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Lead Concentration in Farmlands in Southern Spain: Influence of the Use of Sewage Sludge as Fertilizer

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Lead content in soils is closely linked to the nature of the parent materials, although this relation can change or even disappear due to other factors involved in soil formation. Such factors include the acid-base and oxidation-reduction reaction, ion binding by organic compounds, Pb absorption by clays and organic compounds, and local dissolution and transport by organic acids. In addition, soil Pb content is also affected by biogeochemical cycles. Soil pH is another factor that influences Pb levels; in general, this element is more mobile in acid than in alkaline soils, and tends to form residual concentrations in the latter (Cannon and Hopps 1970). The distribution of Pb varies in soil horizons of different depths, and is more abundant in more superficial horizons. This accumulation depends not only on the composition of the soil, but also on atmospheric contamination and the proximity of heavily transited roads or other sources of exhaust products from motor vehicles (Reaves and Berrow 1984). An additional source of pollution is Pb in pesticides, and in sewage sludges used as fertilizers in farmlands. Within the ecosystem, soils retain a portion of the products that are applied to them, and thus behave as a reservoir of toxic substances, including Pb. These deposits represent an important route through which toxins are incorporated into subterranean and surface bodies of water, into plant tissues and into the human food chain (Goyer 1988; Alegría et al. 1991).

In this study we determined the degree of Pb contamination in farmlands on the Mediterranean coast of the province of Granada in southern Spain (Figure 1). The area studied is farmed by intensive cropping of sugarcane, green vegetables, grains and tropical fruits, and contains industries, heavily-travelled highways and many small towns and cities, in addition to farmlands. Pesticides and fertilizers are frequently applied, and sewage sludge recovered from industrial and urban wastes is also used as a fertilizer. We therefore also measured Pb in sewage sludge sampled from river beds running alongside farm plots. We sought correlations between the presence of Pb in different samples and their proximity to potential sources of pollution (e.g. highways or industries), and examined the influence of sewage sludge as a source of Pb in soils. In addition, we analyzed the geochemical characteristics of the area, their influence on Pb fixation and retention, and Pb availability to nearby vegetation and groundwater tables.

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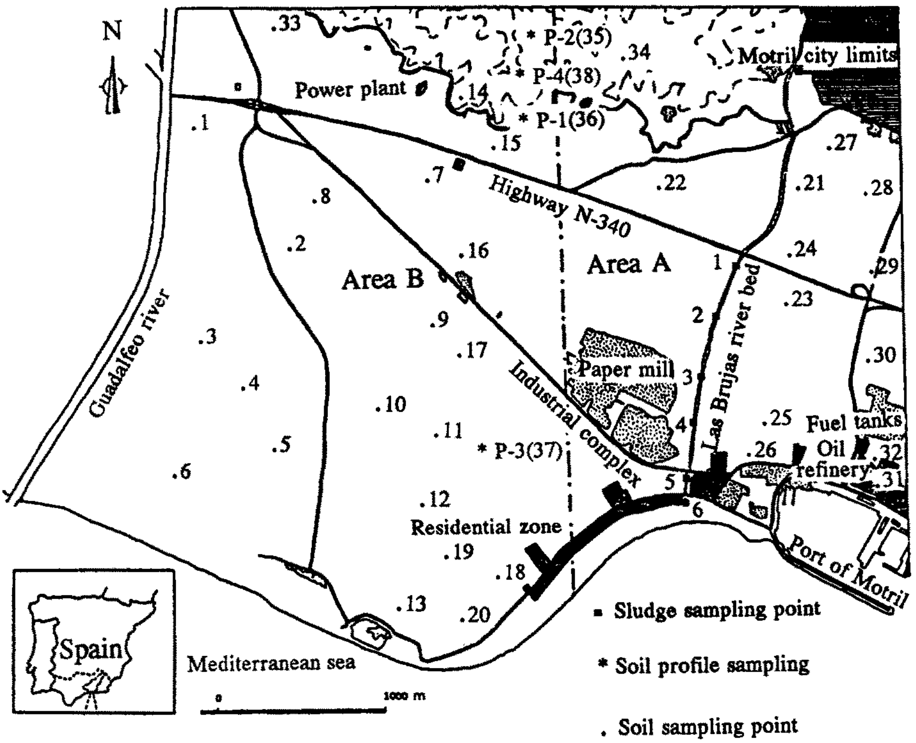

Figure 1. Geographical location of the study area and sampling points used to determine concentrations of Pb in soils and sewage sludge from farmlands on the Mediterranean coast of the province of Granada in southern Spain.

MATERIALS AND METHODS

The arable layer of soil was sampled at 38 different sites, according to the random sampling method proposed by Bridges and Davison (1982). Each sample consisted of 2 kg of soil taken from a depth of 0 to 30 cm. For soil studies, four soil profiles were examined to establish their type and analytical characteristics, in accordance with the rules proposed by the FAO (1977). Soil types were classified according to the systems recommended by the FAO (1989) and the USDA Soil Survey Staff (1990).

Triplicate samples of 500 g of sewage sludge were collected from six sewer outlets opening into the Las Brujas River bed, which crossed the study area. These sewers drained large amounts of waste from the nearby paper mill, cement factory, fuel deposits and refineries, distilleries and sugar mills, as well as urban waste from the city of Motril.

The samples of soil and sewage sludge were dried at room temperature for 2 wk, then homogenized, sieved through a 2-mm sieve (USDA Soil Survey Staff 1975), and stored in polyethylene containers at 4°C until analysis. Sieved soil samples were divided into two portions; one was used for routine analysis as the fine soil fraction (<2 mm) (Ministerio de Agricultura 1971; Soil Conservation Service 1972), and the other was ground in an agate mill for the determination of organic carbon (Tyurin 1951), nitrogen, carbonates (Ministerio de Agricultura 1971), bases and cationic exchange capacity (Soil Conservation Service 1972).

Before Pb determinations were done, the samples were mineralized in a microwave acid digestion bomb (Parr 4782), which was heated in a Moulinex FM-460 microwave oven set at 15-100% full power (600 W) in 25% increments. Two-hundred-fifty mg of dried, homogenized soil or sludge was weighed in the internal capsule of the digestion bomb. Then 4 mL of 65% nitric acid (Merck Suprapure) were added to the capsule, and the bomb was sealed and placed in the microwave oven at the maximum setting for 90 sec. The bomb was cooled to -18°C over 45 min before the capsule containing the sample was removed. Four mL of 40% hydrofluoric acid (Merck Suprapure) and 2 mL 70% perchloric acid (Merck Suprapure) were added, and the capsule was heated in a sand bath to 130°C for 90 min. The capsule was then cooled, 1 mL nitric acid was added, and the mixture was brought to a final volume of 100 mL with ultrapure water (resistivity 18 MΩ cm, Millipore Milli-Q system). This solution was filtered through Whatman filter paper to remove solid residues. All samples were analyzed in triplicate.

In accordance with the recommendations of several authors, we took the physicochemical characteristics of the soil samples into account in optimizing the digestion process (Bettinelli et al. 1986).

Lead concentrations in soils and sludges were determined by electrothermal atomization-atomic absorption spectrometry (ETA-AAS), with a Perkin-Elmer 2380 double-beam AAS apparatus equipped with a deuterium arc background corrector and a 11 mA hollow cathode lamp, at a slit width of 0.7 mm. The samples were atomized in a Perkin-Elmer HGA-400 furnace and pyrolytic graphite tube with a L'vov platform at 283.3 nm. The samples were injected manually with a Pipetman micropipet. Signals were recorded with a Perkin-Elmer 024 potentiometric recorder. The temperature-time program for the graphite furnace was optimized on the basis of previous assays with standard reference material (River sediment, SRM 2704) certified by the National Bureau of Standards (NBS). Samples were mineralized at 750°C, with 200 μg $NH_4H_2PO_4$ and 10 μg NH_4NO_3 as a matrix modifier per 10 μL aliquot of solution to be analyzed. The atomization temperature that yielded maximum signals was 2000°C, with an integration time of 6 sec.

The calibration plot was obtained from a standard solution of 1.00 ± 0.002 g Pb (Titrisol, Merck). The equation for the calibration plot was: absorbance = $8.95 \cdot 10^{-4} + 2.47 \cdot 10^{-3}$ [Pb, ng/mL], with $r = 0.9998$ and $\alpha = 1\%$ (α = level of significance). The equation was linear between 0.04 ng/mL and 1 μg/mL. To rule out possible interferences from the matrix, we used the method of standard additions of analyte.

The accuracy and precision of the analytical method were checked with recovery assays. The percent recoveries from three assays of each of five different samples (soils and sludges) ranged from 97.88% to 100.61%. The results of 10 determinations in NBS-certified reference material (River sediment, SRM 2704) showed a Pb content of 165.5 ± 6.0 μg/g, as compared with a certified value of 161 ± 17 μg/g. These results are expresed as mean ± standard deviation with a confidence interval of 95% about the mean ($p < 0.05$ and Student's t of 2.262).

Once the analytical conditions had been optimized, Pb concentrations in samples of soil and sewage sludge were determined.

For statistical analysis, we used one-way ANOVA followed by Tukey's test, with levels of significance of 5%, 1% and 0.1% (BMDP statistical software package).

RESULTS AND DISCUSSION

The analytical technique we propose is suitable for the determination of Pb in soils and sewage sludges. Our findings were comparable to those reported by several authors (Bettinelli et al. 1986; Kemp and Brown 1990; AOAC 1990) who analyzed similar materials. The accuracy, precision, sensitivity and detection limits we obtained were sufficient within the range of Pb concentrations in the samples analyzed in the present study (Horwitz 1982). Our technique can be used as a routine analysis in quality control assays of soils, and to analyze products used in agricultural treatments; in addition, our method is potentially useful as an indicator of the degree of environmental contamination, and of the possible middle- and long-term risk to vegetation, subterranean and superficial bodies of water, and higher links in the food chain.

Mean levels of Pb and the range of concentrations in soils and sewage sludges analyzed are shown in Table 1.

Table 1. Concentrations of Pb (dry weight) in soils and sewage sludge from farmlands on the Mediterranean coast of the province of Granada in southern Spain.

		Pb concentrations (μg/g)	
Sample	**Source**	**Mean ± SD**	**Range**
Soils (n=38)	Farmlands	115.69 ± 67.91	10.40 - 313.60
Sewage sludges (n=18)	Las Brujas River bed	371.87 ± 634.12	88.00 - 1664.00

The mean concentrations of Pb in farmlands was 115.69 ± 67.91 μg/g dry weight. The variability between different sampling sites may have been due to a number of factors that can raise the natural concentration of Pb in soils (normally 10-30 μg/g) (Goyer 1988). The most important factors were atmospheric pollution, the presence of industries that produced contaminating wastes, and the widespread use of Pb-containing fertilizers (including sewage sludge), pesticides and other phytosanitary products. As a result, the concentrations of Pb found were higher than those reported by other authors (McKeague and Wolynetz 1980; Reaves and Berrow 1984; Landry and Celardin 1988; Kabata and Dudka 1991). According to Boon and Soltanpour (1992), soil Pb concentrations above 500 μg/g denote a high degree of contamination and risk, and are usually associated with nearby sources of pollution.

In the present study we were unable to establish a direct correlation between Pb concentration at a given sampling site and proximity to highway N-340, the paper mill or the industrial complex (see Fig. 1). Linear correlation coefficients (r) between the two variables ranged from 0.0206 to -0.0433 in farmlands, and from 0.1567 to -0.6312 in sewage sludges. In contrast, Pb contamination was significantly greater ($p < 0.01$) at sites near the Las Brujas River bed, and near canals transporting industrial and urban wastes (Area A, Figure 1), than at other sites (Area B). We attribute this finding to the use of sewage sludge as fertilizer in farmlands lying along the river bed; in these extensive areas, sugarcane, a traditional local crop, is grown.

Mean concentrations of Pb in sewage sludge was 371.87 ± 634.12 μg/g dry weight (Table 1), a figure that makes it unadvisable to use this material as fertilizer. After a single treatment, this metal can continue to affect crops for years. However, some chemical fertilizers, pesticides and even irrigation water can raise soil Pb concentrations. This may be the cause of the high levels of Pb recorded at some sampling points where sewage sludge was not applied.

Analytical data of the different soil profiles are shown in Table 2. Soils sampled at higher elevations were coarse-textured and poor in organic matter, with low salinity and low cationic exchange capacity. In contrast, farmlands lying closer to sea level were comparatively richer in organic matter, and were characterized by surface salinization caused by groundwater tables at shallow depths, together with the fine-textured nature of these soils. These factors increased Pb accumulation in lower-lying farmlands. Moreover, their alkaline pH favored Pb retention and immobilization, leading to residual concentrations of insoluble Pb compounds that are relatively unavailable to the plant, and that do not usually enter the adjacent groundwater tables. In addition, lead absorption by plants depends on a number of factors such as the accumulation and distribution of the metal in the different soil profiles, and the physiological and metabolic characteristics of the plant itself. Plant development is impaired in soils rich in heavy metals, although adaptive mutations may lead to the accumulation of large amounts of the element in plant tissues (Goyer 1988). The ingestion of contaminated plants by animals raised for human consumption can lead to severe reductions in agricultural production, and can bring heavy metals into the human food chain (Alegría et al. 1991). These considerations, together with the elevated concentrations of Pb found at some sampling points, suggest some degree of middle- and long-term risk for crops grown in this area, and possible repercussions for human health.

Table 2. Analytical data of the soil profiles.

		Depth	%			pH	E.C.^{a}	Organic fraction %		
Soil	Horz.	cm	Sand	Silt	Clay	H_2O	dS m^{-1}	O.C.^{b}	N	C/N
Typic xerorthent										
1055-1	A	0-27	44.8	43.0	12.2	8.4	0.54	0.398	0.063	6.0
	AR	27-70	50.6	37.8	11.6	8.6	0.57	0.195	0.048	4.0
	R	> 70	59.9	31.2	8.9	8.7	0.53	0.140	0.028	5.0
Typic xerorthent										
1055-2	Apz	0-20	53.4	34.5	12.1	8.3	5.13	1.019	0.165	6.0
	C1	20-61	47.6	39.1	13.3	8.3	3.93	0.433	0.083	5.0
	C2	> 61	33.5	52.8	13.7	8.5	4.91	0.405	0.081	5.0
Aquic xerofluvent										
1055-3	Apz	0-18	49.4	34.8	15.8	8.7	7.02	1.676	0.194	8.6
	Cg1	18-42	46.0	27.8	26.2	8.6	1.46	0.989	0.188	5.3
	2Cg2	42-62	85.4	8.6	6.0	8.7	1.05	0.175	0.028	6.3
	2Cg3	> 62	24.8	60.1	15.1	8.6	0.85	0.442	0.078	5.7
Fluventic xerochrept										
1055-4	Apz	0-18	41.2	41.9	16.9	8.4	0.59	1.257	0.154	8.0
	Bw	18-55	21.5	59.5	19.0	8.6	0.93	1.396	0.171	8.0
	C	> 55	4.9	76.3	18.8	8.5	0.99	0.861	0.121	7.0

		Exchangeable cations,cmol(+)kg^{1}					%		KPa^{d}	
Soil	Horz.	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	CEC^{c}	V	$CaCO_3$	33	1500
Typic xerorthent										
1055-1	A	Sat.	1.20	0.58	1.40	7.1	100	13.4	16.21	6.77
	AR	Sat.	2.77	0.67	0.70	12.2	100	6.6	15.53	6.83
	R	Sat.	3.50	0.53	0.52	9.2	100	5.2	9.91	5.34
Typic xerorthent										
1055-2	Apz	Sat.	3.08	0.43	1.25	8.1	100	1.7	13.36	3.92
	C1	Sat.	2.77	0.24	1.06	6.0	100	3.4	15.10	3.90
	C2	Sat.	3.47	0.10	1.06	5.0	100	4.1	17.69	3.97
Aquic xerofluvent										
1055-3	Apz	Sat.	9.84	1.01	1.82	11.1	100	8.4	24.68	6.32
	Cg1	Sat.	3.40	0.01	0.19	9.2	100	8.0	20.78	4.67
	2Cg2	Sat.	0.98	0.02	0.08	3.0	100	2.9	5.08	1.37
	2Cg3	Sat.	6.16	0.05	0.14	7.0	100	7.3	31.17	4.87
Fluventic xerochrept										
1055-4	Apz	Sat.	1.86	0.29	0.01	8.1	100	4.2	21.95	5.20
	Bw	Sat.	3.08	0.14	0.10	9.1	100	6.2	28.67	6.23
	C	Sat.	4.69	0.19	0.10	7.1	100	4.6	38.58	6.47

[a] Electrical conductivity. [b] Organic carbon. [c] Cations exchangeable capacity [cmol(+)kg^{-1}]. [d] Water content (%).

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