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Toxicity of Lead to Soil Respiration: Mediation by Clay Minerals, Humic Acids, and Compost

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The natural background concentration of lead (Pb) in soils in the United States ranges from 10 to 700 ppm, with an average of 20 ppm (Demayo et al., 1982). However, as a result of anthropogenic activities, soils may be contaminated with elevated levels of Pb. For example, gasoline combustion releases Pb into the atmosphere, and this Pb can be deposited onto roadside soils. 1,225 ppm Pb was noted in soil 0.3 m from a highway along which 8,100 vehicles/day traveled, whereas at 100 and 200 m from the highway, the level of Pb in the surface soil was only 13 ppm. For a highway on which 550 vehicles/day traveled, levels of 35 and 13 ppm Pb were noted 0.3 and 25 to 200 m, respectively, from the highway (Wheeler and Rolfe, 1979). Another source of Pb in soil is from deteriorating Pb-based paints: soil sampled within 2 feet of old wooden-frame houses painted with Pb-based paints contained 1,586 to 2,349 ppm Pb, whereas samples from within 2 feet of brick-veneer houses contained 351 to 501 ppm Pb (Demayo et al., 1982). Extremely high levels of Pb occur in soils near smelters: e.g., the level of Pb in soil samples was 28,000, 8,333, 4,800, 3,654, and 703 ppm at 15, 90, 150, 180, and 1,000 m, respectively, from a secondary Pb smelter (Bisessar, 1982). Levels greater than 24,000 ppm Pb occurred in soils in the immediate vicinity of a Pb mine and smelter, whereas noncontaminated soil contained from 1 to 37 ppm Pb (Djuric et al., 1971).

As Pb has no known biological function, elevated levels of Pb in soils and in other natural environments may adversely affect the indigenous biota, including the microbiota. For example, populations of bacteria, actinomycetes, and fungi were decreased in soils surrounding a secondary Pb smelter (Bisessar, 1982). Elevated levels of Pb in soil may also adversely affect microbe-mediated ecologic processes. For example, amendments of soils with Pb resulted in reductions in carbon (C) mineralization (Mikkelsen, 1974; Doelman and Haanstra, 1979a), nitrogen (N) mineralization, nitrification (Bhuiya and Cornfield, 1974; Rother et al., 1982) denitrification (Bollag and Barabasz, 1979), decomposition of animal (Doelman and Haanstra, 1979b) and plant (Strojan, 1978) litter, and activities of soil enzymes (Doelman and Haanstra, 1979a).

There is, however, relatively little information on the mediating influence of the physicochemical factors of the recipient environment on the toxicity of Pb to microbe-mediated ecologic processes. Mikkelsen (1974) and Doelman and Haanstra (1979a) showed that Pb was more inhibitory to soil respiration in sandy soils of low cation exchange capacity (CEC) than in clay or peat soils with a higher CEC. This present study evaluated the influence of the clay minerals, kaolinite and montmorillonite, particulate humic acids, and compost on the degradation of glucose in soil.

MATERIALS AND METHODS

Soil, with a pH of 5.0, a CEC of 8.2 meq/100 g, consisting of 57% sand, 34% silt, and 9% clay, and naturally containing the clay minerals, kaolinite, vermiculite, and mica-illite and a background concentration of 25 ppm Pb (acid extractable) was obtained from the Kitchawan Research Laboratory of the Brooklyn Botanic Garden at Ossining, New York. The soil was amended with either 9% (v/v) kaolinite (Continental, R.T. Vanderbilt Co., with a CEC of approximately 6.5 meq/100g) or montmorillonite (Volclay, Panther Creek-Aberdeen, American Colloid Co., with a CEC of approximately 60 meq/100 g) to yield a pH of 4.6 and 5.3, respectively, and a CEC of 9.0 and 13.7 meq/100 g, respectively. A more detailed description of the physicochemical properties of these soils is presented elsewhere (Babich and Stotzky, 1982). The soils, both unamended and clay-amended were stored essentially air-dry. In some studies, the soil was amended with particulate humic acids (Aldrich Chemical Co.) or compost (obtained from the aerobic composting of domestic sewage sludge and sawdust in a Kneer Bioreactor in Gissen, Germany). One week before each experiment, the soils were preincubated with 12% water, with intermittent mixing, to reactivate their microbial activity. One day before the experiment, the soils were brought to their 1/3 bar tension water content, stored overnight at 4 C, passed through a 2 mm sieve, and 100 g samples of each soil mixture were placed into wide-mouth incubation vessels. The incubation vessels were connected to a manifold and continuously aerated with water-saturated CO_2-free air at 24 $\pm$ 2 C. The amount of C released as CO_2 was determined titrimetrically with HCl after absorption in NaOH and precipitation with $BaCl_2$ (Stotzky, 1965). Amendments (e.g., Pb as $Pb(NO_3)_2$, glucose, inorganic salts) were made in the water used to bring the soils to their 1/3 bar tension. The pH of the soil systems was determined on a 1:1 soil:water mixture.

The natural and clay-amended soils were supplemented with 2.5 g glucose/100 g soil, 0.04% (w/w) P as Na_2HPO_4-KH_2PO_4, and 0, 500, 1,000, or 10,000 ppm Pb. To compensate for the added N in soils amended with 10,000 ppm Pb, soils amended with 0, 500, or 1,000 ppm Pb were supplemented with NH_4NO_3 to yield a N level of 0.14% (w/w) (i.e., the amount of N added with 10,000 ppm Pb). The addition of 10,000 ppm Pb lowered the pH of the unamended soil to 4.0, of the kaolinite-amended soil to 3.9, and of the montmorillonite-amended soil to 5.0. The soils were incubated for 16 days.

The soil supplemented with either 0.5 or 2% (w/w) humic acids or with 1 or 4% (w/w) compost was amended with 1 g glucose/100 g soil and either 0 or 20,000 ppm Pb. To compensate for the additional N in the Pb-amended soils, the various soil controls (i.e., without Pb) were supplemented with an equivalent level of NO_3^- (i.e., 11,970 ppm) as $Mg(NO_3)_2 \cdot 6H_2O$. The addition of 20,000 ppm Pb lowered the pH of the soil without the supplements of humic acids or compost to 3.6. The pH of control soils (i.e., no Pb) supplemented with 0.5 to 2% humic acids was 5.0 and 6.0, respectively, and of those supplemented with 1 or 4% compost was 4.5 and 4.8, respectively; the respective pH values for these soils amended with Pb were 3.8, 4.2, 3.6, and 3.6. The soils were incubated for 20 days.

RESULTS AND DISCUSSION

In the absence of Pb, the amount of glucose degraded, as indicated by the total amount of CO_2 evolved, was lower in the montmorillonite-amended than in the kaolinite-amended or natural soil. The addition of 500 or 1,000 ppm Pb to the natural or clay-amended soils did not have an appreciably adverse effect on the extent of C mineralized after 16 days of incubation. The addition of 10,000 ppm Pb resulted in a 28, 21, and 1% decrease in the total amount of C mineralized in the natural, kaolinite-amended, and montmorillonite-amended soils, respectively, as compared to their respective control soils. The lag in C mineralization caused by the addition of 10,000 ppm Pb was reduced in the montmorillonite-amended soil: an accelerated rate of C mineralization occurred after 3 days in the montmorillonite-amended soil but after 4 to 5 days in the kaolinite-amended or natural soils. The rate of C mineralization in the montmorillonite-amended soil supplemented with 10,000 ppm Pb was equivalent to that in its control soil (i.e., amended with montmorillonite but no Pb) after 6 days of incubation, whereas the rates of mineralization in the kaolinite-amended and natural soils were approximately equivalent to that in their respective control soils only after 10 days of incubation (Fig. 1).

The lower inhibition of C mineralization by Pb in the montmorillonite-amended soil was probably the result of the higher CEC of this than of the kaolinite-amended and natural soils. Pb adsorbs to clay minerals, with montmorillonite adsorbing more than comparable concentrations of kaolinite (Hildebrand and Blum, 1974a; Farrah and Pickering, 1977), and the greater protection provided by montmorillonite than by comparable concentrations of kaolinite against the toxicity of Pb to mycelial growth of fungi *in vitro* was correlated with the CEC of the clays (Babich and Stotzky, 1979). Doelman and Haanstra (1979a) also showed that the inhibitory effect of Pb on CO_2 evolution from a variety of soil types was inversely correlated with their CEC.

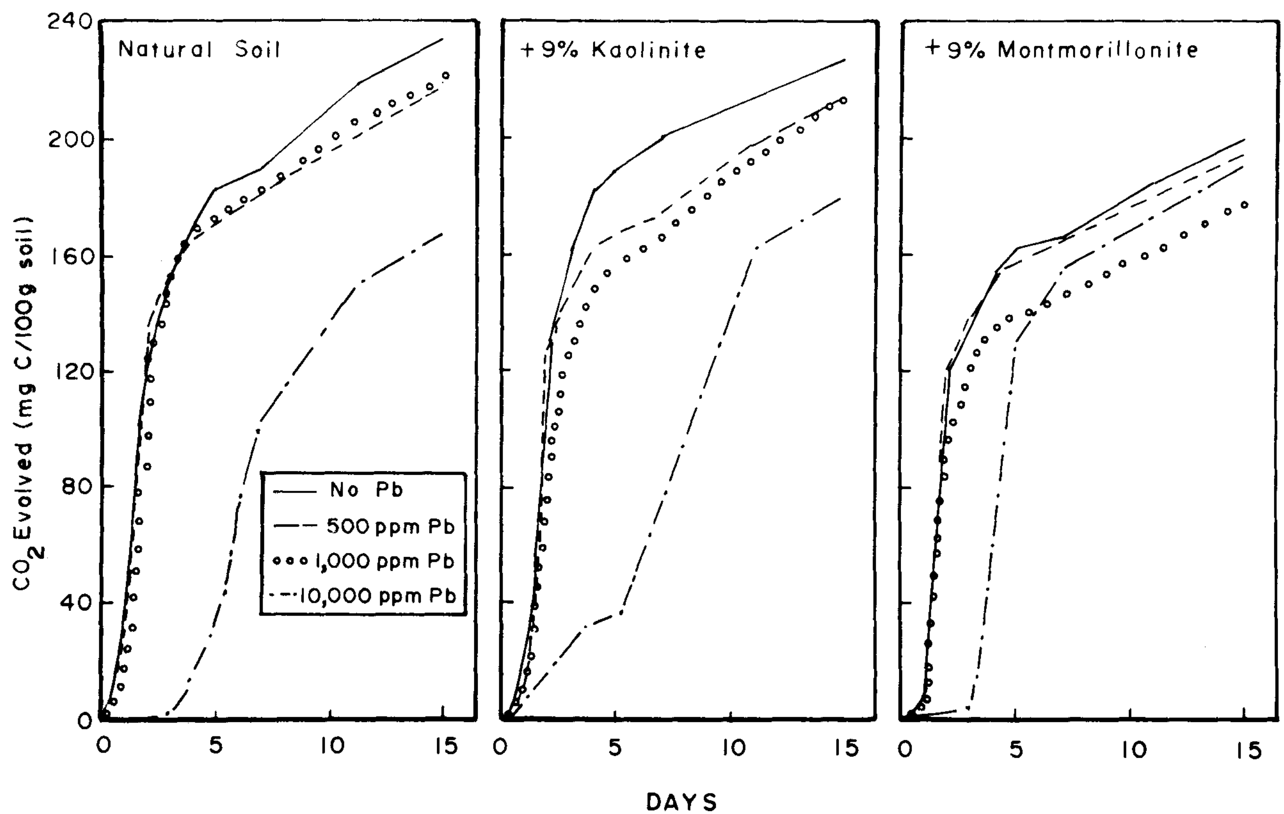

Figure 1. Cumulative amounts of carbon (mg/100 g soil) evolved as CO_2 from natural soil or soil amended with 9% (v/v) kaolinite or montmorillonite treated with 0, 500, 1,000, or 10,000 ppm lead and glucose (2.5 g/100 g soil).

In the absence of Pb, the addition of 0.5 or 2% humic acids did not appreciably affect the rate or extent of C mineralization. After 20 days of incubation in the presence of 20,000 ppm Pb, no CO_2 evolution was detected in the natural soil or in the soil amended with 0.5% humic acids. However, in soil amended with 20,000 ppm Pb and 2% humic acids, there was some evolution of CO_2 (Fig. 2), indicating that the higher concentration of humic acids resulted in some reduction in the toxicity of Pb. Preliminary studies using the natural soil adjusted to pH 7 and amended with 15,000 ppm Pb, showed that 2% humic acids completely, and 0.5% humic acids greatly, reduced the inhibitory effects of Pb on C mineralization. Pb forms stable complexes with humic acids (Hildebrand and Blum, 1974b; Stevenson, 1976), and humic acids protected fungi against Pb toxicity in vitro, probably by complexing the Pb and, thereby, reducing its availability for uptake by the fungi (Babich and Stotzky, 1979).

In the absence of Pb, 1 and 4% compost did not affect the extent of C mineralization. In soil amended with 20,000 ppm Pb and 1% compost, C mineralization occurred at an exceedingly reduced rate that slowly increased with time. In soil amended with 20,000 ppm Pb and 4% compost, the low but progressively increasing rate of mineralization occurred until day 10 of incubation, but then mineralization proceeded very rapidly and approached the rates in the natural and compost-amended soils without Pb, and by day 20, the amount of C mineralized was almost equivalent to that in the natural and compost-amended soils without Pb (Fig. 3). The addition of compost probably increased the CEC of the soil: the application of 40 and 240 metric tons/ha of dry sludge compost to a silt loam soil with a CEC of 5.5 meq/100 g increased the CEC to 6.3 and 10.7 meq/100g (Epstein et al., 1976). The compost apparently provided additional exchange sites in the soil for the sorption and sequestering of the Pb, thereby affording protection against the toxicity of Pb towards the microbiota.

The protection afforded by compost against metal toxicity was in contrast to what usually occurs with the addition of uncomposted sewage sludge. If the sewage sludge contains high concentrations of heavy metals, its use for landfill and fertilizer may result in elevated levels of heavy metals in crops (e.g., Weber, 1972; Page, 1974; Valdares et al., 1983). In contrast, the bioavailability to plants of cadmium and zinc from composted sludge was less than that from uncomposted sludge (Chaney et al., 1975; Giordano et al., 1975; Simeoni et al., 1984), probably because the chemical speciation of the heavy metals changed during composting to reduce their bioavailability and, hence, toxicity.

The toxicity of Pb, as well as of other heavy metals (e.g., cadmium and zinc; Bewley and Stotzky, 1983a, b), to C mineralization in soil is dependent on the physicochemical characteristics of the specific soil into which the metals are deposited. For example, the toxicity of Pb to C mineralization was reduced in soils with a high CEC (Doelman and Haanstra, 1979a; this study). Environments

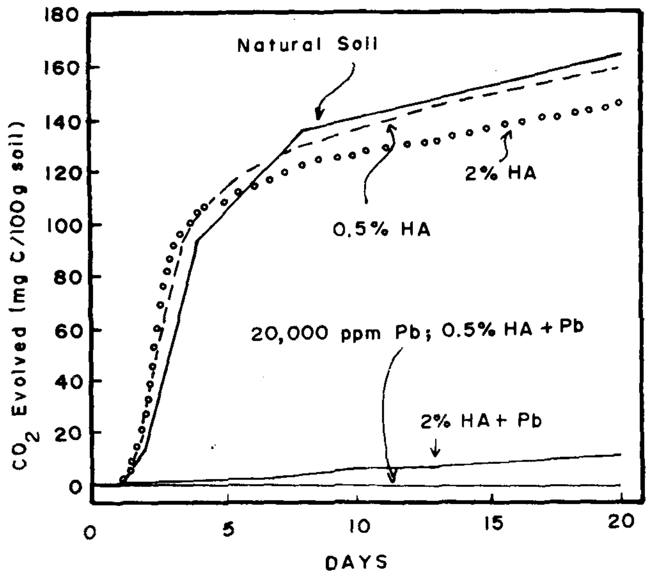

Figure 2. Cumulative amounts of carbon (mg/100 g soil) evolved as CO_2 from natural soil or soil amended with 0.5 or 2% (w/w) humic acids (HA) treated with 0 or 20,000 ppm lead and glucose (1 g/100 g soil).

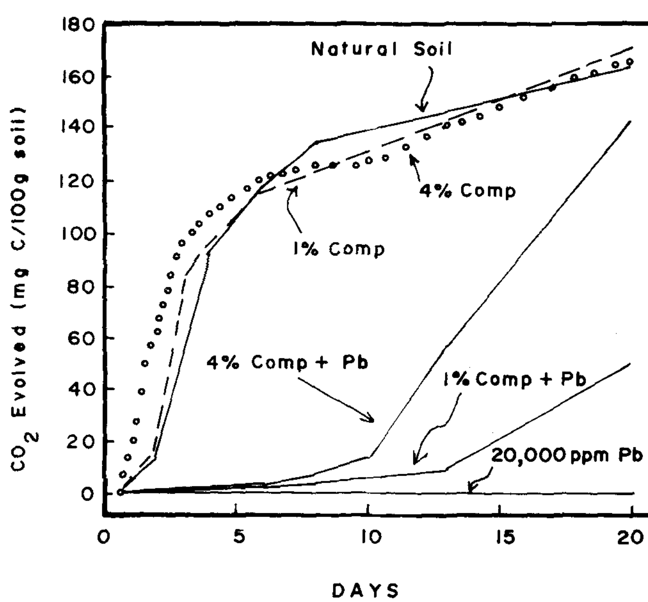

Figure 3. Cumulative amounts of carbon (mg/100 g soil) evolved as CO_2 from natural soil or soil amended with 1 or 4% (w/w) compost (Comp) treated with 0 or 20,000 ppm lead and glucose (1 g/100 g soil).

in which the physicochemical characteristics tend to potentiate the toxicity of a pollutant have been referred to as "high risk" environments, and those in which the toxicity of a pollutant is reduced have been referred to as "low risk" environments (Babich and Stotzky, 1983; Babich et al., 1983). Such differential toxicities of pollutants in environments that differ in physicochemical characteristics must be recognized by regulatory agencies when setting criteria and standards for toxicants in the environment (Babich and Stotzky, 1985).

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