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Adsorption of Cadmium on Biosolids-Amended Soils

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ABSTRACT

Debate exists over the biosolid phase (organic or inorganic) responsible for the reduction in phytoavailable Cd in soils amended with biosolids as compared with soils amended with inorganic salts. To test the importance of these two phases, adsorption isotherms were developed for soil samples (nine biosolids-amended soils and their five companion controls) and two biosolids samples from five experimental sites with documented histories of biosolids application. Subsamples were treated with 0.7 M NaClO to remove organic carbon. Cadmium nitrate was added to both moist soil samples and their soil inorganic fractions (SIF) in a 0.01 M Ca(NO$_3$)$_2$ solution at three pH levels (6.5, 5.5, and 4.5), and equilibrated at 22 ± 1°C for at least 48 h. Isotherms of Cd adsorption for biosolids-amended soil were intermediate to the control soil and biosolids. Decreasing pH did not remove the difference between these isotherms, although adsorption of Cd decreased with decreasing pH level. Organic matter removal reduced Cd adsorption on all soils but had little influence on the observed difference between biosolids-amended and control soils. Thus, increased adsorption associated with biosolids application was not limited to the organic matter addition from biosolids; rather, the biosolids application also altered the adsorptive properties of the SIF. The greater affinity of the inorganic fraction of biosolids-amended soils to adsorb Cd suggests that the increased retention of Cd on biosolids-amended soils is independent of the added organic matter and of a persistent nature.

EVALUATION of phytoavailability of biosolids metals has illustrated that metals added to soils as constituents of biosolids are less phytoavailable than metal salts added to the soils with the biosolids. Further, metal salts added with biosolids are less phytoavailable than metal salts added without biosolids (Brown et al., 1998; Hooda and Alloway, 1993; Bell et al., 1991; Mahler et al., 1987; Singh, 1981; Street et al., 1977; Gaynor and Halstead, 1976; Cunningham et al., 1975a,b,c). The

amount of metals required to cause phytotoxicity or yield reductions are always less with salts as compared with biosolids. Studies have shown that phytoavailability of metals is normally higher in the first year of biosolids application, then decreases with time after application ceased, and stays at a lower level for an extended time (Canet et al., 1998; Bidwell and Dowdy, 1987; Chang et al., 1997). These results have been interpreted as indicating that biosolids add adsorptive phases to soils, which reduce metal availability to plants (Hooda and Alloway, 1993; Corey et al., 1987). However, these studies were of insufficient length of time for all of the biosolids-added organic matter to decompose. Thus, if the added organic matter is the phase responsible for the reduced phytoavailability (Beckett et al., 1979), then the long-term efficacy of the biosolids on phytoavilability remains open to question.

Phytoavailability of added Cd was less for soils with a history of biosolids application than non-biosolids-amended control soils. This decreased phytoavailability was even true for biosolids-amended soils where the organic matter content was less than that of the non-biosolids-amended control soil (Mahler et al., 1987). In the study of Mahler et al. (1987), Wea (fine-loamy, mixed, active, mesic Typic Argiudoll) and Morley (fine, illitic, mesic Oxyaquic Hapludalf) soils both contained less organic carbon in the biosolids-amended treatments than the corresponding control soils (3.2 vs. 4.0% and 2.9 vs. 2.3%, respectively), indicating that the added biosolids organic carbon had decomposed. Comparison of Swiss Chard [*Beta vulgaris* var. *cicla* (L.)] Cd concentration in response to Cd added as a salt (CdSO$_4$) in limed soils with comparable pH values (7.1–7.3) illustrated that Cd phytoavailability was significantly reduced in the biosolids-amended soils (Fig. 1). Therefore, the reduced phytoavailability in biosolids-amended soil was still significant even when the added organic carbon

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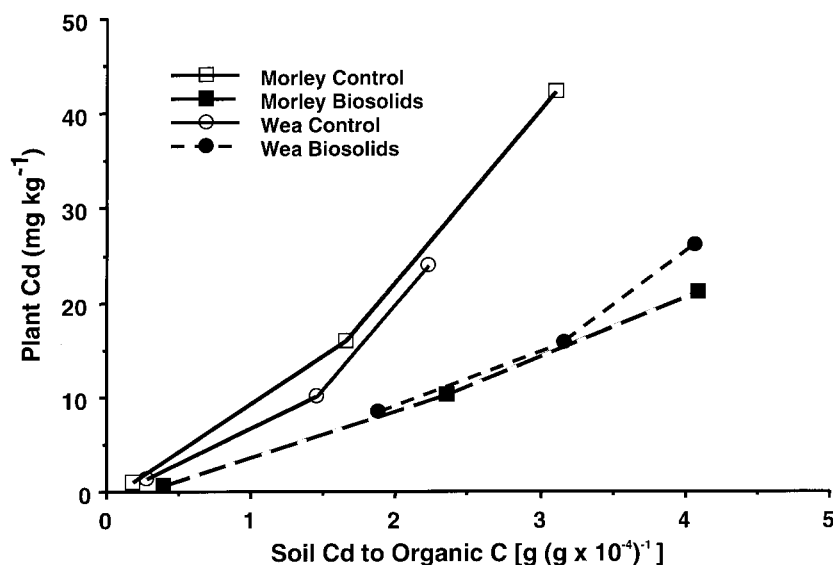
Abbreviations: SIF, soil inorganic fractions.

Fig. 1. Phytoavailability of Cd in soils with history of biosolids amendments. Developed from Mahler et al. (1987). The Cd to organic carbon (OC) ratio was used to normalize Cd loading to compensate for the lower OC content in the biosolids-amended soils.

from biosolids had disappeared. Further, Brown et al. (1998) found that even though organic carbon on biosolids-amended soil had decreased to background soil organic carbon levels, plant uptake did not increase and was unchanged from that observed in the early years of the experiment. Plant uptake was still significantly less from the biosolids application than from an equivalent salt metal loading.

These observations were responsible for using plant response from biosolids-amended soils as the basis for development of regulation for metal loadings by the USEPA (Chaney et al., 1999; Chaney and Ryan, 1994; Ryan and Chaney, 1993; USEPA, 1993). This is a contentious issue for those who believe the time bomb hypothesis of Beckett et al. (1979). The time bomb philosophy assumes the biosolids-associated organic matter is responsible for the observed reductions in phytoavailability and as the organic material decomposes, its complexing nature will be lost with a subsequent release of metal to the inorganic system, where it will behave as a salt addition to the soil (McBride, 1995).

Organic carbon decomposition with time after application of biosolids has been observed (Hyun et al., 1998; Hooda and Alloway, 1993), while metal leaching and/or removal by harvest are usually very minimal (Li and Shuman, 1996, 1997; Lamy et al., 1993; Dowdy et al., 1991; Williams et al., 1984). As the metals added by biosolids can be accounted for in the zone of application (Sloan et al., 1998), the concern for metal retention and phytoavailability by the soil as organic carbon disappears is valid. Additionally, studies indicate that a greater proportion of Cd exists in exchangeable or organic fractions (Li and Shuman, 1996; Sloan et al., 1997), implying the importance of the organic fraction in metal binding. However, the contribution of inorganic fractions cannot be ignored, as digested primary biosolids contain from 30 to 60% inorganic mineral forms (e.g., Fe, Mn, and Al oxides; silicates; phosphates; and carbonates) (Sommers et al., 1976; McCalla et al., 1977) that

are highly reactive with trace metals. Scientists have documented the role of the inorganic components contained in biosolids (Fe, Mn, and Al oxide minerals) in the formation of heterogeneous precipitates as well as the precipitates' ability to adsorb metals such as Cd (Corey, 1981; Corey et al., 1987; Essington and Mattigod, 1991; Kuo, 1986). The phytoavailability of trace metals specifically adsorbed by these inorganic phases would not be expected to increase with time, and could become less phytoavailable with time as surfaces become occluded. Studies demonstrated that Cd was associated with Fe-oxides in biosolids-amended soils (paracrystalline Fe oxides) (Bell et al., 1991) or an Fe–Mn oxide fraction in biosolids (Dudka and Chlopecka, 1990). Schulte and Beese (1994) argued that Cd adsorption was closely related to the specific surface area represented by Al-hydroxide, silicates, and carbonates at different pH ranges. Cadmium availability in biosolids-amended soils was controlled by phosphatic clay instead of organic matter when phosphatic clay was added to the soil system (Gonzalez et al., 1992). Jing and Logan (1992) found a relation between Cd/P and Sudax Cd uptake, suggesting that biosolids P reduced solubility of Cd by precipitating Cd as various phosphates, as had been suggested by others (Corey et al., 1987; Logan and Feltz, 1984). Application of biosolids into soils can also redistribute Cd into carbonate forms (Sposito et al., 1982; Chang et al., 1984) that possess a high capacity for adsorption of Cd (McBride, 1980). Any coprecipation or aggregate mixture of carbonates, phosphates, silicates, or Fe, Mn, and Al oxides may behave quite different from pure compounds, and may greatly affect the phytoavailability of Cd in soil systems.

The different patterns of plant uptake of Cd in soils with biosolids application raises questions about the major phases responsible for this alteration, the specific chemical and surface properties, and the mechanism responsible for the different behavior in biosolids-amended soils and its long-term efficacy. Unfortunately,

few long-term experimental studies in which the organic matter added by biosolids has equilibrated to background soil organic matter content have been reported, causing a lack of extensive definitive experimental data to support the assumption that plant uptake remains at low levels after the organic matter has decomposed. Those studies where the organic matter of the biosolids-amended soils has reached a level equivalent to the control soils illustrate that the change in chemistry and phytoavailability of metals caused by biosolids application are unaltered by decomposition of the added organic matter (Mahler et al., 1987; Brown et al., 1998). This result implies that an inorganic or a very recalcitrant organic phase is responsible for the biosolids-induced reductions in Cd phytoavailability.

As no definitive data on the added biosolids phase responsible and/or the mechanism of metal adsorption–retention by this added biosolids phase exist, and minimal data on phytoavailability after the disappearance of the biosolids-added organic carbon have been reported, the contentious issue of the long-term fate of the added metals persists. The objective of this study was to determine the effects of biosolids application and removal of organic matter on metal adsorption. To demonstrate the different adsorption behavior of biosolids-amended soils, Cd adsorption isotherms were developed on soils with past histories of biosolids amendments and their companion control soils as a function of pH. To evaluate the importance of organic matter on these adsorption isotherms, Cd adsorption on the soils was examined after treatment to remove organic matter.

MATERIALS AND METHODS

Sediment Material

Five experimental sites with five different soil types where controlled long-term biosolids experiments had been conducted were sampled. Surface soil samples (0 to 10 cm) of nine biosolids-amended soils with various rates of biosolids application and their experimental controls (five soil types) as well as two of the biosolids used in the field experiments were collected. Soil samples were placed in a well-sealed plastic bag, and stored in a refrigerator at 4°C. These moist soil samples were used in the Cd adsorption study. The final results were corrected to an air-dry weight basis by measuring the moisture content of subsamples.

Soils were sampled from a composted biosolids experiment established in 1976 at the Moreno Field Station of the University of California, near Riverside, CA. The experimental site was on a Ramona sandy loam soil (fine-loamy, mixed, thermic Typic Haploxeralf). Composted biosolids from the Joint Water Pollution Control Plant of the County Sanitation District of Los Angeles County (61, 1856, 1042, 482, 1996, and 3547 mg kg^{-1} for Cd, Cr, Cu, Ni, Pb, and Zn, respectively) was applied at rates up to 180 Mg ha^{-1} yr^{-1} from 1976 to 1991. Each year the annual application was incorporated to a depth of about 15 cm by roto-tilling with split application of half the rate in early spring and again in early fall. Throughout the years, as much as 2880 Mg ha^{-1} of composted biosolids was applied. For more detail on the experimental site see Chang et al. (1997).

Soils were sampled from a digested biosolids and composted biosolids experiment established in 1976 at the Hayden Farm

Research Facility of the University of Maryland in conjunction with the USDA Agricultural Research Center near Beltsville, MD. The experimental site was on a Christiana fine sandy loam (fine, kaolinitic, mesic Typic Paleudult). A lime-treated digested biosolids from the Piscataway treatment plant in Upper Marlboro, MD (5.9, 259, 15, 217, and 639 mg kg^{-1} for Cd, Cu, Ni, Pb, and Zn, respectively) and a limed composted biosolids from the Blue Plains treatment plant in Washington, DC (7.2, 274, 201, 272, and 731 mg kg^{-1} for Cd, Cu, Ni, Pb, and Zn) were applied at rates of 448 Mg ha^{-1} in 1976. For more detail on the experimental site see Brown et al. (1998).

Soils were sampled from a waste-activated dewatered biosolids experiment established in 1976 at the Rosemount Experiment Station of the University on Minnesota, near Rosemount, MN. The experimental site was on a well-drained Waukegan soil (fine-silty over sandy or sandy-skeletal, mixed, mesic Typic Hapludoll). Waste-activated dewatered biosolids from the Metropolitan Sewage District of the Twin Cities (140, 785, 706, 235, 1209, and 1758 mg kg^{-1} for Cd, Cr, Cu, Ni, Pb, and Zn, respectively) was applied at rates of 90 Mg ha^{-1} yr^{-1} in 1976 and 45 Mg ha^{-1} in 1977 and 1978. Each year the annual application was immediately incorporated to a depth of about 15 cm with a moldboard plow. For more detail on the experimental site see Sloan et al. (1998).

Soils were sampled from an anaerobically digested dewatered biosolids experiment established in 1990 at the Agronomy Farm of The Ohio State University in Columbus, OH. The experimental site was on a Miamian silt loam soil (fine, mixed, active, mesic Oxyaquic Hapludalf). Anaerobically digested dewatered biosolids from the City of Columbus Jackson Pike sewage treatment plant (46, 433, 67, 185, and 2334 mg kg^{-1} for Cd, Cu, Ni, Pb, and Zn, respectively) was applied at rates of up to 300 Mg ha^{-1} in 1990. Biosolids was mixed with 15 cm of soil and placed back on the plot area. For more detail on the experimental site see Logan et al. (1997).

Soils were sampled from an anaerobically digested biosolids experiment established in 1975 at the Pack Forest of the University of Washington, located 100 km south of Seattle, WA. The experimental site was on an extremely coarse textured outwash Everett soil (sandy-skeletal, isotic, mesic Vitrandic Dystroxerept). Anaerobically digested biosolids from the Metropolitan Seattle Wastewater Treatment Plant (32, 448, 727, 89, 737, and 5850 mg kg^{-1} for Cd, Cr, Cu, Ni, Pb, and Zn, respectively) was applied at a rate of 500 Mg ha^{-1} in 1975. The biosolids was disked into the surface soil layer to a depth of 30 cm. Because of poor controls on the application rate it is estimated that the actual application rate ranged from 400 to 600 Mg ha^{-1} over the 10-ha plot size. For more detail on the experimental site see Brallier (1992).

Soil Property Analysis

Subsamples of each soil were air-dried, disaggregated, and sieved through a 2-mm sieve prior to analysis. Soil pH (soil to water = 1:1) was measured according to USEPA Method 9045C (USEPA, 2001). Organic matter contents of soils were measured by the Walkley–Black method (Nelson and Sommers, 1996). Soil cation exchange capacity was determined by summation of cations in 1 M NH$_4$Cl extraction (Sumner and Miller, 1996). Soil free Fe oxide contents were determined with the citrate–dithionite extraction method (Loeppert and Inskeep, 1996; Holmgren, 1967). Soil samples were digested with concentrated HNO$_3$ in a microwave oven (USEPA Method 3051; USEPA, 2001), and total metals in the digested samples were determined by inductively coupled plasma–atomic emission spectrometry (ICP–AES) (USEPA Method 6010B; USEPA, 2001).

Organic Carbon Removal

To distinguish the contribution in Cd adsorption of the mineral phase from organic matter, 0.7 M NaClO was used as an oxidant to remove organic carbon. This reagent has been used to remove organic carbon in evaluating soil mineralogy (Anderson, 1963) and for evaluation of adsorption of organic compounds by soil components (O'Connor and Anderson, 1974). Further, it had been recommended by Shuman (1983, 1995) because it is more effective than H_2O_2 for extracting organic matter with less destruction of carbonates and oxides. To oxidize organic carbon, 20 mL 0.7 M NaClO (pH 8.5) was added to a 50-mL centrifuge tube containing 0.95 to 1.05 g of sample weighed to ±0.01 g. The suspension was heated in a boiling water bath for 2 h with occasional stirring. After cooling, the tube was centrifuged, and the clear supernatant discarded. After repeating the oxidation step a second time the sample was washed three times with 30 mL 0.01 M Ca(NO$_3$)$_2$ at pH 7.0. This soil inorganic fraction (SIF) was used in the Cd adsorption study. The organic carbon content of the SIF was determined by Walkley–Black method after washing with Milli-Q water (Millipore, Bedford, MA) several times to remove Cl$^-$ left in the SIF. Removal of Cl$^-$ was verified by reaction in acidic AgNO$_3$ solution.

Adsorption of Cadmium

For the moist soil samples and the SIF, samples of known weight (0.95 to 1.05 g) accurate to ± 0.01 g of dry solids were suspended in 20 mL 0.01 M Ca(NO$_3$)$_2$. Solution pH in 0.01 M Ca(NO$_3$)$_2$ was adjusted to the desired level (i.e., 6.5, 5.5, and 4.5) using 0.01 M NaOH or 0.01 M HNO$_3$. The suspension was shaken on a platform shaker at 140 rpm for 24 h, centrifuged, and the supernatant discarded. The sample was resuspended in 20 mL 0.01 M Ca(NO$_3$)$_2$, and Cd(NO$_3$)$_2$ solution was quantitatively added to give four known Cd concentrations. The 0.01 M Ca(NO$_3$)$_2$ solution was added to maintain an ionic strength in the adsorption medium similar to the soil environment (Turner et al., 1984; Filius et al., 1998). The total volume of solution was adjusted to a final volume of 25 mL. All adsorption samples were then shaken on a platform shaker at 140 rpm at 22 ± 1°C for 48 h. During the equilibration period, pH was maintained by periodic addition of 0.01 M NaOH or 0.01 M HNO$_3$. After the minimum 48-h equilibration or at least 12 h after the pH had stabilized, the suspension was centrifuged, and clear supernatant was filtered thorough a 0.45-μm filter. The pH of the filtrate [0.01 M Ca(NO$_3$)$_2$ solution] was determined and, if within 0.1 pH unit of the desired value, the solution was analyzed for Cd on ICP–AES using USEPA Method 6010B (USEPA, 2001). The amount of adsorbed Cd was calculated as the difference between the known initial Cd content and final equilibrium concentration. Results reported are from duplicated samples, and are based on the mass of air-dried soil.

RESULTS AND DISCUSSION

Treatment of the samples with NaClO removed a minimum of 95% of the organic carbon (Table 1), indicating the effectiveness of this treatment. The remaining organic carbon might be inter-layered inside the minerals, which would physically prevent oxidation, or they may be nondegradable compounds such as plastic-like polymers or charcoal. In either case they would probably have limited capacity for metal adsorption. It can be argued that chemical treatment such as NaClO alters surface properties of soil inorganic fraction so that the SIF may behave differently from the soil inorganic phases without NaClO treatment. We believe, however, that alterations should be comparable on both biosolids-amended and control soils. Therefore, differences in the behavior between biosolids-amended and control SIF

Table 1. Soil properties and biosolids amendments.

Rate	pH	Soil OC†	SIF OC‡	Free Fe$_2$O$_3$	CEC§	Cd
Mg ha^{-1}			mg g^{-1}		cmol kg^{-1}	mg kg^{-1}
		Ramona sandy loam (Typic Haploxeralf) from California composted biosolids amendments				
0	6.5	5.8	0.4	3.14	5.33	0.50
540	6.7	17.1	0.5	5.53	12.5	7.89
720	6.8	24.6	1.1	7.79	16.0	15.1
2880	6.4	56.0	2.5	13.5	31.1	39.0
		Christiana fine sandy loam (Typic Paleudult) from Maryland lime-treated digested biosolids and lime-composted biosolids amendments				
0	6.7	13.8	0.5	10.2	5.59	0.20
448 D¶	7.1	21.4	0.7	13.0	21.8	2.12
448 C¶	7.1	20.2	0.5	10.0	18.9	1.62
		Waukegan silty loam (Typic Hapludoll) from Minnesota waste-activated, lime-treated biosolids amendments				
0	6.2	20.6	0.6	8.0	19.9	0.52
180	6.4	23.4	0.5	7.8	17.8	7.46
		Miamian silt loam (Oxyaquic Hapludalf) from Ohio anaerobically digested biosolids amendments				
0	6.6	13.9	0.5	15.6	15.0	0.20
90	6.6	19.3	1.0	14.6	22.3	4.13
300	6.8	26.3	1.1	16.5	22.4	6.39
Biosolids	7.8	200	5.2	9.2	134	15.3
		Everett soil (Vitrandic Dystroxerept) from Washington anaerobically digested biosolids amendments				
0	6.6	48.4	1.4	7.9	11.3	1.06
500	6.2	78.8	2.8	18.4	23.0	32.8
Biosolids	7.2	160	4.8	10.3	77.4	32.3

† Soil organic carbon content.
‡ Organic carbon content in residues (soil inorganic fraction) after the soil samples were treated by 0.7 M NaClO twice.
§ Cation exchange capacity.
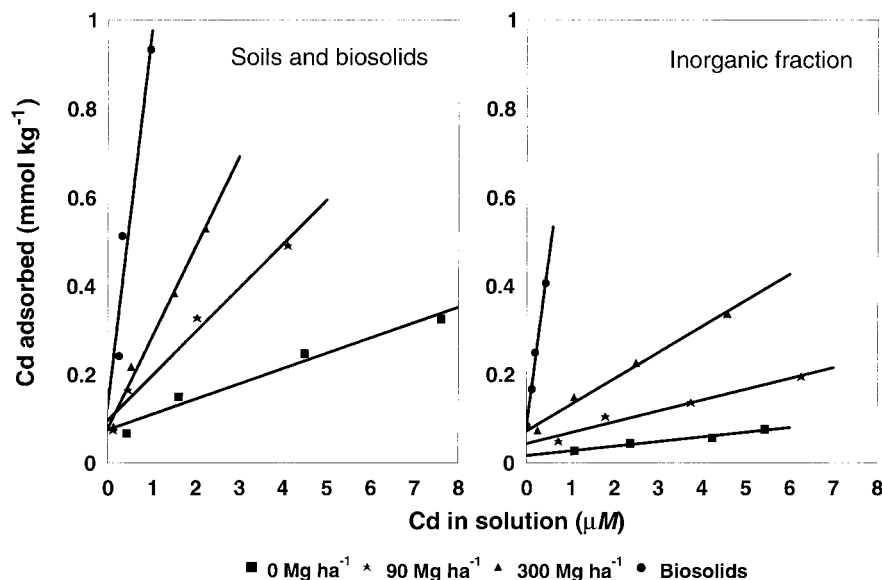¶ D, digested biosolids; C, composted biosolids.

Fig. 2. Effects of biosolids and organic carbon removal on Cd adsorption isotherms on Miamian silt loam at pH 5.5 in 0.01 M Ca(NO$_3$)$_2$ solution.

cannot be attributed to alterations caused by organic carbon removal. Thus, any differences between the adsorption isotherms of the biosolids-amended soils and their controls after NaClO treatment should be due to differences in inorganic phases in these two soil systems, not due to treatment with NaClO.

Results reveal that the adsorption isotherm for samples from different experimental sites behaved in a similar fashion with respect to biosolids application at all experimental pH levels. The Miamian silt loam at pH 5.5 serves as an example (Fig. 2). For a given sample the adsorption isotherm can be fitted by a linear model with a coefficient of determination of 0.90 to 0.99. Cadmium adsorption on the control soil was lower than that on biosolids-amended soils. Cadmium adsorption on the biosolids from the same sources as amended into soils was even greater than the biosolids-amended soils. In-

creasing the rate of biosolids application increased the adsorption of Cd for the amended soils, making the isotherms become more like that of the biosolids itself. The addition of 90 Mg ha^{-1} of biosolids resulted in a threefold increase in the slope of the adsorption isotherm as compared with the control. Further addition of the biosolids to a rate of 300 Mg ha^{-1} caused an additional twofold increase in the slope of the adsorption isotherm as compared with the 90 Mg ha^{-1} biosolids rate of addition. Adsorption of Cd on SIF exhibited similar trends to that of the soil, although the amount adsorbed was lower (Fig. 2). Therefore, we can conclude that both the organic carbon and inorganic fraction contributed to the increased adsorption of Cd on the biosolids-amended soil. Further, the removal of the organic carbon did not cause the biosolids-amended soil to behave like the control. For SIF, the increases in the slope
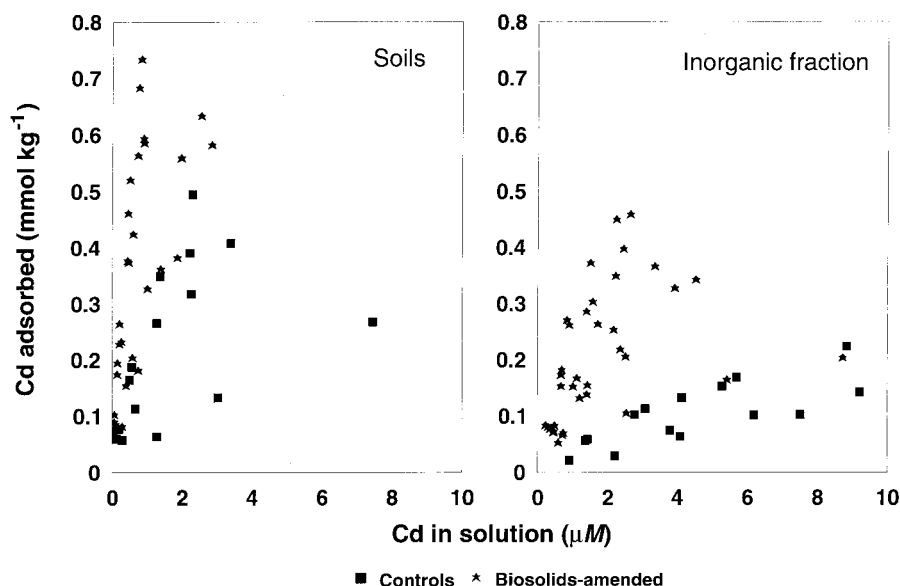

Fig. 3. Effect of biosolids and organic carbon removal on Cd adsorption on soils at pH 6.5 in 0.01 M Ca(NO$_3$)$_2$ solution.

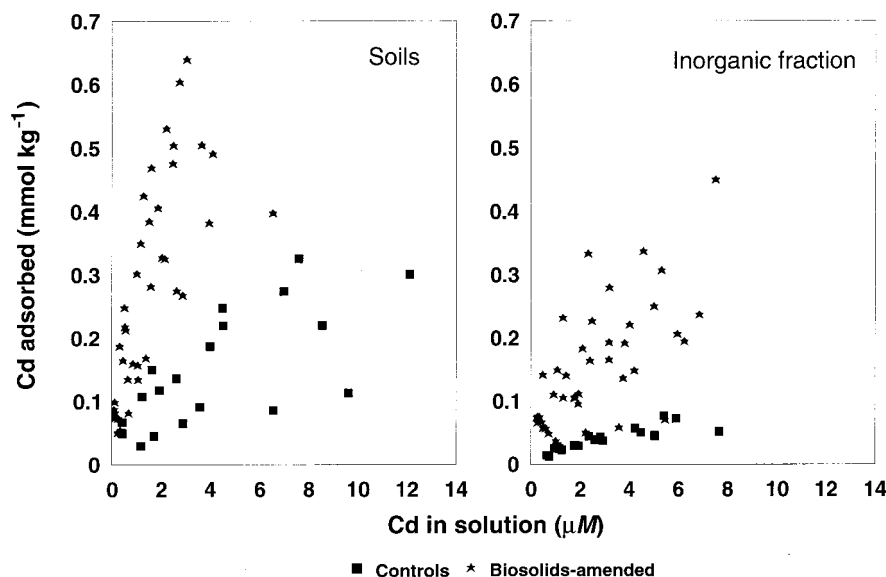**Fig. 4. Effect of biosolids and organic carbon removal on Cd adsorption on soils at pH 5.5 in 0.01 M Ca(NO$_3$)$_2$ solution.**

of the Cd adsorption isotherm on biosolids-amended SIF as compared with the control SIF were approximately the same as those for the soil. Thus, the inorganic fraction of the biosolids-amended soils was an important adsorptive surface and would be important in explaining the difference in Cd adsorption between amended soils and the control soil.

When all of the data at pH 6.5 [in 0.01 M Ca(NO$_3$)$_2$ solution] for the soil samples from the five experimental sites were combined into one graph (Fig. 3), adsorption of Cd on the control soils was distinctly lower than on the biosolids-amended soils. The difference was still apparent when organic carbon had been removed from these soils (Fig. 3). When the pH was decreased to pH 5.5, there was a reduction in the adsorption but the difference between biosolids-amended soils and their controls was even more apparent, and the difference

was still clear in the SIF (Fig. 4), indicating that lowering the pH does not diminish the difference between the biosolids-amended and control soils. Further reduction of pH to 4.5 lowered the slope of the adsorption isotherms but the differences associated with biosolids application were still apparent (Fig. 5). The removal of the organic carbon and reduction of pH did not remove the difference between the biosolids-amended and control soils (Fig. 5).

The difference between biosolid-amended and control soil was still apparent when all the data at all pHs are plotted together (Fig. 6). When comparing the SIF with the soils, a reduction of Cd adsorption was evident. However, the removal of organic carbon did not diminish the difference between biosolids-amended and the control soils, indicating that the inorganic fraction contributed to Cd adsorption and this contribution is proba-
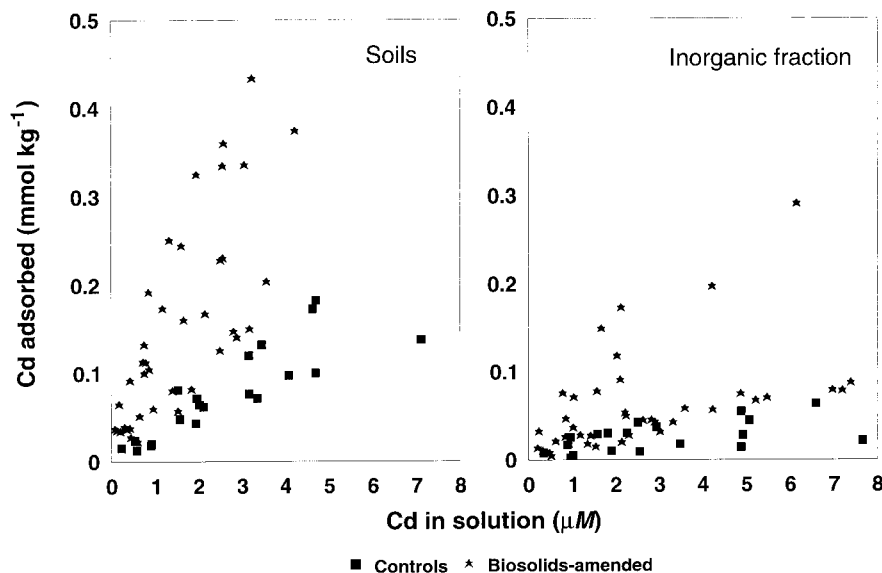

Fig. 5. Effect of biosolids and organic carbon removal on Cd adsorption on soils at pH 4.5 in 0.01 M Ca(NO$_3$)$_2$ solution.

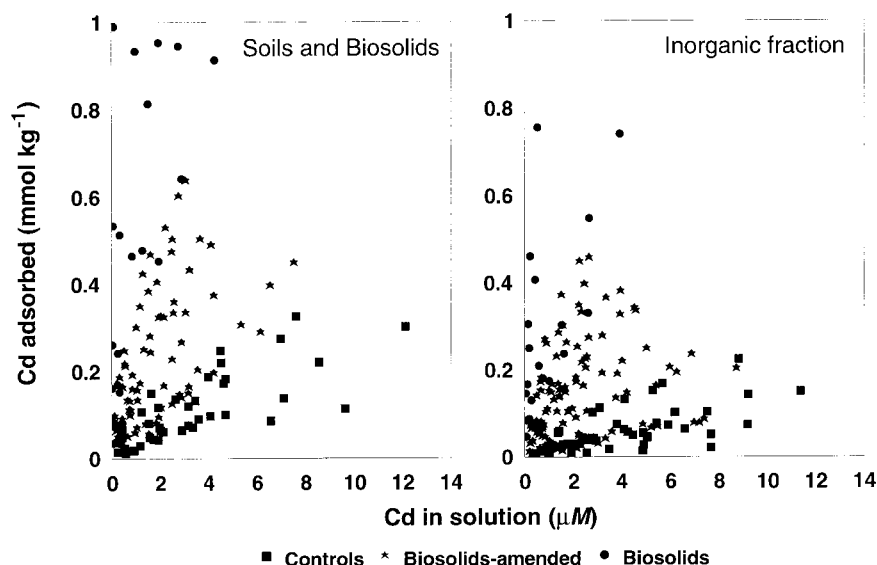Fig. 6. Effect of biosolids and organic carbon removal on Cd adsorption on soils in 0.01 M Ca(NO$_3$)$_2$ solution.

bly due to influences of the inorganic fraction of biosolids.

Fitting a linear model to each of the adsorption isotherms resulted in coefficients of determination of 0.90 to 0.99 (SAS Institute, 1989). Therefore, the slopes of the isotherm (K_d) were used to calculate the percentage of adsorption associated with the inorganic fraction, the increase in adsorption due to the biosolids amendments in soils, and the portion of the increase attributed to the inorganic fractions. That is:

$$P_i = \left[\frac{K_d I}{K_d}\right] 100$$

where P_i = percent of adsorption due to the inorganic fraction; $K_d I$ = slope of the adsorption isotherm for inorganic fraction, SIF; and K_d = slope of the adsorption isotherm for soil sample,

$$IP_s = \left[\frac{K_d B - K_d C}{K_d C}\right] 100$$

where IP_s = increase in percentage due to biosolids amendments; $K_d B$ = slope of the adsorption isotherm for the biosolids-amended soil; and $K_d C$ = slope of the adsorption isotherm for the control soil, and

$$IP_i = \left[\frac{K_d BI - K_d CI}{K_d B - K_d C}\right] 100$$

where IP_i = increase in percentage of adsorption due to the inorganic fraction of biosolids-amended soil; $K_d BI$ = slope of the adsorption isotherm for the inorganic fraction of biosolids-amended soil; $K_d CI$ = slope of the adsorption isotherm for the inorganic fraction of control soil; $K_d B$ = slope of the adsorption isotherm for the biosolids-amended soil; and $K_d C$ = slope of the adsorption isotherm for the control soil.

For the five control soils the percent adsorption by the inorganic fraction accounted for 29% (11–59%) of the adsorption observed on the soil samples. For the biosolids-amended soils the percent adsorption by the inorganic fraction accounted for 33% (6–93%) of the adsorption observed on the biosolids-amended soil samples. For the two biosolids samples the percent adsorption by the inorganic fraction accounted for 61% (52–69%) of the adsorption observed on the biosolids samples. Thus, assuming that treatment of the samples with NaClO did not alter the adsorptive characteristics of the inorganic fraction, we can conclude that the addition of biosolids increases the importance of the inorganic fraction to the overall Cd adsorption by the sample.

The application of biosolids increased soil Cd adsorption capacity by an average of 125% (28 to 210%) at pH 6.5 for four of the five experimental sites. The observations from the Christiana fine sandy loam were not included as the addition of biosolids increased the adsorption isotherm by 2500%. For samples from an experimental site, the rate of application of biosolids was related to the increase in Cd adsorption (i.e., California and Ohio). However, across all experimental sites the increases were not proportionally related to the rates of biosolids application. Rather, some of the biosolids had a larger effect, implying that not all biosolids had equal effects on increased Cd adsorption. Fifty percent (4 to 100%) of the increased adsorption of the biosolids-amended sample was attributed to the inorganic fraction in biosolids-amended soils at pH 6.5. Thus, the inorganic fraction of biosolids can have as great a contribution to Cd adsorption as the soil, indicating its importance in metal adsorption in biosolids-amended soils.

Normalizing the average slope of the adsorption isotherms (K_d) for each of the various samples as a percentage of the average of the control soils at pH 6.5 allows an evaluation of the importance of the various fractions as a function of pH (Fig. 7). Regardless of change in pH within the range studied the slope of the adsorption isotherms (K_d) of the biosolids-amended soil was at least three times the control soil, and the SIF of the
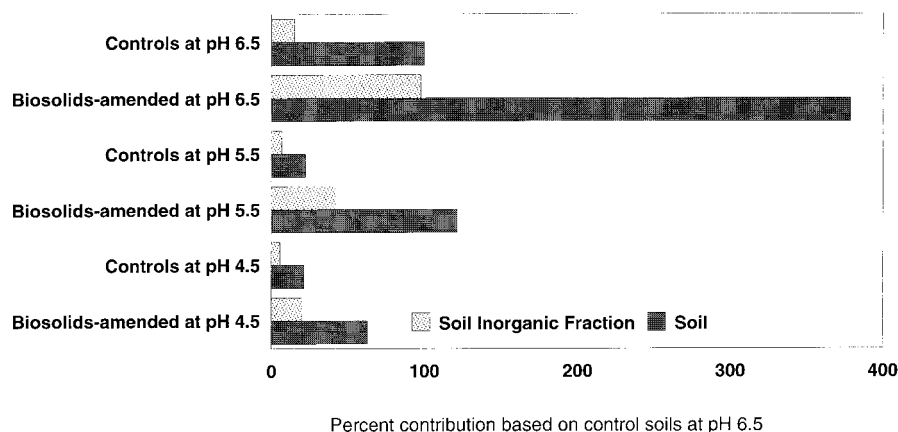
Fig. 7. Average contribution of biosolids-amended and control soils and their inorganic fraction to Cd adsorption (percentage based on average of control soils at pH 6.5).

biosolids-amended soil was approximately equal to that of the control soil. Therefore, even if all organic matter was degraded in biosolids-amended soils, the inorganic fraction can still retain Cd at a similar level as the control soils with both an organic and inorganic fraction.

SUMMARY

These results illustrate that cadmium adsorption is increased in soil with a history of biosolids amendments. Removal of organic carbon caused a reduction of Cd adsorption, but the difference between biosolids-amended samples and their control soils was still apparent. The difference persisted in the pH range from 4.5 to 6.5 in both soils and SIF. Thus, even when the organic carbon added by biosolids has disappeared, the soil that received biosolids will have a greater capacity to retain Cd from solution. As the inorganic fraction contributes significantly to Cd adsorption on soils, and the addition of biosolids increased the contribution from the inorganic fraction, the biosolids either added some inorganic adsorptive phase(s) or increased the adsorptive characteristics of the inorganic phase(s) present in the soil. In either case it becomes important to identify the inorganic phase(s) responsible and understand the mechanisms of adsorption. The responsible inorganic phases possibly include Fe, Mn, and Al oxides, silicates, carbonates, or phosphates, which have all been reported as important in metal adsorption (Schulte and Beese, 1994; Gonzalez et al., 1992; Jing and Logan, 1992; Bell et al., 1991; Corey et al., 1987; Chang et al., 1984; Logan and Feltz 1984; Sposito et al., 1982; McBride, 1980). However, the inorganic phase(s) and the mechanism by which it operates still evade us and will only be revealed by methodically pulling these complex systems apart.

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