

## Lignite Reduces the Solubility and Plant Uptake of Cadmium in Pasturelands

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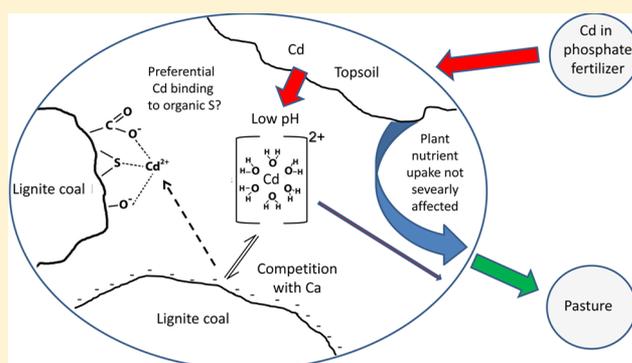
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### Supporting Information

**ABSTRACT:** Repeated application of Cd-rich phosphate fertilizers can lead to the accumulation of this nonessential element in soil. This can result in increased plant uptake, with possible breaches of food or feed safety standards. We aimed to determine whether lignite (brown coal) can reduce Cd solubility and plant uptake in New Zealand pasture soils. In batch sorption experiments, we tested the capacity of lignite and lignite-soil mixtures to sorb Cd at various soil pH and Cd loadings. Over a pH range of 4–7, Cd sorption by lignite was 1–2 orders of magnitude greater than by a typical immature pallic soil containing 2% carbon. The addition of 5 wt % lignite to a range of soils revealed that lignite addition was most effective in reducing soluble Cd in soils with low pH. In a greenhouse experiment, we tested the effect of lignite on the accumulation of Cd and other elements by perennial ryegrass, *Lolium perenne* (L.). The addition of just 1 wt % lignite to the aforementioned soil reduced plant Cd uptake by 30%, without adversely affecting biomass or the uptake of essential nutrient elements including copper and zinc. This may be due to preferential binding of Cd to organic sulfur in lignite.



## INTRODUCTION

Cadmium (Cd) is a nonessential element<sup>1</sup> that is readily taken up by plants and transferred through fodder and food products into animals and humans.<sup>2</sup> Enrichment of Cd in soils has been reported worldwide, through the land application of biosolids, industrial effluents, and Cd-rich phosphate fertilizers.<sup>1,3,4</sup> In a New Zealand (NZ) soil survey, Taylor et al.<sup>5</sup> reported an average Cd concentration in pasture soils of 0.43 mg/kg ( $N = 825$ ). This is more than double the background concentration of 0.16 mg/kg ( $N = 372$ ).<sup>5</sup> The main sources of Cd in these soils are phosphate fertilizers containing Cd as an impurity that originates from the phosphate rock used for their production.<sup>6</sup> Grazing animals take up Cd mainly via consumption of herbage; intake through soil ingestion is generally lower.<sup>6,7</sup>

For agricultural soils, a suitable risk-mitigation technology must be low-cost and leave the soil fertile. Potentially, *in situ* fixation may fulfill these requirements. By applying a fixing additive to soil, Cd is transferred to a form that is less available for plant uptake. Organic (e.g., leaves, bark sawdust, peat, compost) and inorganic (e.g., lime, hydroxyapatite) amendments can effectively reduce Cd solubility and plant uptake in contaminated soils and tailings,<sup>8,9</sup> by forming insoluble

organometallic compounds.<sup>10</sup> Lignite is discussed as a source of soil organic matter to improve soil fertility in degraded soils<sup>11</sup> and as a fixing additive in remediation of metal-contaminated soils.<sup>10,12,13</sup> Compared to other organic amendments such as compost, lignite is more resistant to decomposition and mineralization and shows a long-lasting activity in soil.<sup>10</sup> In contrast to some biochars, which also sorb Cd,<sup>14,15</sup> lignite is abundant worldwide and mined in great quantities. The proven recoverable world lignite resources are ca. 195 billion tonnes, with 333 million tonnes located in NZ.<sup>16</sup>

The prevalent mechanism by which metal ions are sorbed to lignite is ion exchange, but specific adsorption also plays a role.<sup>17</sup> Lignite contains large amounts of humic and fulvic acids<sup>18</sup> that have similar properties as their equivalents in soil.<sup>11</sup> Being a chalcophile, Cd is expected to bind strongly to organic sulfur groups,<sup>1</sup> R-SH, R-S-R, R-SS-R and heterocyclic S, which can be present in lignite.<sup>19</sup> Such binding may be important at

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Table 1. Physicochemical Properties for the Biosolids, Lignite, and Soils 1–6<sup>c</sup>

	biosolids	lignite	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6
moisture (%)	53	38	<1	<1	<1	<1	<1	<1
clay/silt/sand (%)	n.d.	<200 $\mu\text{m}$	4/20/76	3/42/55	40/46/14	17/44/39	20/30/50	19/25/56
pH (H <sub>2</sub> O)	4.1	4.5	5.1	5.5	5.3	4.8	6.8	5.5
CEC <sup>a</sup> (meq/100g)	n.d.	44.8	12.3	n.d.	n.d.	n.d.	n.d.	n.d.
BS <sup>b</sup> (%)	n.d.	95.2	50.3	n.d.	n.d.	n.d.	n.d.	n.d.
C (%)	28.0 (0.2)	57.2 (0.2)	3.3 (0.03)	6.1	4.9	8.7	2.0	13.3
N (%)	2.7 (0.03)	0.8 (0.01)	0.3 (0.00)	0.6	0.3	0.6	0.2	1.0
P	4683 (2)	57.6 (0.2)	732 (11)	1470	876	786	605	2108
S	6972 (43)	6539 (35)	383 (6)	784	447	578	217	1381
Ca	9818 (176)	17502 (119)	3229 (58)	4350	3310	8272	11090	4210
Mg	2204 (17)	2815 (11)	3426 (71)	1235	1921	1779	1934	1231
K	4330 (67)	219 (2)	2541 (279)	3781	3768	4422	3585	1256
Cd	2.8 (0.0)	0.06 (0.007)	0.13 (0.00)	0.86	1.34	0.75	1.07	1.53
Zn	878 (13)	9 (1)	70 (2)	43	76	49	67	61
Cu	561 (33)	2 (0)	5 (0)	6	23	6	23	38
Mo	n.d.	0.1 (0.00)	0.1 (0.01)	0.3	0.6	0.2	0.2	0.9
B	n.d.	36.3 (0.1)	7.3 (1.0)	4.1	4.6	3.1	5.6	4.5
Fe	n.d.	12918 (145)	17727 (353)	21039	38664	20501	34912	33082
Mn	n.d.	280 (3)	357 (20)	154	2346	320	577	814

<sup>a</sup>Cation Exchange Capacity. <sup>b</sup>Base Saturation. <sup>c</sup>Values in brackets represent standard error (SE) of the mean. ( $N = 3$  when SE is given;  $N = 1$  when no SE is given). All units are in mg/kg unless otherwise indicated. Soil type according to the New Zealand Fundamental Soil Layer<sup>50</sup> given at the bottom. n.d. = not determined. **Soil 1:** typical immature pallic soil (43°38'11.35" S, 172°26'17.00" E), **Soil 2:** typical orthic brown soil (42°20'18.51" S, 171°33'54.34" E), **Soil 3:** weathered rendzic melanic soil (40°56'36.24" S, 172°53'33.53" E), **Soil 4:** typical sandy recent soil (43°22'4.00" S, 170°11'12.20" E), **Soil 5:** acidic orthic brown soil (41°23'18.27" S, 172°48'47.73" E), **Soil 6:** pallic orthic brown soil (38°29'5.48" S, 174°59'49.38" E).

low, biologically relevant Cd concentrations, typical for low to medium level polluted agricultural soil (e.g., Taylor<sup>5</sup>). In batch sorption experiments, lignite and other low rank coals effectively sorbed Cd from aqueous solution containing high Cd concentrations.<sup>17,20–27</sup> These studies are not representative of agricultural soils though, where Cd concentrations typically reach a few mg/kg at most.<sup>28</sup> Other studies found a decrease in plant uptake of Cd when Cd-contaminated soil was blended with lignite. The metal concentrations used in these treatments were usually high and resulted in reduced plant growth.<sup>10,12,13</sup> The findings of these studies nevertheless indicate that lignite application could potentially reduce the plant uptake of Cd from pasture soils with subphytotoxic levels of Cd contamination originating from Cd-containing P fertilizer applications.

The goal of this study was to investigate whether lignite could be used as soil amendment for *in situ* fixation of Cd in NZ pastureland. Specifically we sought to determine the following:

- 1) Cd sorption by lignite at biologically relevant concentrations and pH values,
- 2) the effect of lignite amendments on Cd sorption and pH of various NZ pasture soils,
- 3) lignite treatment effects on plant growth and uptake of elements, and
- 4) the influence of liming on the lignite treatment effects.

## MATERIALS AND METHODS

Powdered lignite (particle size <200  $\mu\text{m}$ ) mined in the New Vale open cast mine in Southland (NZ) was provided by Solid Energy New Zealand Ltd. The lignite was obtained from the W7 rider seam, which is low calorific value lignite ~14.5 MJ/kg, compared to the main W6 seam that is mined for thermal coal (~15.5 MJ/kg). The lower calorific value is due to partial oxidation of the W7 seam as this rider seam is shallower and

closer to ground level. Biosolids, a soil amendment with typically elevated Cd concentrations, were obtained from Kaikoura regional treatment works, NZ, homogenized, and sieved to <20 mm. Relevant properties of the biosolids used are given in Table 1. Six pasture soils from NZ were used. The soil types and properties are given in Table 1. Soil 1 was collected on the Lincoln University Commercial Dairy Farm. Soils 2–6 were selected from a survey of a total of 69 soils from both islands on the rationale of covering a broad range of soil pH values, carbon contents, and textures. All soils had been modified by agriculture, i.e. amendment of liming agents and fertilizers, and occasionally tilling and sowing. Table 1 also gives the properties of the lignite used.

**Batch Sorption Experiments.** The influence of pH and spiked Cd solution concentration on Cd sorption by lignite and soil was studied in Batch Experiment 1 (BE1). The influence of lignite addition on Cd adsorption in contrasting soil types was investigated in Batch Experiment 2 (BE2).

The soils used for the experiments were dried and passed through a 2 mm nylon sieve. The lignite powder was used without drying to avoid hydrophobicity. The moisture content of the lignite was taken into account in determining solid-solution ratios. Both sorption experiments were conducted using 40 mL centrifuge tubes with 4 replicates per treatment. Three replicates per treatment were used for element analysis and one for pH determination.

The tubes were continuously agitated for 2 h on an end-overend shaker in order to reach sorption equilibrium (determined in a previous experiment). The pH of the slurry was measured after shaking. The tubes were centrifuged for 10 min at 3300 rpm. The supernatant was decanted and filtered through Whatman 52 filter paper (pore size 7  $\mu\text{m}$ ). Solution element concentrations were measured by ICP-OES (Varian

720-ES). Total and organic carbon in solution was determined using a total carbon analyzer (Shimadzu TOC-5000A).

**Treatments BE1.** Five grams of lignite or Soil 1 was added to 30 mL of 0.05 M  $\text{Ca}(\text{NO}_3)_2$  (BDH AnalaR  $\text{Ca}(\text{NO}_3)_2 \bullet 4\text{H}_2\text{O}$ ) solution spiked with various amounts of Cd (BDH AnalaR  $3\text{Cd}(\text{SO}_4) \bullet 8\text{H}_2\text{O}$ ). The initial solution Cd concentrations were 0, 0.12, 0.39, 1.26, and 3.75 mg/L. The solution pH was adjusted to values ranging from 2.8 to 8.3 after addition of the sorbent by using  $\text{HNO}_3$  (BDH ARISTAR nitric acid 70%) or KOH (BDH AnalaR KOH) to decrease or increase pH, respectively (Table S1). Centrifuge tubes containing solutions without soil or lignite were prepared as a control for each Cd concentration to determine the extent of any Cd sorption by the tubes or filter papers. The results indicated that such sorption was negligible.

**Treatments BE2.** In this experiment we compared the effect of lignite addition on Cd sorption of Soil 1 with five other soils (Soil 2–6). For this purpose, we prepared mixtures of 4.75 g of soil with 0.25 g of lignite (5 wt %) and for Soil 1 additionally mixtures of 4.5 g of soil with 0.5 g of lignite (10 wt %). Five grams of soil or soil/lignite mixture was added to 30 mL of 0.05 M  $\text{Ca}(\text{NO}_3)_2$  solution without spiking or spiked with 0.39 mg/L Cd, respectively. Were most of this added Cd sorbed by the soil, the soil concentration would be ca. 2.34 mg/kg, which is at the high end of the Cd concentrations found in NZ soils.<sup>5</sup>

**Pot Experiment.** In a greenhouse at Lincoln University (NZ), we grew *Lolium perenne* (L.) in 2.5-L pots holding ca. 3 kg of Soil 1, an alluvial soil similar to that found on many NZ lowland farms. Soil treatments included no spiking, spiking with 1.1 mg/kg Cd (added as  $\text{CdSO}_4$  solution), or blending with 10% biosolids by volume (equivalent to 3.7 wt %). The Cd-spiked treatment was intended to simulate a future scenario where soil Cd concentrations exceed guideline values due to the continued application of Cd-containing phosphate fertilizers. The biosolids treatment raised the Cd concentration of Soil 1 from 0.13 mg/kg to 0.23 mg/kg. Undried lignite (38 wt %  $\text{H}_2\text{O}$ ) was mixed into the unspiked and the biosolid-treated soil treatments at rates of 0, 25, 100, and 250 g per pot (equivalent to dry weight lignite concentrations of 0, 1.0, 3.4, and 7.1 wt %). The spiked soils were amended with 0, 1.0, and 3.4 wt % lignite. Two treatment series, one with and one without lime addition (65 g Ravensdown AgLime per pot, average particle size <0.5 mm), were prepared in five replicates each. Before filling into the pots, the soils were mixed using a concrete mixer. All treatments were added at the same time. The filled pots were placed in a randomized block design and allowed to stand for 2 weeks. Soil samples for chemical analysis were taken prior to sowing. *L. perenne* was sown directly on the wet soil surface at a rate of ca. 100 seeds per pot without any further soil working. A dense cover of seedlings developed in all pots. Plants were irrigated daily, and no fertilizer was applied. The above-ground biomass was harvested 29 days after sowing, washed thoroughly in deionized water, and dried at 60 °C until a constant weight was obtained.

**Sample Analysis.** The C and N content of the lignite, soil, and plant material was determined using an Elementar vario MAX CN element analyzer. Pseudototal element concentrations were measured in acid digests using ICP-OES. For both lignite and soil, 0.5 g was digested in 5 mL of  $\text{HNO}_3$ /1 mL of  $\text{H}_2\text{O}_2$  (Merck hydrogen peroxide 30%). The digest was diluted with Milli Q (Barnstead, EASYpure RF, 18.3 M $\Omega$ -cm) to a volume of 25 mL and filtered with a Whatman 52 filter paper. Plant material (0.3 g) was digested in 5 mL of  $\text{HNO}_3$

and subsequently diluted to a volume of 20 mL. Wageningen reference soil (ISE 989) and plant (IPE 100) material were analyzed for quality assurance (giving recoveries of >95% for all elements).<sup>29</sup> Soluble element concentrations, henceforth referred to as “solution concentrations”, in soil samples were measured in calcium nitrate extracts using ICP-OES. Five grams of soil was weighted into centrifuge tubes ( $V = 40$  mL), and 30 mL of 0.05 M  $\text{Ca}(\text{NO}_3)_2$  was added. Tubes were agitated for 2 h on an end-over-end shaker, subsequently centrifuged for 10 min at 3300 rpm, and finally filtered using a Whatman 52 filter paper. Extracts were stored at 4 °C. Soil pH was measured in Milli Q water at a solid-solution ratio of 1:2.5 using a Mettler Toledo pH meter. The cation exchange capacity (CEC) and base saturation (BS) for the lignite powder and Soil 1 was determined using the silver thio-urea method of Blakemore et al.<sup>30</sup> The grain size distribution of the Soils 1–6 was determined using the pipet method according to the reference methods of the Swiss federal agricultural research stations.<sup>31</sup>

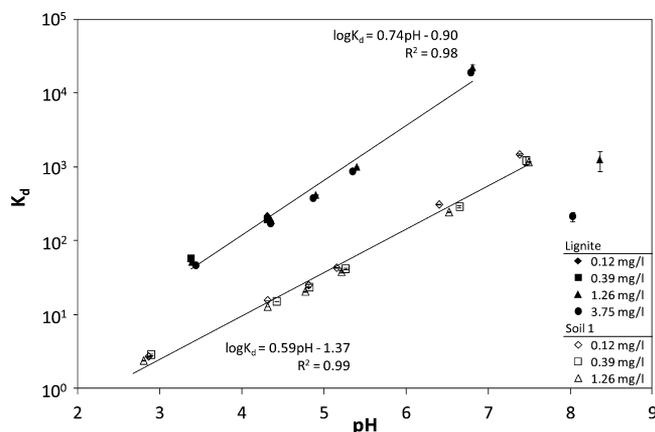
**Data Analysis.** Solid-solution distribution coefficients  $K_d$  were calculated from the experimental results using eq 1, where  $C_f$  is the Cd solution concentration after equilibration in a given batch with Cd spiking,  $C_o$  is the Cd solution concentration in the corresponding batch without Cd spiking, and  $C_i$  is the initial Cd solution concentration. Following the review by Degryse et al.<sup>32</sup> these  $K_d$  values characterize the equilibrium of labile Cd sorption.

$$K_d = \frac{\text{Cd adsorbed (mg/kg)}}{\text{Cd in solution (mg/L)}} = \frac{(C_i - (C_f - C_o)) \text{ (mg/L)} * \frac{0.031}{0.005 \text{ kg}}}{(C_f - C_o) \text{ (mg/L)}} \quad (1)$$

Microsoft Excel 2007 was used for general data analysis and visualization. (Log-)linear regressions and Fisher's least significant difference tests (LSD-test) were computed using the statistical software R (<http://www.r-project.org/>). For Fisher's test the R package *Agricolae* was used (<http://tarwi.lamolina.edu.pe/~fmendiburu>).

## RESULTS AND DISCUSSION

**Cd Adsorption As a Function of pH and Cd Loading (BE1).** Figure 1 shows that in the experimental range of solution pH between 3.4 and 6.8 and at a range of Cd concentrations found in pasturelands, the lignite used in this study sorbed 1 to 2 orders of magnitude more Cd than Soil 1. Sorption isotherms were linear in the experimental range of Cd loadings. Thus, the  $K_d$  values were independent of Cd loading, indicating that Cd binding was due to adsorption to sites that are well below saturation. On the log scale,  $K_d$  values increased linearly with pH for both materials up to neutral pH values. For lignite, where we had also batches with pH values of 8.0 and 8.4, sorption then decreased again by more than 1 order of magnitude between the maximum at the experimental pH value of 6.8 and these alkaline conditions. Although the difference in  $K_d$  between lignite and Soil 1 was greater at higher pH, the difference in terms of percentage adsorbed was highest at lower pH and diminished with increasing pH. Using the regression functions given in Figure 1 and assuming a solid-solution ratio of 1:6, 87% and 42% of the Cd was calculated to be bound to lignite and Soil 1, respectively, at pH 3.4, whereas respective >99% and 96% were obtained for pH 6. Thus, lignite addition to soil might be most effective at low pH.



**Figure 1.**  $K_d$  for Cd adsorption onto lignite or Soil 1 as a function of solution pH and different spiked Cd solution concentrations as measured in BE1 (mean  $\pm$  SE,  $N = 3$ ). The ambient solution was 0.05 M  $\text{Ca}(\text{NO}_3)_2$ . Lines represent fitted log–linear model (formula and  $R^2$  given in the figure). The equation data set included all observations for Soil 1 and observations in the pH range  $\leq$  pH 6.8 for lignite. Dissolution of the lignite at pH  $>$  pH 6.8 may be responsible for the anomalously low values of these points (connected with dashed lines).

The phenomenon of increasing  $K_d$  with increasing pH is well-known for soils and was also described for lignite.<sup>20,24</sup> The log–linear relationship indicates that the sorption mechanism is dominated by a competition reaction with  $\text{H}^+$  following the law of mass action. Dissociation of acid groups and complexation of Cd with the charged conjugate groups is expected to account for the observed pH effect on Cd sorption of lignite. Phenolic and thiol groups typically have  $\text{p}K_a$  values above pH 8<sup>24,33</sup> and are therefore not expected to deprotonate in great quantities under acidic conditions. Adsorption onto dissociated carboxylic ( $\text{COO}^-$ ) groups may account for the increase in Cd adsorption onto lignite with increasing pH. Titration of the lignite slurry produced a gradual change of pH over the whole pH range (Figure S1) and no distinct titration edges. This indicates that our lignite contained functional groups with a relative broad range of  $\text{p}K_a$  values typical for carboxylic groups.<sup>25</sup> This does not rule out sorption onto other functional groups, such as sulfur groups. Karlsson et al.<sup>33</sup> found that surface complexation with sulfur groups might be the dominant mechanism of Cd binding in soils with a concentration of  $<5$  mg Cd/g organic C.<sup>33</sup> Lignite contains a sufficient number of sulfur groups that can play an important role in Cd binding at these concentrations. The large percentage of spiked Cd adsorbed at pH 3.4 may indicate sulfur binding, as the amount of Cd bound to reduced sulfur is expected to be approximately constant over the pH range investigated (see modeling by Karlsson et al.<sup>33</sup>).

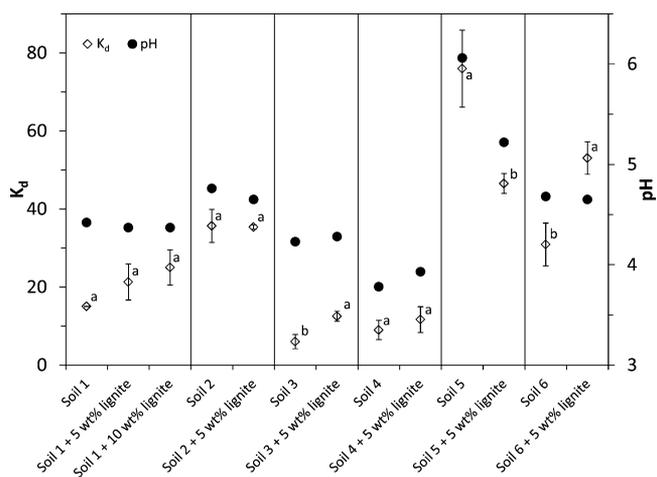
The decrease in Cd sorption by lignite above neutral pH might be due to dissolution of humic acids. An increase of such organic ligands in solution increases the solution concentration of Cd by forming soluble Cd-humic acid complexes. This is a well-known phenomenon for Cu.<sup>34</sup> The dissolved organic carbon (DOC) concentration released from the lignite in BE1 increased exponentially with increasing pH according to eq 2:

$$\log \text{DOC} \quad (\text{mg/L}) = 0.19\text{pH} + 0.42 \quad R^2 = 0.94 \quad (2)$$

However, at low pH values ( $<5.5$ ) the DOC approached an approximately constant level of 14 mg/L. At these pH values, DOM is largely composed of fulvic acids. With increasing

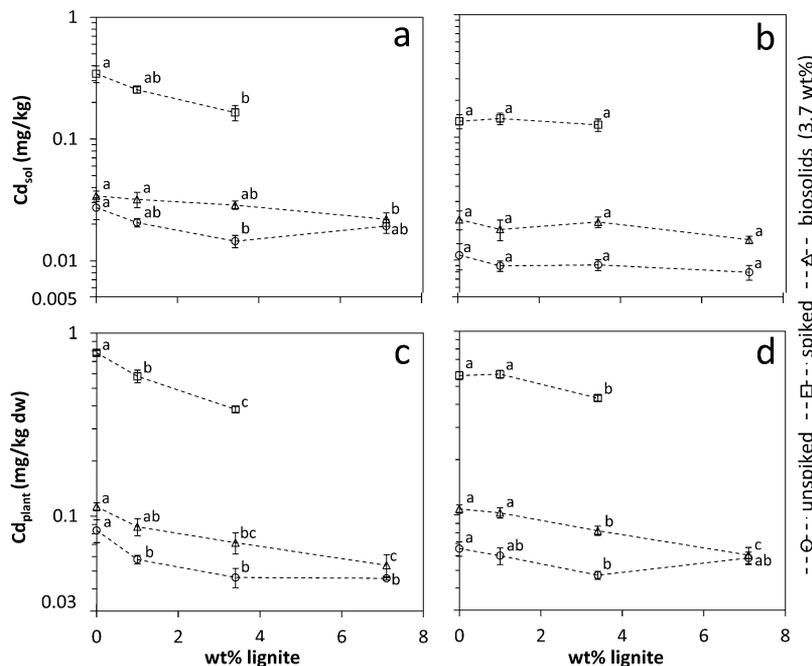
solution pH the fraction of humic acids, which are not soluble at pH  $< 2$ , increases in solution. This is consistent with a higher concentration of humic as opposed to fulvic acids in lignite.<sup>18</sup> A fraction of the fulvic and humic acids in solution may actually be present in the form of submicrometer colloids and not truly dissolved. The dissolved organic carbon released from Soil 1 was almost constant (ca. 120 mg/L) over the studied pH range (pH 2.8–7.5), indicating that it was dominated by fulvic acids, and thus no similar decrease in  $K_d$  should be expected at pH  $> 7$  as for lignite. Whether lignite addition to soil might fail to lower plant Cd concentrations finally depends on whether or not humic acid–Cd complexes contribute to the availability of soil Cd for plant uptake. Antoniadis and Alloway<sup>35</sup> found that the application of dissolved organic matter (DOM) significantly increased the uptake of Cd by *L. perenne*.<sup>35</sup> Evangelou et al.<sup>36</sup> observed that humic acid amendment to soil increased Cd uptake by *Nicotiana tabacum* (L.).<sup>36</sup> The bioavailability of metal-DOC/DOM complexes depends on a number of factors including the nature of organic compounds in DOC, the solubility, and dissociation constants of these complexes.<sup>37,38</sup>

**Cd Sorption of Various Soils Amended with Lignite (BE2).** The capacity of lignite to decrease the solubility of Cd in soil varied strongly with soil type (Figure 2). Lignite addition

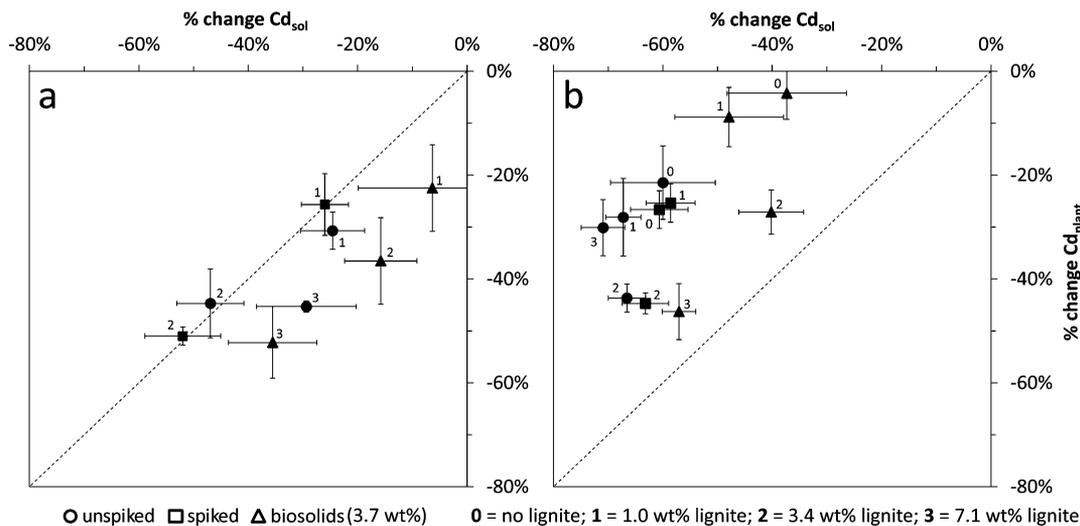


**Figure 2.**  $K_d$  and pH values as a function of sorbent type (Soils 1–6 with 0, 5, or 10 wt % lignite addition) as measured in BE2 ( $K_d$ : mean  $\pm$  SE,  $N = 3$ , pH: no replicate). The ambient solution was 0.05 M  $\text{Ca}(\text{NO}_3)_2$ . Means with the same letter are not significantly different.

may affect the affinity of a soil to sorb Cd directly by changing the density and composition of sorption sites as well as indirectly by changing conditions that affect sorption, in particular pH. Given that Cd sorption was stronger by lignite than by soil, an increase in Cd sorption should be expected upon lignite addition as long as this direct effect was not outmatched by Cd solubilization due to a decrease in pH. With the addition of the lignite amendment, the soil pH showed slight changes in all soils except Soil 5. Of these soils,  $K_d$  was either unchanged (Soils 1, 2, and 4) or significantly increased (Soils 3 and 6). In Soil 5, lignite addition caused a 0.8 unit drop in pH and a significant decrease in  $K_d$ . Comparing Soil 2 and 6 reveals that they differ remarkably in clay content, total carbon content, and concentrations of the (hydr)oxide forming metals Fe and Mn (Table 1). Therefore, interactions of lignite with soil minerals as well as soil organic matter may be different in Soil 2 and Soil 6.



**Figure 3.** Concentration of  $\text{Ca}(\text{NO}_3)_2$ -extractable Cd in soil ( $\text{Cd}_{\text{sol}}$ ) and Cd concentration in *Lolium perenne* ( $\text{Cd}_{\text{plant}}$ ) as a function of wt% lignite addition (mean  $\pm$  SE,  $N = 5$ ). Means with the same letter are not significantly different. The graphs a/c and b/d refer to the treatment series without and with lime addition respectively.

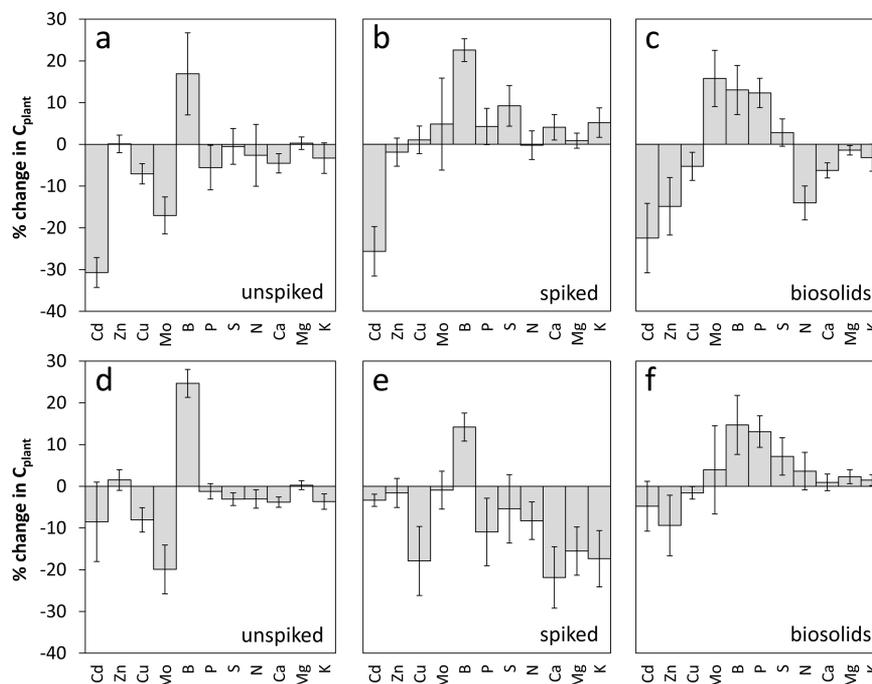


**Figure 4.** Change in  $\text{Ca}(\text{NO}_3)_2$ -extractable Cd versus changes in plant Cd as observed relative to the concentrations in the corresponding unlimed treatments without lignite addition (mean  $\pm$  SE,  $N = 5$ ). The Graphs 'a' and 'b' refer to the treatment series without and with lime addition respectively. Note that the treatments without lignite addition in Graph 'a' are at the origin as they are the reference treatments.

Lignite alone equilibrated with the  $\text{Ca}(\text{NO}_3)_2$  solution at pH 4.3. Soil 1 came to equilibrium at approximately the same pH. Therefore, the pH of the Soil 1–lignite mixture would be expected to also be around 4.3, and this is what was observed. For a soil that equilibrates with the solution above pH 4.3, a decrease in pH should be expected when it is blended with lignite. Likewise, an increase in pH is expected for a soil equilibrating with the solution below pH 4.3. The data in Figure 2 confirm these expectations. The critical pH value is a function of the lignite type and pretreatment and is also expected to vary between different lignites, depending on the acidic properties of their functional groups and their base saturation.

**Effect of Lignite Addition on Plant Uptake of Cd.**

Figures 3 and 4 show that lignite addition reduced  $\text{Ca}(\text{NO}_3)_2$ -extractable Cd concentrations and accumulation in ryegrass by up to 52% in the treatments without lime addition (Figure 3a, Figure 4a). In the treatments with lime addition (Figure 3b, Figure 4b), 3.4 wt % lignite addition did not reduce the  $\text{Ca}(\text{NO}_3)_2$ -extractable concentration of Cd but still reduced plant uptake. Although significant, this reduction was less than without liming (Figure 3c, Figure 4a). That the effect of lignite on plant uptake was less at higher pH values is consistent with the findings from batch experiments. When lignite was added to the soils, the pH decreased by up to 0.1 units without liming and by 0.6 pH units with liming. As the pH decrease was more pronounced in the limed treatments, we expect a stronger



**Figure 5.** Difference in element content in *Lolium perenne* for the treatments with 1.0 wt % lignite addition relative to the corresponding treatment without lignite addition (Mean  $\pm$  SE). a - c refer to the unspiked, spiked, and biosolids treatment in series without lime addition. d - f refer to the unspiked, spiked, and biosolids treatment in the series with lime addition. Note the difference in normalization of plot d - f as compared to Figure 4.

negative effect on Cd adsorption. This may be responsible for the differences in efficiency of lignite addition in reducing Cd solubility and plant uptake between unlimed and limed soil.

Potentially, lignite could be blended with a sufficient amount of lime to buffer the pH drop. Several authors recommended reducing soil acidity by liming as a suitable measure to reduce Cd plant uptake.<sup>6,39</sup> Calcium may compete with Cd for exchange sites on root surfaces, further reducing uptake. Therefore, the application of a combination of lignite and lime is expected to be more effective in reducing Cd plant uptake than lignite alone. In this study, liming did not enhance the ability of lignite to reduce plant Cd-uptake (Figure 4 a and b). The lack of effect of liming on Cd plant uptake under certain conditions was described by several authors.<sup>40–42</sup> Loganathan et al.<sup>40</sup> stated that the large amount of Ca added via lime might compete with Cd for sorption to soil if the pH is not sufficiently increased by the lime application to specifically sorb and immobilize Cd.<sup>40</sup> This would imply that outer sphere complexation is an important Cd sorption mechanism in the soil/lignite mixtures as Ca is known to bind generally via ion exchange mechanism and is not expected to compete in inner sphere sorption. The importance of outer and inner sphere sorption in soil at biologically relevant concentrations (<5 mg/kg) is debated. Experimental evidence is scarce as most of the studies investigating sorption mechanisms to soil used high concentrations not found in pasturelands. At a low Cd loading the effect of pH on Cd sorption is much lower and Cd tends to bind increasingly as inner sphere complexes.<sup>40</sup> Harter and Naidu<sup>42</sup> suggested this lack of pH effect in high affinity soils at low Cd loading might explain the absence of effect of liming on plant uptake.<sup>42</sup> Neither Ca competition nor lack of pH effect on Cd sorption in high affinity soils explains the lack of liming effect on plant uptake in this study as the solubility of Cd was significantly reduced. Other possible reasons are that lime increases root growth (not measured) by supplying Ca and

ameliorating soil acidity; lime decreases Zn availability, thereby reducing Zn competition with Cd for plant uptake; and Ca from lime increases root cell permeability, thereby facilitating root Cd uptake.<sup>41</sup> Due to plant and/or microbial activity the pH in the rhizosphere between the treatments with and without lime addition may be more similar than the pH values observed in the bulk soil.<sup>43–46</sup> Local buffering of the pH in the rhizosphere by biological activity might explain the lack of effect of lime addition on Cd plant uptake. Whether and how *L. perenne* and/or microorganisms changed the rhizosphere pH value in our experiment cannot be deduced from the results.

**Effect of Lignite on the Concentrations of Other Elements in Pasture.** Figure 5 shows that plant concentrations of Ca, Cu, and Mo were significantly reduced for 1 wt % lignite addition, except in the unlimed spiked treatment, where there is a marginal increase (Figure 5 A2) and in the limed biosolids treatment (Figure 5 B3), where plant Ca was unchanged. Plant Zn uptake was significantly reduced in the biosolids treatments that had elevated Zn concentrations. Plant B concentrations significantly increased with increasing lignite addition. In the unlimed soil, the reduction in Cd concentration was greater than the reduction in plant concentration of other elements measured.

Table S2 and Table S3 show the influence of lignite addition on soil pH and soluble concentrations of nutrients. Assuming that the bioavailability of Cd, Zn, and Cu is a function of their solubility in a 0.05 M  $\text{Ca}(\text{NO}_3)_2$  extractant, this observation is surprising as Zn and especially Cu are often cited to show higher affinity to organic matter than Cd.<sup>47</sup> However, Cu and Zn also form complexes with dissolved organic matter, some of which may be bioavailable.<sup>34</sup> This may further indicate the importance of S groups in complexation of Cd by lignite at biologically relevant concentrations. In contrast to sorption on carboxylic groups, Cd is usually more competitive than Zn in binding to reduced sulfur groups.<sup>48</sup> Martinez et al.<sup>48</sup> found that

peat had a higher affinity for Cd than for Zn and concluded that this might indicate high importance of sulfur groups in the binding of Cd in peat.<sup>48</sup>

**Effect on the Lignite on Pasture Growth.** Lignite additions of 1.0 and 3.4 wt % had no significant effect on biomass, while the highest addition of lignite (7.1 wt %) decreased pasture biomass, where it was applied, by 10–20% in most treatments (Table S4). In contrast, other authors showed significant increase in plant biomass when lignite was applied.<sup>10,12</sup> In these studies, soil was highly contaminated with heavy metals. Lignite addition might have eased phytotoxic effects by rendering metals at toxic levels unavailable to the plant which in turn might have caused the increase in biomass. The decrease in biomass observed in this study might be caused by the sorption of limiting plant nutrients, such as Cu, which were significantly reduced in some treatments (Tables S4 and S5). The decrease in biomass was most pronounced for the treatments fertilized with biosolids. Therefore lignite might have locked up plant nutrients that were released from the biosolids. Alternatively, the biomass reduction may have come from incipient B toxicity as this element was significantly increased in all lignite treatments (Table S5).

**Potential for Lignite to Mitigate Plant Cd-Uptake in Pasturelands.** The addition of 1 wt % (dry matter) lignite to the top 120 mm of the soil profile, where most Cd occurs,<sup>49</sup> may be an effective and relative selective amendment for *in situ* fixation of fertilizer-borne Cd in soil without adversely affecting plant growth. This represents a rate of 23.2 tonnes (fresh weight) per hectare, assuming a soil density of 1.2 g/cm<sup>3</sup>. However, the effectiveness of the lignite depends on the soil type and lignite amendment might be ineffective in rendering Cd less bioavailable in some soils. Future work should investigate the effect of lignite on the fluxes of Cd and other elements in the soil-plant system over a longer period of time. While lignite has been shown to be relatively persistent in soil,<sup>10</sup> it is unclear how its ability to bind Cd or other elements would change.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Table S1 lists the treatments of BE1. Figure S1 shows pH as a function of acid/base addition as observed in BE1. Table S2 and Table S3 show the influence of lignite addition on soil pH and soluble concentrations of nutrients and Table S4 and Table S5 the influence of lignite addition on biomass and the concentrations of nutrients in *L. perenne* (pot experiment). Figure S2 shows the difference in element concentration in *L. perenne* for the treatments with 3.4 wt % lignite addition relative to the corresponding treatment without lignite addition analogous to Figure 5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

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