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Cadmium contamination of agricultural soils and crops resulting from sphalerite weathering

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Abstract

The biogeochemistry and bioavailability of cadmium, released during sphalerite weathering in soils, were investigated under contrasting agricultural scenarios to assess health risks associated with sphalerite dust transport to productive soils from mining.

Laboratory experiments (365 d) on temperate and sub-tropical soils amended with sphalerite (< 63 μm, 0.92 wt.% Cd) showed continuous, slow dissolution (0.6 – 1.2 % y^{-1}). Wheat grown in spiked temperate soil accumulated ≈ 38 % (29 μmol kg^{-1}) of the liberated Cd, exceeding food safety limits. In contrast, rice grown in flooded sub-tropical soil accumulated far less Cd (0.60 μmol kg^{-1}) due to neutral soil pH and Cd bioavailability was possibly also controlled by secondary sulfide formation. The results demonstrate long-term release of Cd to soil porewaters during sphalerite weathering. Under oxic conditions, Cd may be sufficiently bioavailable to contaminate crops destined for human consumption; however flooded rice production limits the impact of sphalerite contamination.

Capsule:

Sphalerite dissolves steadily in oxic agricultural soils and can release highly bioavailable Cd, which may contaminate food crops destined for human consumption.

Keywords: metals; sulfide weathering; human health; rice; risk assessment

Introduction

Cadmium (Cd) is considerably environmentally mobile, bioavailable and toxic to humans (Smolders and Mertens, 2013) and there are linkages between mineral exploitation, Cd soil contamination and human health hazards, for example the contamination of soils by Japan's Jinzu River and its association with the debilitating 'itai-itai' disease (Ishihara et al., 2001). In the region bordering Guangdong and Hunan provinces (China), decades of metal production were shown to have contaminated river sediments and agricultural soils (e.g. Chenzhou) as far as 60 km from the source (> 9 μmol Cd kg^{-1}) (Limei et al., 2008) and inhabitants are considered at risk of chronic health effects from consuming locally grown rice and vegetables (H. Zhao et al., 2012; Zhuang et al., 2009). Crop safety is a concern because the primary human intake routes for Cd are tobacco smoking and diet (Järup, 2003), both of which link human exposure to soil contamination. Chronic

toxicity may arise because Cd has a long biological half-life (15 – 30 years) and accumulates in the body, resulting in kidney disease, osteoporosis, lung and prostate cancer and endocrine disruption (Henson and Chedrese, 2004; Järup, 2003).

Mining and ore processing produces fine mineral particles enriched with potentially toxic metals and metalloids (e.g. As, Cd, Hg). These particles are vulnerable to fluvial (Miller et al., 2004; Simmons et al., 2005) and aeolian (Castillo et al., 2013; Zota et al., 2009) transport, for example through erosion from exposed tailings, so they can behave as vectors for toxic elements. Several investigators have reported the spatial distribution and concentration of toxic metals in soils affected by mineral exploitation, but less is understood about how transported mineral particles influence soil quality in terms of the biogeochemical cycling of toxic metals and the risk they pose to human health through crop contamination.

Commonly exploited sulfide ores (e.g. sphalerite) are vulnerable to oxidative and acid-promoted dissolution under moist, oxic surface conditions and may release metals into soil porewater and surface waters, providing a source of potentially toxic metals for plant uptake. This situation is most likely to affect communities in developing and rapidly industrialising countries, where environmental regulations may be either weak or poorly enforced and soils impacted by mining may be used for agriculture (Miller et al., 2004; Zhuang et al., 2009).

Sphalerite (ZnS), the primary geologic source of zinc (Zn) and Cd, occurs commonly around the world. Sphalerite is notable for its tendency for isomorphic substitution of Zn by other metals and Cd is generally present in solid solution at 0.2–1 % (Smolders and Mertens, 2013). The alteration mechanisms proposed for sphalerite include oxidative dissolution, either by molecular oxygen (Eq. 1) or Fe(III) (Eq. 2), and acid-promoted dissolution (Eq. 3) (Heidel et al., 2011). Cd is released from solid solution during sphalerite dissolution (Stanton et al., 2008).

$$ZnS + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-} \quad \text{(Eq. 1)}$$

$$ZnS + 8Fe^{3+} + 4H_2O \rightarrow Zn^{2+} + 8Fe^{2+} + SO_4^{2-} + 8H^+ \quad \text{(Eq. 2)}$$

$$ZnS + 2H^+ \rightarrow Zn^{2+} + H_2S_{(aq)} \quad \text{(Eq. 3)}$$

Laboratory experiments in aqueous media (Acero et al., 2007; Stanton et al., 2008) showed that sphalerite dissolution follows a first order reaction with respect to $[H^+]$ (pH 1 – 4.2); the rate increases with temperature (25 – 70 ˚C) and is independent of dissolved oxygen concentrations (6.3 – 270 μM $_dO_2$), suggesting that the process described by Eq. 1 is of minimal importance. Apart from differences in experimental design, the iron (Fe) content of the sphalerite is also proposed to influence the dissolution rate (Weisener et al., 2003).

The aim of this study was to determine the rate of sphalerite dissolution and Cd release in soils of contrasting geologic and climatic provenance, and the bioavailability of the Cd to key crops under relevant agricultural scenarios.

Methods

Investigative approach

This study comprised of: (1) Laboratory batch incubations of sphalerite-spiked (0.1 % m/m) soils to determine sphalerite dissolution behaviour and (2) Phytoavailability experiments where *Triticum aestivum* (spring wheat) and *Oryza sativa* (rice) were grown in samples of the temperate and flooded sub-tropical soils, respectively, to evaluate the bioavailability of Cd released from sphalerite.

Reagents and materials

Reagents were of analytical grade or higher (ROMIL, Sigma-Aldrich, Fisher) and ultra-high purity water (UHP, ≥ 18.2 MΩ cm^{-1}) was used for all experiments. Specimen sphalerite was obtained from a private collection (Richard Tayler Minerals, Cobham, UK).

Soil and mineral sampling, preparation and characterisation

A temperate soil (inceptisol from the Tamar Valley, Cornwall, United Kingdom) was sampled from low-intensity grassland, used only for haymaking for the past decade. The sub-tropical soil (The University of Hong Kong Kadoorie Centre) comprised sub-surface oxisol from secondary forest and horticultural soil, in equal parts by volume.

Experimental soils (< 2 mm, dried at 40 ˚C) were fertilised with dried (50 ˚C, ≥ 72 h) well-rotted animal dung (milled and sieved to < 2 mm) at 10 % m/m, bringing the organic matter content to the upper range for productive soils. Sphalerite was finely ground, sieved (ball mill, < 63 μm) and stored in a desiccating, N_2-purged atmosphere (see Laboratory batch incubation experiments). The < 63 μm fraction represents clay and silt size particles, which are thought to account for the majority of fugitive dust mass flux (Kon et al., 2007).

Experimental soils were characterised using standard methods (Carter and Gregorich, 2007): total sulfur (S), nitrogen, organic/inorganic carbon (NC2500 elemental analyser, Carlo Erba), eCEC, organic matter, texture and pH (United States Environmental Protection Agency, 2004). For elemental analyses, soils and sphalerite were microwave-digested (MarsXpress, CEM) in 50 % v/v 1:3 HNO_3:HCl. Bulk mineralogy was evaluated using powder X-ray diffraction (XRD) (Cu-Kα, 2-70˚ 2θ, 0.02˚/S, D5000, Siemens). The sphalerite was also examined using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) (JSM-7100F, JEOL/Aztec EDS, Oxford Instruments).

Laboratory batch incubation experiments

Batch incubations (≤ 12 months) were conducted in polypropylene beakers using 100 g aliquots of the experimental soils. The soils were either spiked with 0.1 g ground sphalerite or left as controls (no ZnS) and then their moisture was maintained gravimetrically at 75 % field capacity. Triplicate incubation batches were sacrificed and analysed after 0 hours, 7, 30, 90, 180, 270 and 365 days under laboratory conditions. Sacrificed soils were freeze-dried, homogenized and sub-sampled for analyses. Soluble major ions (NO_3^-, SO_4^{2-}), cation-exchangeable Cd/Zn and EDTA-extractable Cd/Zn were extracted in UHP water (1:5), 0.01 M $CaCl_2$ (1:5) and 0.1 M EDTA (1:30, pH 7.5),

respectively (2 h agitation, reciprocating shaker). Extracts were centrifuged, filtered (0.45 μm) and preserved until analysis (freezing, acidification or refrigeration).

An abiotic control experiment, analogous to the first 30 days of the batch incubation experiments, was performed using sterile soils. Soils were fractionally sterilised to ensure overkill of both microorganisms and endospores, using three cycles of stem heating (97 ± 2 ˚C, 2 h) and overnight incubated (37 ± 1 ˚C). The incubations were performed in autoclaved (121 ˚C, 1 h), foam-bunged (tortuous path filter) glass conical flasks. Sterility was maintained by using only heat-sterilised (≥ 250 ˚C) implements, filter-sterilised (0.22 μm) water and observing best practise for sterile handling.

Phytoavailability experiments

Larger (2 kg), analogous, soil incubations were established in polypropylene pots and maintained in parallel with those of the batch experiment. After 180 days, 10-day wheat seedlings (350 seeds m^{-2}) were transplanted into the temperate soils. The plants were matured to ripeness (112 days) under glasshouse conditions (24 ± 3 ˚C, 66 ± 3 % RH) and then the stems and ears were rinsed (≥ 5 times) with water and freeze-dried. The tissues were comminuted (food processor) and 0.5 ± 0.01 g (n = 3) of tissue was microwave-digested in 10 mL HNO_3 (50 % v/v conc.).

The sub-tropical soils received 14-day rice seedlings, were flooded with 6 cm standing water and plants matured (152 days) inside a growth chamber (Fitotron PG660, Sanyo; 16 h light, 8 h dark at 27 ˚C, followed by 12 h light, 12 h dark at 24 ˚C) and then treated as per the wheat. The drained, saturated soils were core-sampled (∅ 2.5 cm, n = 5) inside an anoxic chamber (Coy laboratory products). Bulked cores were sub-sampled for aqueous extraction, capped and sealed with Parafilm and then extracted as previously described (see Laboratory batch incubation experiments). Dissolved sulfide was determined in soil water extracts (in an anoxic chamber) using the methylene blue method (Cline, 1969). Solid-phase Fe speciation and acid-volatile sulfide were determined after Lovley and Phillips (1986) and Allen et al. (1993), respectively. Porewater pH and Eh were determined in the water that collected in the core voids.

Analytical techniques

Anion, Fe (II) and dissolved sulfide (S^{2-}) concentrations were determined using ion chromatography (DX-500, Dionex Corporation) or spectrophotometry (8453 UV-Vis, Agilent), respectively. Aqueous metal concentrations were determined using ICP-OES (725-ES, Varian) and ICP-MS (X-series 2 + Collision Cell, Thermo Scientific). Half-cell redox potentials (Hanna HI9025, BDR Gelplas ORP) were corrected against ZoBell's solution. Certified reference materials (BCR 320R channel sediment, IRMM 804 rice flour and PACS-1 marine sediment) were used to verify the satisfactory accuracy and performance of the methods (Table S1). Statistical analyses were performed using the Sigmaplot 12 software package (Systat Software).

Results and discussion

Experimental soil and sphalerite characterisation

Both experimental soils were of circum-neutral pH, rich in organic matter, with a similar moderate eCEC (Table 1). Both soils were Fe rich (5.5 – 6.3 % Fe m/m) but the sub-tropical soil contained 7 times less manganese, more aluminium (6.2 % vs. 3.9 %) and a lower proportion of poorly crystalline Fe and aluminium oxides/hydroxides (factor of 2 – 4). Both soils had similar S, Zn and Cd concentrations, which fell within (Cd) or just above (Zn) the range expected for uncontaminated soils (Mertens and Smolders, 2013). The main crystalline phases were clinochlore ($(Mg,Fe^{2+})_5Si_3Al_2O_{10}(OH)_8$), muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), illite ($(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$) and quartz ($SiO_2$) in the temperate soil (sandy loam) and kaolinite ($Al_2Si_2O_5(OH)_4$), orthoclase ($KAlSi_3O_8$), microcline ($KAlSi_3O_8$), gibbsite ($Al(OH)_3$) and quartz in the sub-tropical soil (silt loam).

Elemental (wet) analyses and SEM-EDS examination showed that the experimental mineral consisted of ZnS ($Zn_{1.01}S_{0.99}$) with 0.3 % m/m Fe and 0.9 % m/m Cd. An XRD analysis and reference to mineral databases also confirmed the crystalline structure to be that of sphalerite and not the sphalerite polymorph, wurtzite (Figure S1).

Soil biogeochemical conditions throughout oxic incubations

The pH was not controlled during the experiment and a notable decrease was observed in the pH of both temperate (- 1.05 pH units) and sub-tropical (- 0.43 pH units) soils during the initial 30 days of incubation. After 30 days, the temperate and sub-tropical soils fluctuated around pH 5.53 ± 0.13 and pH 6.40 ± 0.08, respectively. Acid buffering experiments, performed after Magdoff and Bartlett (1985), demonstrated that the sub-tropical soil had significantly greater buffering capacity (≈ 43 % at neutral-acid pH) than the temperate soil, which was devoid of carbonate, partly explaining the disparate pH decline in the early stages of the experiment (Figure S2).

Data from an abiotic control experiment covering the initial 30 days incubation of the temperate soil (Figure 1) indicate that the pH decline was mediated by soil microbiota, and was coupled with sharp increases in nitrate and sulfate concentrations, reflecting ammonium and sulfur-oxidising bacterial activity. Both can contribute to soil acidity especially if percolation is prevented, as was the case in these experiments.

[Approximate location for Figure 1]

Sphalerite dissolution had a negligible effect on soil pH, since control and spiked incubation soil pH generally differed by < 0.1 pH unit throughout the batch incubations. Redox potential (Eh) was determined in soil extracts, which were performed as for the pH determinations (see Soil and mineral sampling, preparation and characterisation). The data indicated consistently oxic conditions (350 – 400 mV) throughout the experiment.

Geochemical conditions in sub-tropical soil during rice cultivation

After rice cultivation (180 days oxic, 152 days flooded) the sub-tropical soils had attained neutral pH (7.01 ± 0.08) and moderately reducing conditions (Eh - 23 ± 6 mV) (Figure 2 b). Flooded paddy soils often attain neutral pH as many important reduction reactions, e.g. Fe(III) > Fe(II), consume free protons (Ponnamperuma, 1972).

228 [Approximate location for Figure 2.]

229 Redox indicators and $CaCl_2$-extractable metal concentrations suggest that the
230 availability of Cd in porewater, and therefore to the rice plants, was limited by the
231 formation of secondary Fe/Cd/Zn sulfide phases. Depleted soluble nitrate (> 99 %) and
232 sulfate (≥ 94 %) (Figure 2 a), together with a significant proportion of acid-extractable
233 Fe(II) (66 ± 10 %), indicated the influence of nitrate, Fe and sulfate-reducing anaerobes
234 (Inglett et al., 2005). No dissolved sulfide was detected in soil extracts but acid-volatile
235 sulfide (AVS) was found in the reduced control soils (200 ± 16 μmol S^{2-} kg^{-1}), providing
236 evidence for the formation of amorphous secondary sulfides (e.g. greigite, mackinawite).
237 An AVS determination was not possible in the spiked soils because sphalerite itself is
238 acid-volatile. Concurrent with sulfide formation, net (control-corrected) $CaCl_2$-
239 extractable Cd and Zn concentrations were considerably lower in the reduced soils,
240 compared with their oxic equivalents (Figure 2 c), and net EDTA-extractable Cd (Cd_{net})
241 concentrations also fell from 0.23 ± 0.02 to 0.12 ± 0.02 μmol kg^{-1}. Much of the depleted
242 sulfate was unaccounted for by AVS formation, suggesting other contributory
243 mechanisms. There was no olfactory evidence for $H_2S_{(g)}$ evolution and sulfate adsorption
244 is minimal in pH neutral soils (Scherer, 2009), excluding adsorption effects. Other
245 potential mechanisms for the observed sulfate and extractable Cd depletion were the
246 formation of non-acid-volatile sulfides (e.g. pyrite, greenockite) and plant uptake,
247 respectively, and these are given further consideration in the section 'Uptake by paddy
248 rice grown in sub-tropical soil'.

249 **Sphalerite dissolution**

250 Cd and Zn extraction protocols

251 The 0.01 M $CaCl_2$ protocol was applied to provide a 'snapshot' reflecting plant-available
252 concentrations at a given time (Meers et al., 2007). The 0.1 M EDTA extraction protocol
253 was selected because it effectively scavenges metal cations from solid soil phases (Lo
254 and Yang, 1999; Schecher, 2001), providing an indication of the total Cd and Zn release
255 from sphalerite and total plant-available concentrations over a longer timescale.

Cd and Zn release trends

The clear distinction between Cd concentrations obtained from control and spiked incubations (Figure 3a/a_i & b/b_i) evidences the release of Cd from sphalerite dissolution. This divergence can be seen after 7 days incubation of both the temperate and sub-tropical soils. Cd concentrations extracted from control incubations were relatively constant throughout the incubation duration, which demonstrates that Cd extractability was not affected by changes in soil pH during the oxic incubations.

[Approximate location for Figure 3.]

Extractable Zn concentrations (Figure 3c/c_i & d/d_i) were considerably higher than Cd concentrations, reflecting the molar Zn:Cd ratio in the sphalerite. In the temperate soil (Figure 3c & d), comparison with the control shows that Zn was released from sphalerite with increasing incubation time and, as with the Cd, the release curve did not exhibit a change in slope over the last 180 days of the experiment. In the temperate control soils, Zn concentrations from the beginning and the end of the experiment did not significantly differ ($p = 0.05$).

The $CaCl_2$-extractable Zn concentrations in spiked sub-tropical soils were higher than in the control soil (Figure 3c_i), most notably during the last 180 days of the experiment; however the $CaCl_2$-extractable concentrations in control soils varied significantly ($p > 0.05$, ANOVA) during incubation. The EDTA-extractable Zn concentrations in spiked and control sub-tropical soils (Figure 3d_i) fluctuated throughout the incubation time and there was no significant difference between concentrations at the beginning and end of the experiment ($p < 0.05$, ANOVA). Comparison of the Zn release trends with those of Cd, which were linear with incubation time, suggest that Zn released from the sphalerite was in equilibrium with another solid phase and recalcitrant to EDTA complexation. The net release indicated by $CaCl_2$-extractable concentrations (Figure 3c_i) was masked in the EDTA-extractable data, as the EDTA extraction was not sensitive to minor variations in Zn lability.

Dissolution rate, trends and limits

EDTA-extractable Cd concentrations were the most suitable indicator of the extent and rate of sphalerite dissolution, in this case meaning alteration from the original sulfide species. Unlike Zn, Cd release trends were clear and consistent (concentration vs. time) in both experimental soils. Additionally, Cd release is directly correlated with sphalerite dissolution rate (Stanton et al., 2008) and EDTA dissolves sphalerite oxidation products but not the sulfide itself (Rumball and Richmond, 1996), as confirmed by preliminary experiments (data not shown).

Net Cd release (Cd_{net}) from the sphalerite was calculated by subtracting EDTA-extractable concentrations obtained from control incubations from those obtained from the respective spiked incubations. The Cd_{net} data were used to estimate the percentage sphalerite dissolved at each incubation time point (Table 2). The relationship between Cd_{net} and incubation duration was linear ($R^2 \geq 0.96$) for both temperate and sub-tropical soils, indicating a constant rate of Cd release, and therefore sphalerite dissolution, throughout the experiments. Several studies on sphalerite dissolution in aqueous solution showed that dissolution rates decline during the initial few hundred hours of exposure and then attain an apparent steady state (Acero et al., 2007; Stanton et al., 2008; Weisener et al., 2003). It was proposed that this change is concurrent with the formation of Zn-deficient, polysulfide and elemental S product layers on sphalerite particles, and a shift from reaction rate-limited dissolution to dissolution limited by reagent diffusion (i.e. H_3O^+, O_2, Zn^{2+}, Cd^{2+} and/or S) through those product layers (Weisener et al., 2003). Acero et al. (2007) argued that, because steady state was attained, the layers were not passivating and initially high dissolution rates probably resulted from micro-crystals and oxidised phases on the pre-exposure sphalerite surfaces. In this study the slower dissolution rate remained constant over long durations (hundreds of days), regardless of whether these product layers are porous, and therefore not diffusion limiting, or whether they are in equilibrium with bulk solution, and therefore do not accumulate.

The data from this study are consistent with slow steady-state dissolution. The constant Cd release excludes the significant formation of stable secondary Cd phases, which

would have produced declining $CaCl_2$ and EDTA-extractable concentrations with increasing incubation duration by sequestering Cd^{2+} from the porewater. The absence of secondary phases was evidenced by SEM-EDS examination of sphalerite platelets exposed to field conditions for 2 years. Full details of this method are provided in Robson et al. (2013).

Dissolution rates observed at 365 days are indicative of the annual average, approximately 1 and 0.5 μmol Cd g^{-1} ZnS a^{-1} for the temperate and sub-tropical soils, respectively. Accounting for the reducing surface area of the given mass of dissolving sphalerite and assuming proportionality between dissolution rate and surface area (shrinking particle model) (Pradhan et al., 2010; Safari et al., 2009), the half-life of the sphalerite was estimated to be 50 and 94 years in the temperate and sub-tropical soils, respectively.

The slower dissolution rates observed in the sub-tropical soil were attributed to the prevailing soil pH. Based on kinetics data from Acero et al. (2007), a change in porewater pH from 5.53 (temperate soil) to 6.40 (sub-tropical soil) would result in dissolution rates being reduced by 66 %; therefore pH is likely to be the most significant factor affecting sphalerite dissolution in oxic soils. The shift to neutral pH observed in flooded sub-tropical soils (from pH 6.40) is associated with a further 53 % reduction in the dissolution rate, based on pH alone.

Cd uptake by crops

Uptake by wheat grown in temperate soil

Grain and stem Cd concentrations in the spring wheat grown in the sphalerite-spiked temperate soil were considerably higher (by a factor of ≥ 75) than in plants grown in the control soil (Figure 4). The wheat grain contained 29.0 ± 3.3 μmol Cd kg^{-1}, around 8 times higher than the international food safety limit of 3.6 μmol kg^{-1} (FAO/WHO, 2006).

[Approximate location for Figure 4.]

The data suggest that high Cd concentrations in grain produced from the spiked soil were proportional to the magnitude of the bioavailable Cd pool in that soil. Stem-to-grain transfer factors (TF) were the same for plants grown in spiked and control soil; therefore the translocation rate was independent of the phytoaccessible Cd concentration in the soil and the stem Cd concentration (Figure 4).

Stem bioconcentration factors (BCF), based on Cd_{net} values, for plants grown in spiked soils were 25 times higher than for those grown in control soils. The probable explanation for this observation is soil 'ageing'. Cd is generally regarded as exhibiting minimal ageing effect (Smolders and Mertens, 2013) but Hamon et al. (1998) demonstrated that around 1 % of soil Cd could be rendered unavailable for plant uptake per year of soil residence time. Ageing may have rendered the antecedent Cd in the soils far less phytoavailable than the Cd recently introduced by sphalerite dissolution.

Uptake by paddy rice grown in sub-tropical soil

Rice stem and grain Cd concentrations of plants grown in spiked soils were 3 – 4 times higher than in control soil plants (Figure 4). Although the plants were contaminated by the sphalerite, the edible tissue concentration (0.597 ± 0.019 μmol Cd kg^{-1}) was well below applicable Chinese (1.78 μmol Cd kg^{-1}) and international (3.56 μmol Cd kg^{-1}) food safety limits (FAO/WHO, 2006; USDA Foreign Agriculture Service, 2010). For comparison, Cd concentrations in the wheat (spiked soil) were higher than those for rice by a factor of 49 in seeds and 24 in stems. Given that the rate of sphalerite dissolution in the experimental soils only varied by a factor of 2, the tissue concentrations illustrate significant differences in the Cd bioavailability and/or uptake behaviour in the rice and wheat soil-plant systems.

The data suggest that, all factors being equal, the rice had a propensity for Cd uptake similar to or greater than the wheat. In control soils, the wheat and rice stem concentrations were similar (0.74 – 0.85 μmol kg^{-1} Cd) and the rice stem BCF was much higher than for the wheat (Figure 4). Also, the rice TF increased in spiked soils (+ 53 %), indicating that the plants responded to higher Cd availability by enhancing stem-to-grain translocation. In light of this apparent propensity for uptake, the relatively low

rice tissue Cd concentrations suggest that decreased Cd availability in the paddy soil porewater limited uptake. This proposition is supported by $CaCl_2$-extractable Cd concentrations that were below the detection limit (Figure 2 c), Cd_{net} concentrations that were reduced by 49 % (versus oxic incubation) and stem BCF values that were the same (6.36 – 6.40) in spiked and control soils (i.e. equal bioavailability).

Soil-to-rice Cd transfer was examined to determine if this could explain the depleted extractable Cd concentrations obtained from the sub-tropical soils (see Geochemical conditions in sub-tropical soil during rice cultivation). The plant roots were not analysed but their biomass is always much smaller than the stem biomass and therefore assuming equal contribution by the root and stems provided a conservative estimate (Kibria and Ahmed, 2006). Although the neutral soil pH and plant uptake might explain the depletion of $CaCl_2$-extractable Cd, these factors cannot entirely explain the decreased Cd_{net}. Firstly the EDTA extraction, from which Cd_{net} is derived, would have been insensitive to the shift towards neutral soil pH. Secondly, after considering the estimated total Cd uptake by rice, a 33 % decrease in Cd_{net} still remained unaccounted for. Therefore it is likely that the formation of non-acid-volatile secondary sulfides (see Geochemical conditions in sub-tropical soil during rice cultivation) contributed to the low bioavailability and rice uptake of Cd in this study (de Livera et al., 2011).

Lowland rice is traditionally grown under near-constant standing water; however increasing global population and freshwater demand have catalysed the adoption of new agricultural practises such as 'system of rice intensification' (SRI), a set of management principles that discourage flooded agriculture (Africare et al., 2010; L. Zhao et al., 2010). A shift towards more oxic soil management will remove the protective biogeochemical conditions afforded by soil flooding and enhance the bioavailability of Cd in soils.

Conclusions

Sphalerite exhibits slow, steady dissolution behaviour in oxic agricultural soils developed under contrasting geoclimatic conditions and is accompanied by the release of the guest element Cd. Sphalerite contamination impacts soil quality for decades to

centuries, long after its introduction to soils ceases. The liberated Cd is highly bioavailable under oxic conditions, as indicated by *Triticum aestivum*, and has the potential to contaminate crops and pose a human health hazard. Data from *Oryza sativa* indicate that flooded rice production can limit these impacts by neutralising soil pH and possibly by providing sulfate-reducing conditions, under which secondary Cd sulfides can form. The recently publicised advantages of ending a reliance upon flooded agriculture (increased yields, reduced water consumption) suggests that growing rice under more oxic conditions will increase in popularity. Adopters of these new practices working Cd or sphalerite-impacted soil will sacrifice the protective biogeochemical conditions afforded by flooding, increasing the risk of producing contaminated food.

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542 Table 1: **Characterisation data for the temperate and sub-tropical experimental**
543 **soils.** Uncertainties reported as ± 1 standard deviation (n = 5). eCEC = Effective cation
544 exchange capacity; LOI = Organic matter content, determined by loss on ignition.

	Temperate soil	Sub-tropical soil
pH	6.58 ± 0.07	6.83 ± 0.12
eCEC (cmol+ kg^{-1})	14.6 ± 0.3	13.1 ± 0.2
$C_{organic}$ (% m/m)	5.57 ± 0.20	4.62 ± 0.06
$C_{inorganic}$ (% m/m)	< LOD	0.47 ± 0.37
LOI (% m/m)	12.3 ± 0.5	13.1 ± 0.7
Al (mol kg^{-1})	1.44 ± 0.11	2.32 ± 0.11
$Al_{oxalate}$ (mol kg^{-1})	0.121 ± 0.001	0.0975 ± 0.0018
Fe (mol kg^{-1})	0.973 ± 0.018	1.13 ± 0.03
$Fe_{oxalate}$ (mol kg^{-1})	0.202 ± 0.002	0.0602 ± 0.0014
Mn (mmol kg^{-1})	37.6 ± 3.2	5.25 ± 0.31
S (mmol kg^{-1})	17.0 ± 2.2	17.1 ± 1.7
Cd (µmol kg^{-1})	2.70 ± 0.55	2.67 ± 0.27
Zn (mmol kg^{-1})	2.05 ± 0.14	2.13 ± 0.17

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547 Table 2: **Net Cd release (Cd_{net}) and percentage sphalerite dissolution** determined
548 after 7 – 365 days incubation in both temperate and sub-tropical soils. Uncertainties are
549 reported as ± 1 standard deviation (n = 3). Asterisks indicate insignificant differences
550 between the spiked and control incubation values.

Days	Temperate soil		Sub-tropical soil	
	Cd_{net} (nmol Cd g^{-1} ZnS)	**% dissolution**	**Cd_{net} (nmol Cd g^{-1} ZnS)**	**% dissolution**
7	18.2 ± 15.4	0.02 ± 0.02	*	*
30	76.9 ± 21.1	0.09 ± 0.03	73.6 ± 57	0.09 ± 0.07
90	261 ± 38	0.32 ± 0.05	148 ± 24	0.18 ± 0.03
180	475 ± 223	0.58 ± 0.27	228 ± 24	0.28 ± 0.03
270	756 ± 60	0.93 ± 0.07	425 ± 18	0.52 ± 0.02
365	998 ± 212	1.23 ± 0.26	464 ± 27	0.57 ± 0.03

551

Figure 1: **Influence of microbiota upon soil pH:** Sulfate, pH (a) and nitrate (b) in biotic and abiotic control incubations of the temperate soil. Uncertainties are reported as ± 1 standard deviation (n = 3).

Figure 2: **Redox indicators and metal availability in flooded paddy soils:** (a) SO_4^{2-} and NO_3^-, (b) pH and Eh and (c) $CaCl_2$-extractable Zn/Cd in the sub-tropical soil (180-365 days), under both oxic (filled symbols) and anoxic (hollow symbols) conditions. Uncertainties are reported as ± 1 standard deviation (n = 3).

Figure 3: **Cd and Zn release during sphalerite weathering:** $CaCl_2$-extractable and EDTA-extractable Cd (a/b_{I-II}) and Zn (a/b_{III-IV}) concentrations in temperate (a_{I-IV}) and sub-tropical (b_{I-IV}) experimental soils. Uncertainties are reported as ± 1 standard deviation (n = 3). Note that all Cd concentrations were below the detection limit (0.002 µmol Cd kg^{-1}) until day 180 of sub-tropical soil incubation (b_I). Asterisks denote statistically significant ($p > 0.05$, ANOVA) differences between spiked and control soils.

Figure 4: **Plant uptake of cadmium:** total Cd tissue concentrations, stem bioconcentration factors (BCF) based upon Cd_{net} concentrations and stem-to-grain transfer factors (TF) for spring wheat grown in the temperate experimental soil and rice in the flooded sub-tropical experimental soil. Uncertainties based on ± 1 standard deviation.

571 Table S1: Certified and determined concentrations obtained for certified reference
572 materials. Uncertainties are reported as ± 1 standard deviation (n = 5).

Χερτιφιεδ ματεριαλ	Παραμετερσ	Χερτιφιεδ	Δετερμινεδ
IRMM 804 Rice flour	Cd (μmol kg^{-1})	14.3 ± 0.6	14.3 ± 1.1
	Zn (μmol kg^{-1})	353 ± 29	360 ± 32
BCR 320R Channel Sediment	Cd (μmol kg^{-1})	23.5 ± 1.6	21.1 ± 0.2
	Zn (mmol kg^{-1})	4.88 ± 0.31	4.85 ± 0.19

573
574
575
576 Figure S1: **XRD characterisation:** X-ray diffractogram obtained for the experimental
577 sphalerite used in this study, plotted together with an exemplar pattern for wurtzite.
578
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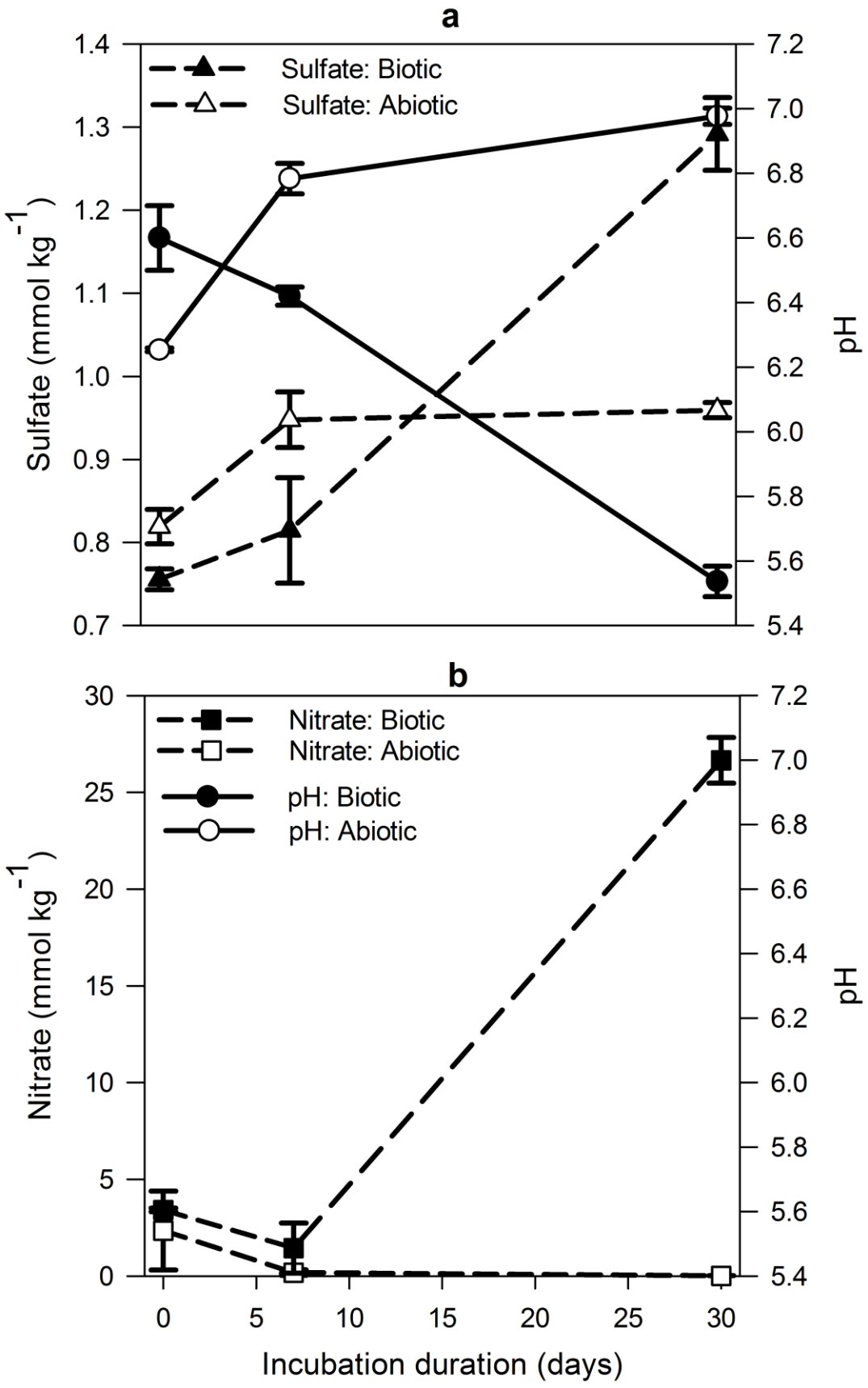
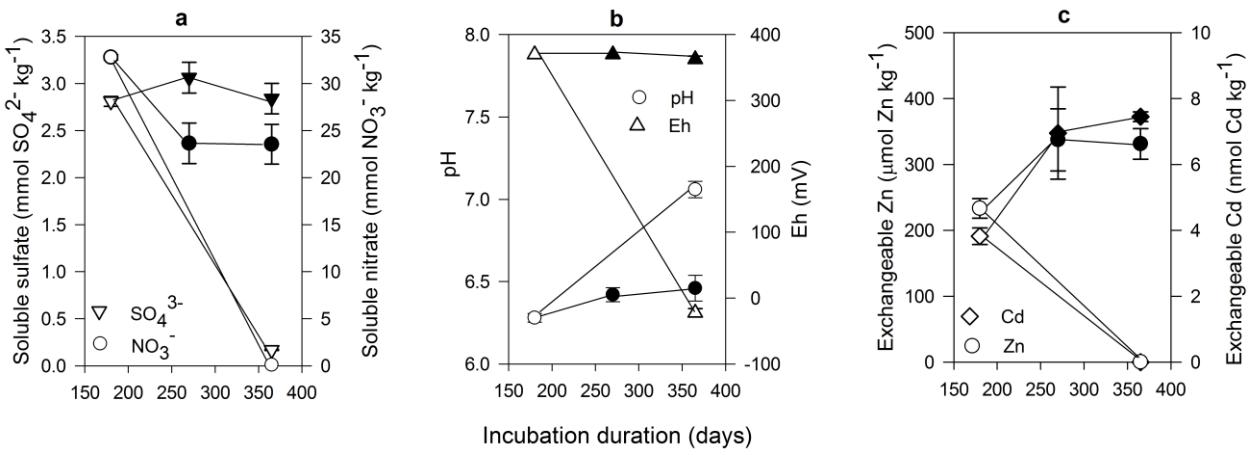
580 Figure S2: **Soil pH buffering curves for temperate and sub-tropical experimental**
581 **soils:** The curves were produced by adding variable concentrations of H_2SO_4 (x-axis) to
582 the soils and determining slurry pH after overnight equilibration (y-axis).
583


a
Sulfate: Biotic
Sulfate: Abiotic
Sulfate (mmol kg-1)
pH
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
b
Nitrate: Biotic
Nitrate: Abiotic
pH: Biotic
pH: Abiotic
Nitrate (mmol kg-1)
pH
30
25
20
15
10
5
0
0
5
10
15
20
25
30
Incubation duration (days)

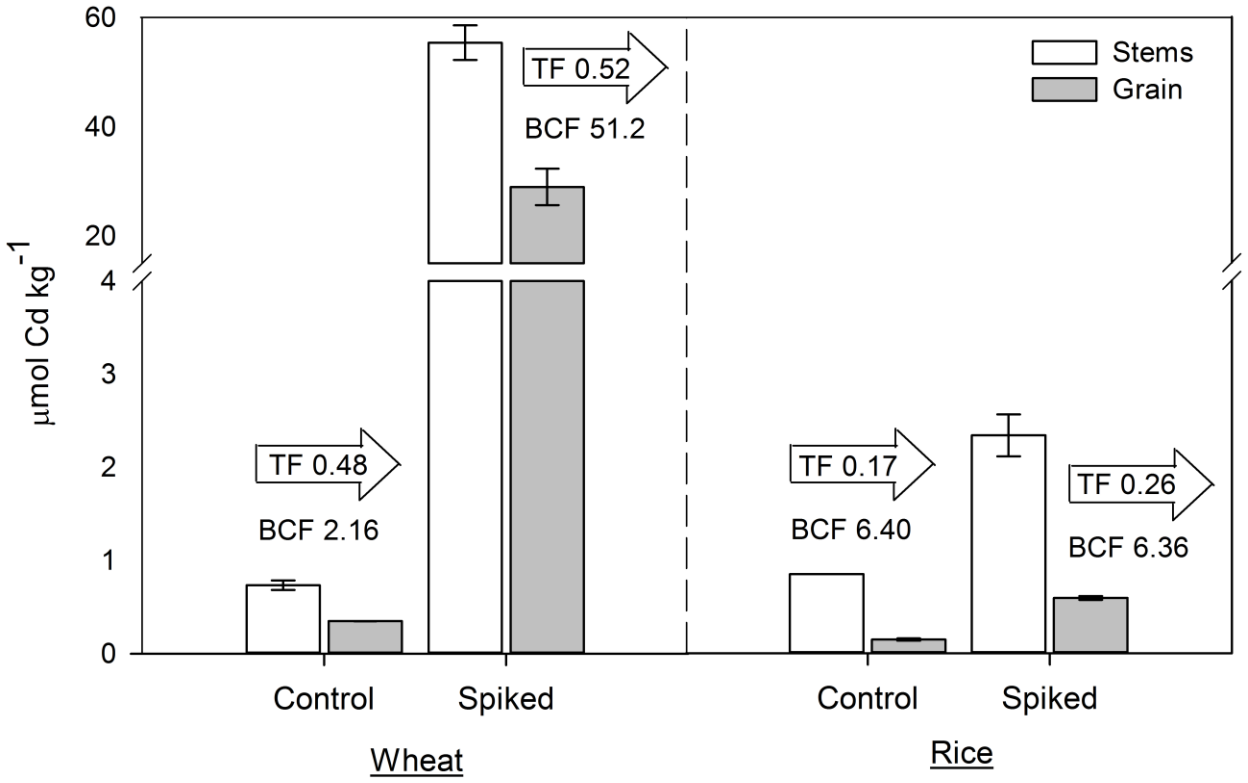
584

585


a
b
c
Soluble sulfate (mmol SO_4^{2-} kg^{-1})
Soluble nitrate (mmol NO_3^- kg^{-1})
SO_4^{3-}
NO_3^-
pH
Eh
Eh (mV)
Exchangeable Zn (µmol Zn kg^{-1})
Exchangeable Cd (nmol Cd kg^{-1})
Cd
Zn
Incubation duration (days)

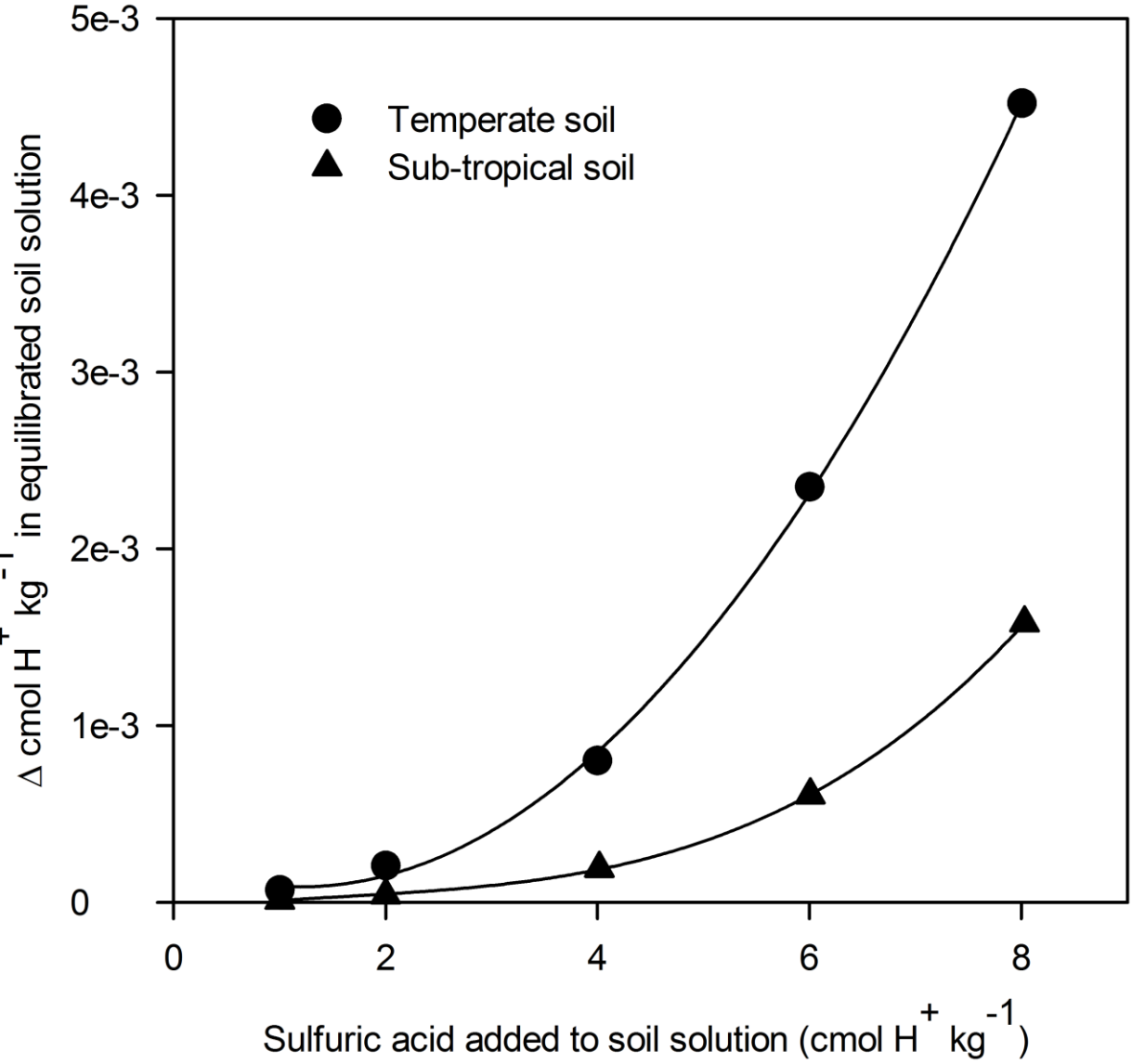
586

587


60
40
20
4
3
2
1
0
µmol Cd kg-1
Stems
Grain
TF 0.52
BCF 51.2
TF 0.48
BCF 2.16
TF 0.17
BCF 6.40
TF 0.26
BCF 6.36
Control
Spiked
Control
Spiked
Wheat
Rice

588

589


5e-3
4e-3
3e-3
2e-3
1e-3
0
Δ cmol H+ kg-1 in equilibrated soil solution
Temperate soil
Sub-tropical soil
0
2
4
6
8
Sulfuric acid added to soil solution (cmol H+ kg-1)

590