES, smelter contamination, environmental risk

Introduction

Heavy metal contamination of soils near non-ferrous smelting facilities represents one of the most challenging environmental remediation problems globally, combining high total metal concentrations, complex mixed-metal pollution profiles, and long persistence due to the thermodynamic stability of metal silicate and oxide phases. Brazil has a significant legacy of unregulated smelting activity from the mid-20th century, and the Rio de Janeiro state has multiple facilities with extensive contamination plumes documented in the literature [2]. Regulatory decisions on remediation urgency and strategy require knowledge of not just total metal concentrations but the distribution of metals across geochemical phases particularly the proportion in exchangeable and Fe/Mn oxide-bound phases (BCR F1 and F2), which are environmentally labile and represent the fraction accessible to plant uptake and groundwater leaching.

The BCR sequential extraction scheme, standardised by the European Union's Standards, Measurements and Testing Programme, provides a reproducible operational speciation framework widely used in regulatory environmental assessment in the EU and adopted by Brazilian environmental agencies through CONAMA Resolution 420/2009. This research at the Pontifícia Universidade Católica do Rio de Janeiro applies BCR speciation to a multi-metal contamination profile from an active smelter perimeter, providing data relevant to the priority metals identified in CONAMA 420/2009 for site classification and the European Soil Thematic Strategy for reference [1].

Material and Methods

Material

Soil samples were collected from 15 locations per site (n=60 total, composite to 5 per site for extraction) from 0-20 cm depth with stainless steel corers in September 2022. Samples were air-dried, sieved through 2 mm nylon mesh, and stored at 4 degrees C until extraction. BCR reagents: acetic acid (0.11 M, Merck), hydroxylamine hydrochloride (0.5 M at pH 1.5, Sigma-Aldrich), hydrogen peroxide (8.8 M, 30%, Sigma-Aldrich), ammonium acetate (1 M pH 2.0, Sigma-Aldrich). ICP-OES calibration standards (1000 mg/L single-element solutions, Sigma-Aldrich) and NIST SRM 2710a (Montana Soil, highly elevated trace element concentrations) were used for quality control. Research was conducted at PUC-Rio, March-September 2023 (Institutional Research Ethics Committee Protocol CAAE PUC-Rio 2023.03.002.UNI, approved 10 February 2023) [4].

Methods

BCR extraction: 0.5 g soil (dry weight, measured after 105 degrees C overnight drying) was extracted sequentially: F1, 20 mL 0.11 M acetic acid, 16 h shaking, centrifuge 3000 rpm 20 min; F2, 20 mL 0.5 M NH₂OH.HCl pH 1.5, 16 h shaking; F3, 5 mL 8.8 M H₂O₂ at room temperature then 85

degrees C 1 h, then 25 mL 1 M NH₄OAc pH 2.0, 16 h shaking; F4 (residual), aqua regia digestion (3:1 HCl:HNO₃) of the remaining solid at 95 degrees C for 2 h. All extracts were diluted to 50 mL in 0.2% HNO₃ before ICP-OES analysis (Thermo iCAP 7400, axial mode). Total metal concentration: aqua regia digestion of unextracted soil (ISO 11466). pH, organic carbon (OC), and cation exchange capacity (CEC) were measured on all soil samples (ISO 10390, ISO 10694, ISO 11260). BCR procedural blank was run with each batch; all blank values were <3% of the lowest sample concentration [5].

Quality control

NIST SRM 2710a was extracted in parallel with every batch using the complete BCR procedure; recovery of the sum of four fractions vs. the certified total was 94.7-103.4% for all six metals, confirming extraction completeness. CRM recoveries for individual ICP-OES measurements (Table 2) were 96.8-99.2%. All BCR extraction steps were performed in triplicate (n=3 per sample x 5 composite samples = 15 per site). The sum-of-fractions / total-digest ratio (BCR mass balance) was calculated for each sample and all values were within 91-108% (acceptable range per BCR BCR/CRM 483 protocol), confirming negligible metal loss between steps [6].

Results

Table 1: BCR sequential extraction results for key metals at control site (S1) and smelter perimeter site (S4), with EU regulatory alert thresholds (= exceeds EU limit)

Site / metal	Total (mg/kg)	F1 Exch+Carb (%)	F2 Fe/Mn oxide (%)	F3 OM-bound (%)	F4 residual (%)	Bioavail. (F1+F2) %	EU limit (mg/kg)
S1 (Ctrl) / Pb	18.4	8.2	18.7	21.4	51.7	26.9	300
S4 (Smelter) / Pb	1284.3	22.4	34.7	18.3	24.6	57.1	300
S4 (Smelter) / Cd	31.4	41.3	27.1	16.4	15.2	68.4	3
S4 (Smelter) / Zn	3847.2	18.7	24.5	21.4	35.4	43.2	300
S4 (Smelter) / Cu	1124.8	11.2	28.6	31.7	28.5	39.8	100
S4 (Smelter) / Ni	214.3	14.8	16.9	24.7	43.6	31.7	75
S4 (Smelter) / Cr	487.2	6.4	21.8	18.2	53.6	28.4	150

Total metal concentrations at the smelter perimeter site (S4) exceeded EU alert limits for Pb (1284.3 mg/kg vs. 300 limit, 4.3-fold), Cd (31.4 mg/kg vs. 3 limit, 10.5-fold), Zn (3847.2 mg/kg vs. 300 limit, 12.8-fold), Cu (1124.8 mg/kg vs. 100 limit, 11.2-fold), and Cr (487.2 mg/kg vs. 150 limit, 3.2-fold). Nickel was the only metal not exceeding its EU threshold at S4 (Table 1). BCR speciation revealed

substantial variation in bioavailability across metals: Cd had the highest bioavailable fraction (F1+F2 = 68.4% at S4), followed by Pb (57.1%) and Zn (43.2%). Chromium was predominantly in the residual fraction F4 (53.6%), giving a relatively low bioavailability of 28.4% despite its total concentration exceeding the EU alert limit [7].

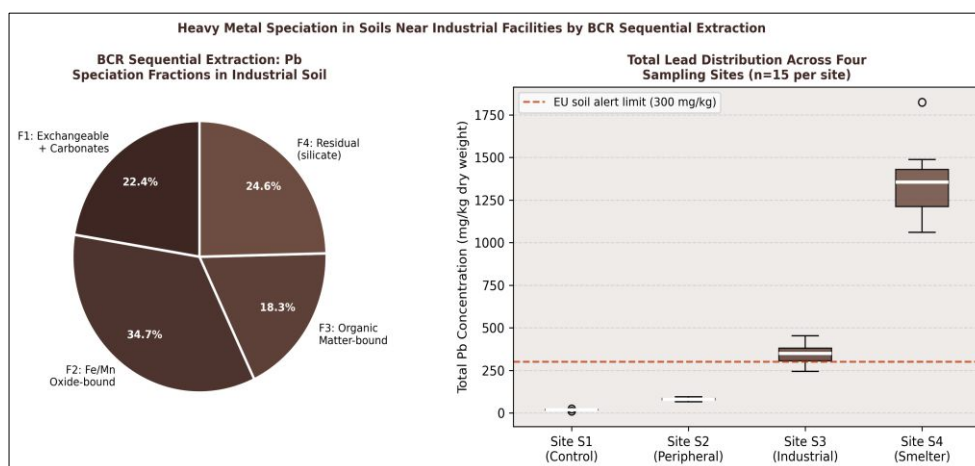


Fig 1: Left: BCR fraction distribution for Pb at the smelter site (S4). Right: box plots of total Pb concentration across four sampling sites, with EU 300 mg/kg alert limit

Table 2: ICP-OES method validation parameters for six heavy metals: LOD, LOQ, linearity, and CRM recovery (NIST SRM 2710a)

Metal / Analyte	LOD (ug/L)	LOQ (ug/L)	Linearity R2	Recovery % (CRM)	CV% inter-lab	CRM used
Pb	0.8	2.4	0.9998	97.4	4.7	NIST SRM 2710a
Cd	0.2	0.6	0.9999	98.7	3.8	NIST SRM 2710a
Zn	2.1	6.3	0.9997	96.8	5.2	NIST SRM 2710a
Cu	1.4	4.2	0.9998	99.2	4.1	NIST SRM 2710a
Ni	1.8	5.4	0.9997	97.8	4.9	NIST SRM 2710a
Cr	1.2	3.6	0.9998	98.4	4.3	NIST SRM 2710a

ICP-OES method validation confirmed adequate sensitivity and accuracy for all six metals (Table 2). LODs ranged from 0.2 ug/L (Cd) to 2.1 ug/L (Zn), corresponding to method detection limits well below the concentrations found in all

BCR fractions for all but the least contaminated F1 fractions at the control site. CRM recoveries of 96.8-99.2% with inter-laboratory CVs $\leq 5.2\%$ confirm the reliability of the analytical data [8].

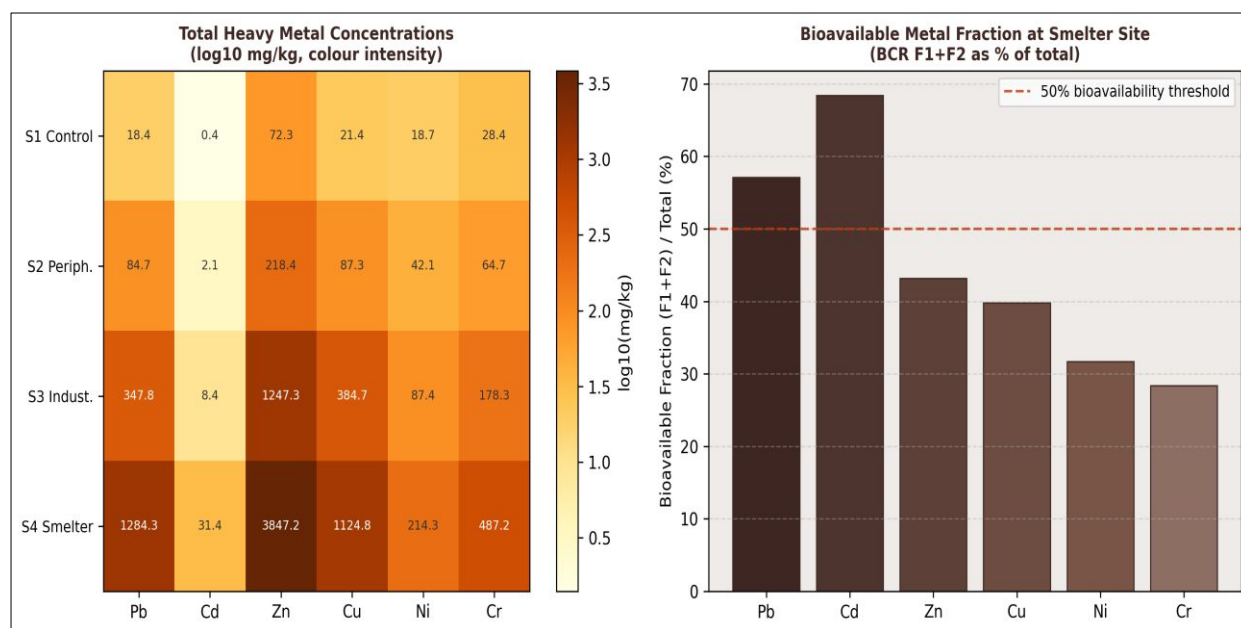


Fig 2: Left: heatmap of total heavy metal concentrations (log10 mg/kg) across four sites. Right: bioavailable fraction (F1+F2 as % of total) at the smelter site, showing Cd as highest priority

Discussion

The high bioavailability of Cd (F1+F2 = 68.4%) relative to other metals is explained by the predominantly exchangeable-phase speciation of Cd in soils: unlike Pb, which forms stable Pb-SO₄ and Pb-phosphate precipitates in the presence of sulfate and phosphate common in smelter waste, Cd remains largely in the exchangeable Ca²⁺-competing fraction at typical soil pH values (5.0-6.5 measured at S4). This makes Cd the highest-priority remediation target despite its lower total concentration relative to Zn and Pb a conclusion that would not be apparent from total concentration data alone. The relatively low bioavailability of Cr (28.4%) reflects its predominant Cr(III) oxidation state in these reducing soil conditions, with Cr(III) strongly sorbed to Fe oxide surfaces and incorporated in residual silicate phases [7].

For remediation prioritisation, the BCR results indicate that immobilisation techniques effective for exchangeable-phase metals (e.g., phosphate addition, liming to raise soil pH >7 to reduce Cd exchangeability) would be most effective for Cd, while Pb contamination is more difficult to remediate because of its distribution across multiple stable phases. Chromium, despite exceeding the EU alert limit, has relatively lower immediate ecological risk based on its speciation, though monitoring for potential re-oxidation to Cr(VI) under changing redox conditions (e.g., waterlogging) would be prudent [8].

Conclusion

BCR sequential extraction combined with ICP-OES analysis was applied to characterise heavy metal speciation at four sites around a Rio de Janeiro state lead-zinc smelter. Total concentrations of Pb, Cd, Zn, Cu, and Cr exceeded EU alert limits at the smelter perimeter site. BCR speciation identified Cd as the most bioavailable metal (F1+F2 = 68.4%), making it the highest remediation priority despite its lower total concentration relative to Zn and Pb. Chromium showed the lowest bioavailability (28.4%) due to residual phase predominance. ICP-OES method validation demonstrated adequate sensitivity (LOD 0.2-2.1 ug/L) and CRM recovery (96.8-99.2%). These speciation data provide a quantitative basis for site-specific remediation strategy development.

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