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Barium uptake by maize plants as affected by sewage sludge in a long-term field study

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ABSTRACT

A long-term experiment was carried out under field conditions in Jaboticabal, SP, Brazil, with the objective of evaluating the concentration of Ba in soil and in maize plants grown in a soil treated with sewage sludge for nine consecutive years. During 2005/2006, maize was used as test plants and the experimental design was in randomized complete blocks with four treatments and five replicates. Treatments consisted of: 0.0, 45.0, 90.0 and 127.5 t ha^{-1} sewage sludge (dry basis). Sewage sludge application increased soil Ba concentration. Barium accumulated in the parts of maize plants were generally affected by the successive applications of sewage sludge to the soil. However, the concentration of Ba in maize grain did not exceed the critical levels of Ba for human consumption. Sewage sludge applied to soil for a long time did not affect dry matter and grain production, nevertheless had the similar effect of mineral fertilization.

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1. Introduction

Although the use of sewage sludge in agriculture represents one of the most viable alternatives for final disposal, the presence of toxic metals may limit its application because of the risk of soil contamination and transfer via the food chain by absorption and translocation of these elements in plants [1]. Among these metals, barium (Ba) has been least studied. However, recently Ba was included in a list of elements that pose a risk to human health and are most commonly found in cases of soil contamination [2,3].

Barium is an alkaline earth element which occurs as a trace metal in igneous and sedimentary rocks. In nature it occurs principally in compound states as barite ($BaSO_4$) and withewrite ($BaCO_3$) [4,5]. Barium is a common and quite ubiquitous element, with a mean concentration in the Earth's crust up to 425 mg kg^{-1} (ranging from 550 to 668 mg kg^{-1} in the upper continental crust) [6]. Barium concentration in natural soils is around 100–3000 mg kg^{-1} [2].

Recently, anthropogenic activities have increased Ba concentrations in soil and water. Barium has been used industrially in a variety of forms, for example: in the manufacture of alloys, soap, rubber, linoleum, and valves, as a loader for paper, and has been found in coal as well as in fuel oils. Barium compounds are also used in cement, specialty arc welding, glass industries, electronics, cosmetics, insecticides, pharmaceuticals, and paints [7]. High concentration of total Ba, ranging from 273 to 600 mg kg^{-1} (dry weight), was found in sewage sludge at Sao Paulo State, Brazil (A. Franco and L.P. Firme, unpublished Ph.D. Thesis, CENA, University of Sao Paulo, Piracicaba, SP, Brazil, 2009).

Barium can enter human body through consumption of foods and/or water. Thus, the monitoring of Ba accumulation in soil and water deserves attention in local and international environmental legislation [8]. The ingestion of Ba in soluble forms is highly toxic to animals and human beings. Barium toxicity in animals and human beings has been studied extensively. For example, ingestion of small quantities of water-soluble Ba can result in several human health problems: muscular paralysis, gastrointestinal disturbances, stomach irritation, changes in nerve reflexes, swelling of the brain and liver, heart damage, high blood pressure, and in some cases even death [9–11]. The lowest lethal dose of barium carbonate has been reported to be 57 mg kg^{-1} body weight, of barium chloride 11.4 mg kg^{-1} [12].

Few investigations have been conducted to investigate the effects of Ba on plants and there is also limited information on the toxic effects of Ba on plants. To date no maximum limit of Ba for food safety has been established [13]. Relative to the amount

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Table 1
Chemical properties[a] of the soil in the 0–20 cm layer of the control plots from 1997 to 2006.

Year	pH ($CaCl_2$)	OM (g dm^{-3})	P_{resin} (mg dm^{-3})	K ($mmol_c$ dm^{-3})	Ca ($mmol_c$ dm^{-3})	Mg ($mmol_c$ dm^{-3})	H + Al ($mmol_c$ dm^{-3})	SB ($mmol_c$ dm^{-3})	CEC ($mmol_c$ dm^{-3})	BS (%)
1997/1998	5.7	34	67	4.9	42	19	22	66	88	75
1998/1999	5.4	32	62	4.7	38	17	26	60	86	70
1999/2000	5.3	26	60	4.2	32	18	30	54	84	64
2000/2001	5.3	28	61	4.5	39	14	34	58	92	63
2001/2002	5.3	24	67	4.1	41	14	38	59	97	61
2002/2003	4.9	32	60	4.1	42	22	38	68	106	64
2003/2004	5.3	28	45	3.1	35	15	31	53	84	63
2004/2005	5.7	29	31	1.7	25	20	22	47	69	68
2005/2006	5.1	25	58	4.8	29	12	42	46	88	52

[a] Values on an air dried basis. OM = organic matter. SB = sum of bases. CEC = cation exchange capacity BS = base saturation.

of Ba found in soils, less is bioconcentrated by plants. Nevertheless, there are plants such as legumes, forage plants, Brazil nuts, and mushrooms that can accumulate Ba. Bioconcentration factors from 2 to 20 have been reported for tomatoes and soybean [7].

The Brazilian National Environment Council published maximum levels of Ba in sewage sludge for safe use in agriculture [14] and recently established value guide of Ba in agricultural soils [15]. However, there is minimal information available in the literature regarding Ba contamination of soil and plants, included food crops. No detailed observations of the environmental consequences of long-term application of sewage with regards to Ba have yet been reported.

The objective of this research was to evaluate the effect of application rates of sewage sludge on Ba concentration in soil and its potential availability to maize plants in a clayey soil in a field experiment carried out for 9 consecutive years.

2. Materials and methods

2.1. Field procedures

A long-term field experiment was carried out in the experiment farm of the Sao Paulo State University (Unesp), at Jaboticabal, State of São Paulo, Brazil (21°15′22″ S and 48°15′18″ W, altitude 618 m), for nine years, beginning in 1997/1998. The experimental design was in randomized complete blocks with four treatments (sewage sludge rates) and five replications.

A clayey soil (clay, 51%; silt, 28%; sand, 21% at a depth of 0–20 cm) classified as a clayey texture Typic Eutrorthox, was used for applying sewage sludge and maize was cropped. In the first year, the rates of sewage sludge applications were 0.0 (control, with no sewage sludge and no mineral fertilizers), 2.5, 5.0 and 10.0 t ha^{-1} (dry weight basis). Starting in the second year, the control plots were fertilized with mineral fertilizers according to soil chemical analysis and the recommendations of van Raij et al. [16]. Starting in the fourth year, the 2.5 rate was replaced by 20.0 t ha^{-1} in order to increase the concentration of metals in the soil. Therefore, the accumulated amounts of sewage sludge over nine years were 0.0, 45.0, 90.0 and 127.5 t ha^{-1}.

Maize (*Zea mays* L.) was used as test plant up to the sixth year, sunflower (*Helianthus annuus* L.) in the seventh year, crotalaria (*Crotalaria juncea* L.) in the eightieth, and maize again in the ninth year. The present work reports the results of all the nine years.

Each year before growing season, soil samples of the control plots were taken at the 0–20 cm depth for chemical analysis according to procedures described by van Raij et al. [17] (Table 1).

Based on the soil test results (Table 1) and lime recommendations to maize plants of the State of Sao Paulo [16], the base saturation (BS) was raised to 70% in the control plot (BS = 52%) and in the 20 t ha^{-1} sewage sludge-treated plot (BS = 47%) by adding 1.8 and 2.5 t ha^{-1} of dolomitic limestone, respectively.

The sewage sludge-residue used during the long-term experiment proceeded from the Wastewater Treatment Plant of SABESP (Company of Basic Sanitation of the State of São Paulo) located at Barueri, metropolitan region of São Paulo city, State of São Paulo, Brazil.

In 2005, the sewage sludge was manually spread out on the soil surface and incorporated by harrowing into the top-10 cm-layer. The control plots received mineral fertilizers manually applied in the plow furrows before sowing as follows (kg ha^{-1}): N = 150, as ammonium sulfate (20% N); P = 277, as simple-superphosphate (18% P); and K = 86, as potassium chloride (58% K). In the SS-treated

Table 2
Mineral fertilizers and sewage sludge application rates of the nine-year experiment.

Cropping year	Sewage sludge rates[a] (t ha^{-1})	N		P	K	
		Sowing (kg ha^{-1})	Side-dressing (kg ha^{-1})	Sowing (kg ha^{-1})	Sowing (kg ha^{-1})	Side-dressing (kg ha^{-1})
1997/1998	0.0	–	–	–	–	–
	2.5	–	–	278	50	–
	5.0	–	–	244	45	–
	10.0	–	–	183	34	–
1998/1999	0.0	75	136	167	52	–
	5.0	–	–	–	43	–
	10.0	–	–	–	34	–
	20.0	–	–	–	17	–
1999/2000	0.0	150	245	278	86	69
	7.5	–	–	–	79	69
	15.0	–	–	–	71	69
	30.0	–	–	–	55	69
2000/2001	0.0	150	267	278	86	69
	20.0	–	–	89	67	69
	27.5[b]	–	–	–	48	69
	40.0	–	–	–	9	69
2001/2002	0.0	150	311	278	86	69
	25.0	–	–	–	59	69
	47.5	–	–	–	29	69
	50.0	–	–	–	–	69
2002/2003	0.0	150	311	278	86	69
	30.0	–	–	–	66	69
	60.0	–	–	–	47	69
	67.5	–	–	–	7	69
2003/2004	0.0	50	89	111	34	–
	35.0	–	–	–	–	14
	70.0	–	–	–	–	–
	87.5	–	–	–	–	–
2004/05	0.0	–	–	100	31	–
	40.0	–	–	–	–	–
	80.0	–	–	–	–	–
	107.5	–	–	–	–	–
2005/06	0.0	150	311	278	86	69
	45.0	–	–	–	41	69
	90.0	–	–	–	–	69
	127.5	–	–	–	–	69

[a] Annual accumulated doses.
[b] Since 2000/2001, it was decided to substitute 2.5 t ha^{-1} by 20 t ha^{-1} of sewage sludge, in a dry basis.

plots, K was added as necessary based on soil analysis, in order to supply all plots with the same N–P–K levels. The N and P quantities in the sludge-treated plots were within the range required by the crop [16].

Two side-dressing applications were conducted, each at 156 kg ha^{-1} N (as urea, 45% N) only in the control plots; and 69 kg ha^{-1} of K (potassium chloride) in all plots, at 27 and 40 days after sowing. The N, P and K quantities applied to the soil during the nine-year experiment are presented in Table 2.

Seeds of the maize 'Syngenta NK Traktor S1' hybrid were sowed on November 26th, 2005, spaced 0.9 m between rows, using 8 plants per meter, in 60 m^2 plots (experimental unit).

2.2. Laboratory analysis

Chemical characteristics of the sewage sludge-residue in the 9-year experiment (Table 3) were determined as follows: total N by a microkjeldahl method [18]; total P and K by vanado-molybdate spectrophotometry and flame-photometry, respectively, after digestion with nitric-perchloric acids [19]; and the heavy metals by Atomic Absorption Spectrophotometer (AAS) in an acetylene-air flame (Model: AVANTA GBC, Australia) in extracts obtained by digestion with $HNO_3 + H_2O_2 + HCl$ [20].

The maize plants were cut just above the soil surface and separated into stem, leaf, straw, cob, and grain. Plant samples (6 plants per plot) were harvested 60 d (stem and leaf) and 120 d (straw, cob, and grain) after sowing. Stem, leaf, and straw were separately washed two to three times with tap water and once with deionized water before being oven dried at 65 °C for 72 h. The dry matter yields of each plant part were recorded, and oven dried plant tissues were ground in a Wiley mill, and submitted to nitric-perchloric acid digestion according to Malavolta et al. [19] for determination of Ba by Atomic Absorption Spectrophotometer (AAS) in an acetylene-air flame (Model: AVANTA GBC, Australia).

Barium accumulated in the parts of the maize plants was calculated using the dry matter production and the Ba concentration in the plants (i.e. $A_{Ba} = C_{Ba}$ DM, A_{Ba} is the amount of accumulated Ba (mg $plant^{-1}$) in the plants, C_{Ba} is the Ba concentration (mg kg^{-1}) in the parts of the plant, and DM is the dry matter yield (g $plant^{-1}$) of the maize plant).

Table 3
Chemical composition of the sewage sludge[a], on a dry basis, used for the nine-year experiment.

Cropping year	$N_{kjeldahl}$ (g kg^{-1})	P (g kg^{-1})	K (g kg^{-1})	Cu (mg kg^{-1})	Mn (mg kg^{-1})	Zn (mg kg^{-1})	Cr (mg kg^{-1})	Cd (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Ba (mg kg^{-1})
1997/1998	32	17	4.8	664	228	1800	290	8	268	152	NA
1998/1999	37	11	1.7	551	294	3810	1190	12	595	371	NA
1999/2000	29	17	1.5	660	257	2328	764	8	360	180	NA
2000/2001	29	15	1.8	719	263	1745	699	10	354	171	NA
2001/2002	37	15	2.7	627	287	2354	778	9	350	155	NA
2002/2003	34	22	1.9	722	222	2159	808	11	231	186	NA
2003/2004	41	19	0.1	690	194	2930	736	10	297	173	NA
2004/2005	34	19	1.3	998	206	2474	798	8	299	169	106
2005/2006	34	19	1.3	998	206	2474	798	8	299	169	106

[a] Samples obtained from the Wastewater Treatment Plant of SABESP (Company of Basic Sanitation of the State of São Paulo), at Barueri, State of São Paulo, Brazil. NA = not available.

For the evaluation of crop production, plants were harvested 120 d after sowing from the two central rows of each plot, dried at 65 °C in a forced air oven, and weighed. The data of grain yield were corrected to 13% moisture.

Soil samples (0–20 cm layer) for Ba analysis were collected 60 d after sowing in the ninth year of experiment. In the area reserved for soil sampling of each plot, 10 single samples were collected 10 cm from the sowing furrow, at the side of a maize plant, and composited. Soil samples were air dried and sieved (2 mm) prior to chemical analysis.

Total recoverable Ba was determined following USEPA-3050B method [20]. Briefly soil sample (2.00 g) was placed in a 100 mL beaker and 10 mL of 1 + 1 (v/v) HNO_3 were added, followed by heating on a hot plate at 90–95 °C for 15 min. After heating, concentrated HNO_3 (6 mL) was added and heated for a further 30 min. This operation was repeated until no more brown fumes were formed and the volume of the sample reached about 5 mL. Deionized water (2 mL) and 3 mL of 30% (w/w) H_2O_2 were added and the sample was heated with repeated additions of 1 mL of H_2O_2 (maximum of 10 mL) until the reaction stopped and the volume of the extract reached about 5 mL. Then concentrated nitric acid (10 ml of 35%, w/w) was added and the extract heated at 90–95 °C for 15 min. The extract was then transferred to a 50 mL volumetric flask and made up to volume with deionized water. The concentration of Ba in the digested solution was determined using the AAS.

Total Ba in soil was determined following the method by Jackson [21]. Briefly soil sample (100 mg) was placed in a 50 mL Teflon crucible. The sample was wetted with a few drops of deionized water. Then, 0.5 mL of concentrated $HClO_4$ and 5 mL of 48% HF were added. The crucible, with the lid covering nine-tenths of the top, was placed on a sand bath at a temperature of 200–225 °C, and the acids were evaporated to dryness. The crucible was then removed from the sand bath, cooled, 6 M HCl (5 mL) was added and the suspension was diluted with 15 mL of deionized water. The crucible was then put on a hot plate and the suspension boiled gently for 5 min. When the soil was totally dissolved, the solution was cooled, transferred to a 100 mL volumetric flask and made up to volume with deionized water.

2.3. Statistical analysis

The data were analyzed for variance and when the *F*-test was significant at $p < 0.01$, the Tukey's test ($p < 0.05$) was used for comparison of means. The correlation coefficients (R) between Ba extracted from the soil and the amounts taken up by maize plants (stem, leaf, straw, cob, and grain) were calculated [22]. Statistical analyses (t test, correlation, mean) were performed using SAS procedures [23].

3. Results and discussion

3.1. Soil chemical properties and sewage sludge composition

The Typic Eutrorthox soil was selected for this study because it occurs in large areas in the State of Sao Paulo. The chemical properties of samples obtained from the control plots for 9 yrs of experimentation are presented in Table 1. These data were used to calculate the mineral fertilizers to be applied to those plots. The chemical properties of the soil before sewage sludge and limestone application (Table 1) indicate a high fertility soil according to the nutrient standards established in Raij et al. [16].

The sewage sludge used in the experiment is rich in OM, plant nutrients (except K) and also in heavy metals such as Ba (Table 3).

Table 4
Total recoverable Ba and total Ba in the soil treated with sewage sludge and mineral fertilizers for nine years.

Sewage sludge	Total recoverable Ba ($mg\ kg^{-1}$ dry basis)	Total Ba ($mg\ kg^{-1}$ dry basis)
0.0 $t\ ha^{-1}$ [a]	27.15[b] ± 1.79 c	41.37 ± 1.36 c
45.0 $t\ ha^{-1}$	32.06 ± 0.98 b	45.42 ± 0.77 bc
90.0 $t\ ha^{-1}$	33.62 ± 1.76 ab	48.50 ± 1.47 b
127.5 $t\ ha^{-1}$	35.30 ± 1.84 a	58.24 ± 1.83 a
Mean	30.56 A	49.39 B

[a] Mineral fertilizers (without sewage sludge application).
[b] Mean ± SE of five replicates.
Means followed by the same letters within the column (small case compare rates and capital letters compare methods) are not significantly different by the Tukey's test at $p < 0.05$.

The high concentration of heavy metals is due to the fact that the treatment plant collected sludge from a highly industrialized region. In August 2006, the CONAMA [14] released a list of critical levels of heavy metals and pollutants to sewage sludge land application, including Ba. Barium limit values for sludge spread on agricultural land are: maximum concentration in sewage sludge (1300 mg Ba kg^{-1}, dry matter); maximum amount in sewage sludge (265 kg Ba ha^{-1}). Barium is found in anaerobic sewage sludge at the concentrations ranging from 100 to 9000 mg kg^{-1} (mean concentration of 800 mg kg^{-1}) and in aerobic sewage sludge at the concentrations ranging from 100 to 300 mg kg^{-1} (mean concentration of 200 mg kg^{-1}) [24].

This study presents the concentrations of Ba only in the last two yrs of experimentation. This is because until then Ba was not an element that causes major environmental concerns. Also, the values of Ba in the sludge (mean concentration of 106 mg Ba kg^{-1}, dry matter) were well below the (1300 mg Ba kg^{-1}, dry matter) allowed by CONAMA. However, since this limit was not established in tropical soils, it becomes important to understand Ba behavior in tropical soils amended with sewage sludge, including forms and availability to plants, and translocation to plant parts in order to establish guidelines for Ba-containing sludge applications in order to minimize the risk for the environment and food chain.

3.2. Total barium in soil

Sewage sludge application to the soil significantly increased total recoverable Ba and total Ba in soils as determined by the USEPA-3050B ($HNO_3 + H_2O_2 + HCl$) and Jackson's ($HClO_4 + HF$) method, respectively (Table 4). Total recoverable Ba ranged from 27.15 (control) to 35.30 mg kg^{-1} (in the 127.5 t ha^{-1} accumulated sewage sludge treatment) while the total soil Ba ranged from 41.37 (control) to 58.24 (in the 127.5 t ha^{-1} accumulated sewage sludge treatment).

The Jackson's method provided 38% higher than those provided by USEPA's method (Table 4) as total recoverable Ba does not include Ba within mineral crystal [25]. The data agree with those obtained by Nogueira et al. [26] after applying sewage sludge for nine consecutive years in the same soil. According to the authors, the mean concentrations of Zn and Pb in soil estimated by Jackson's method ($HClO_4 + HF$) were 62% and 32%, higher than those obtained by USEPA's method ($HNO_3 + H_2O_2 + HCl$), respectively. Melo et al. [25] found, for a Brazilian Oxisol, 47% more Ni by the Jackson's method compared to the USEPA's method. One possible explanation for this finding is that heavy metals may be occluded in iron hydroxides and manganese oxides, in which tropical soils are rich [27].

Whereas the USEPA's method does not dissolve the entire soil sample, the Jackson's method does. A study using sewage sludge enriched with Ni applied to a Typic Haplorthox found that part of the added Ni was not recovered immediately after the application of the residue and considered this fact due to a fraction of soil Ni that was not dissolved by the USEPA's method [28]. The USEPA's method recovers all the metals present in the residual fraction of soil samples except those within the structure of silicates so that the percentage of extraction varies from 60% to 100%.

There was a positive correlation between total recoverable Ba and total Ba in the soil estimated by each of the two procedures (Fig. 1).

Considering that the Environmental Agency of the State of Sao Paulo (Cetesb) establishes the value 300 mg Ba kg^{-1} as a reference value for soils of the São Paulo State [8] after nine years of application of sewage sludge from SABESP-Barueri, soil total Ba was much below that limit value. An interim soil quality criterion of 750 mg Ba kg^{-1} for agricultural soils also has been established in Canada [29]. However, a Ba fractionation study was developed to evaluate the Ba availability after applying sewage sludge for nine consecutive years in the same soil [30]. According to the authors, soil Ba distribution decreased in the various fractions in the following order: soluble + exchangeable > manganese oxide > amorphous iron oxide > organic matter > residual > crystalline iron oxide. Barium is mostly bound to the exchangeable fraction, indicative of Ba-phytoavailability and can be a potential risk for the maize plants contamination.

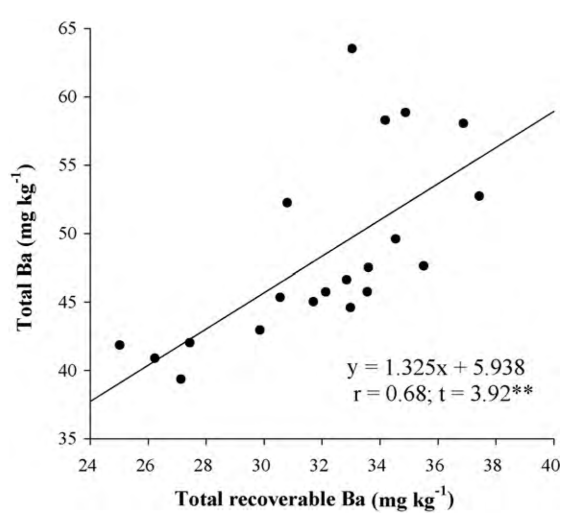

Fig. 1. Correlation coefficients of Pearson (r) and respective statistical significance by t test, obtained between total recoverable Ba and total Ba in a Typic Eutrorthox soil treated with increasing rates of sewage sludge and mineral fertilization for nine consecutive years. **Significant at the $p < 0.01$ level.

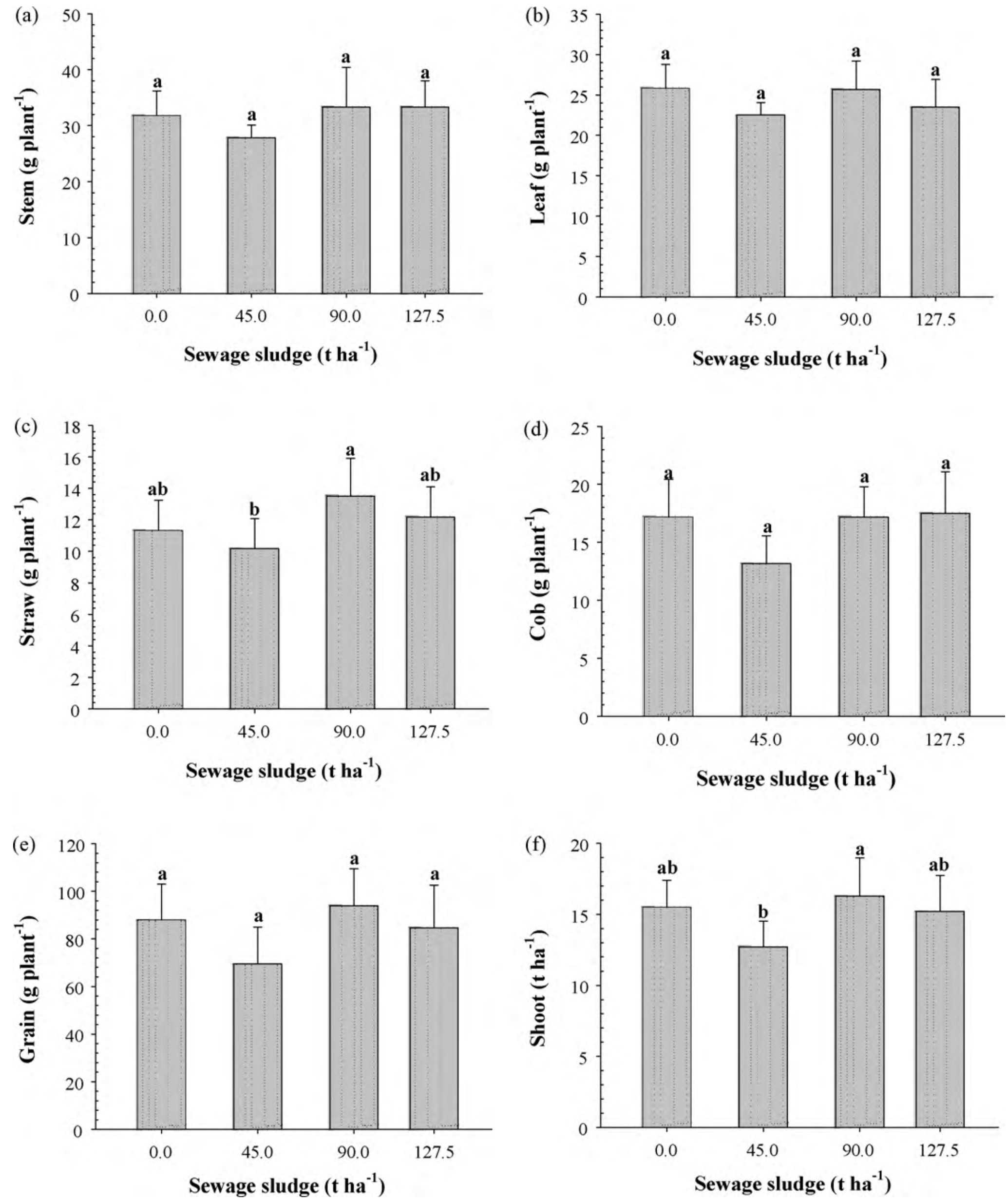

Fig. 2. Dry matter yield by maize plants grown on a Typic Eutrorthox treated with sewage sludge for nine consecutive years. Means followed by the same letters are not significantly different by the Tukey's test at $p < 0.05$. Bars represent the standard error of the mean.

3.3. Maize yield and dry matter production

Dry matter yield of the aerial part of maize plants in the last year of the experiment was affected by the application of sewage sludge; the highest value (16.3 t ha^{-1}) occurred in the treatment plot that received the accumulated amount 90.0 t ha^{-1} and the lowest (12.7 t ha^{-1}) for the treatment pot that received 45.0 t ha^{-1} (Fig. 2f).

The same trend was observed for the different parts of the plant (Fig. 2a–e), except for straw, for which there was a significant difference in dry matter yield between the 45.0 and 90.0 t ha^{-1} treatment. In general, sewage sludge and mineral fertilizers had a similar effect on dry matter yield. These results demonstrate that sewage sludge can be used together with the mineral fertilizer to improve nutritional status and contribute to increase the production of dry matter in maize plants. The data agree with those obtained by Melo [31] after applying sewage sludge for three consecutive years in the same soil. Other reports showed increases in dry matter of maize plants when grown on soil treated with sewage sludge; in a few cases the dry matter yield was higher with sewage sludge than mineral fertilizers [26,32–34].

The sewage sludge has been considered an important urban-waste in cycling plant nutrients and increasing bioavailability of these elements, improving soil fertility and enhancing crop yields [26]. However, in this study, the treatments did not affect grain yield (Fig. 3), likely because of both (sewage sludge and mineral fertilizer) supplying the required amounts of nutrients

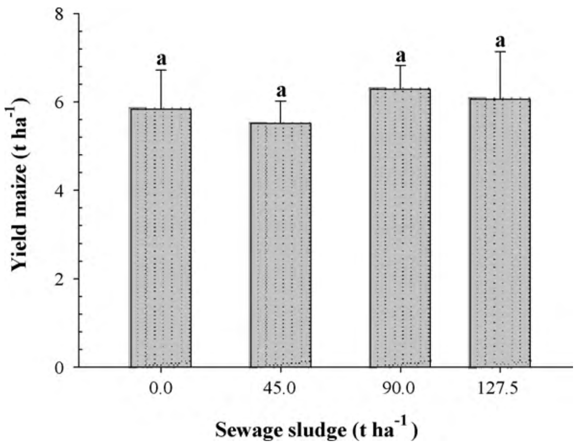

Fig. 3. Yield maize grown on a Typic Eutrorthox soil treated with sewage sludge for nine consecutive years. Means followed by the same letters are not significantly different by the Tukey's test at $p < 0.05$. Bars represent the standard error of the mean.

or the soil being sufficiently fertile so that fertilization was not necessary.

3.4. Barium in maize plants

The concentration of Ba in the stem, leaf, straw, cob, and grain was significantly influenced by sewage sludge application (Fig. 4).

With increasing sewage sludge application rates from 45 to 127.5 t ha^{-1} Ba concentration in the stem, leaf, and straw decreased (Fig. 4a–c) whereas the concentration of Ba in the cob and grain increased with increasing sewage sludge applications rates (Fig. 4d and e). However, Ba concentration in cob was levelled off at the highest sewage sludge application rate (127.5 t ha^{-1}). The inconsistent trend of Ba concentration change with sewage sludge application rates in plant parts may be due to the transfer of Ba from vegetative organs to grain at reproductive growth stage as the plant samples were collected at flowering stage (60 d after germination). The exponential increase in grain Ba concentration with sewage sludge application rate implies that soil Ba accumulation may cause contamination to the food chain and subsequently affect human health. The mechanisms of uptake, transport and accumulation of Ba in crop plants are not fully understood yet and merit great attention in future research.

Barium generally does not accumulate in common plants in sufficient quantities to be toxic to animals. However, large quantities of barium (as high as 1260 mg kg^{-1}) accumulating in legumes, alfalfa, and soybeans grown in soils containing high exchangeable barium content has been reported to cause problems in domestic cattle [35]. In the present work, Ba concentration in stem + leaf + straw is far below critical levels and should not pose any threat to animal health if the plant biomass is used for silage or hay production.

The Ba concentration in the leaves ranged from 90.65 (control) to 105.7 mg kg^{-1} (in the 127.5 t ha^{-1} accumulated sewage sludge treatment). There is very limited information on the toxic effects of Ba in plant tissue [13] which complicates the comparison of results obtained in this study. Also the lack of such information hampers the evaluation of the environmental risk of ambient Ba [36].

The plants did not display any symptoms of Ba toxicity or of deficiency in other nutrients caused by the presence of excess Ba in the soil. Experiment using hydroponic culture indicated Ba toxicity in soybeans by affecting stomatal closure, photosynthetic activity, and overall plant growth [37]. Others investigations of Ba toxicity in plants have been performed [36,38,39]. In general, growth depression has been observed but all these experiments were carried out in greenhouse conditions. One greenhouse experiment using sunflower, mustard, and castor bean grown on soil spiked with 0, 150, and 300 mg Ba kg^{-1} added as $BaSO_4$, Ba did not affect the development of the plants and there was no difference between dry matter productions in soil with or without Ba for each species [40].

Barium concentration in most plants ranges from 2 to 13 mg kg^{-1}, with the exception of blueberries, in which highly elevated Ba levels are reported. The highest concentrations (3000–4000 mg kg^{-1}) have been found in Brazil nut trees, a Ba-accumulating species [6]. Barium concentrations of 200 mg kg^{-1} have been found to be moderately toxic, and an excess of 500 mg kg^{-1} is considered to be toxic [41]. The Ba concentrations in this study were lower in all maize parts, as compared with those previously reported (Fig. 4).

The concentration of Ba in the grains ranged from 0.06 (control) to 1.05 mg kg^{-1} (in the 127.5 t ha^{-1} accumulated sewage sludge treatment) (Fig. 4e). Grain Ba levels did not exceed the normal expected range of 4.2–6.6 mg kg^{-1} in the cereal-grains [6]. Nevertheless, there is no established maximum limit for Ba in food so far. According to Pais and Benton Jones [41], common Ba concentration in foods is less than 0.5 mg kg^{-1}, but Brazil nuts may contain 3 mg kg^{-1} or higher concentrations.

The accumulation of Ba in the stems, leafs, straw, cob, and grain was significantly influenced by mineral fertilization and sewage sludge treatments (Fig. 5).

Considering Ba concentration accumulated in the different parts of maize, the leaves contained the highest values (ranged from 1.7 to 2.7 mg per plant), while the straw and cob were found to have the lowest values (ranged from 0.005 to 0.014 mg per plant).

Barium accumulation decreased in the stem, leafs, and straw with increasing sewage sludge application rate from 90 to 127.5 t ha^{-1} (Fig. 5a–c), similar observations were reported on Ba concentrations in maize plants. The mechanism of the decrease in Ba accumulation with sewage sludge application at high rates is not clear. The application of sewage sludge to the soil significantly increased Ba uptake in the cob and grains (Fig. 5d and e), which is likely due to the transfer of Ba from vegetative organs to cob and/or grain, as also indicated by the decrease in Ba concentration in leaves, stem and straw (Fig. 4). There is little documentation addressing Ba uptake by plants in contaminated environments [42]. Also, there is limited information on the mobility of Ba in plants. Results from Smith [43] showed that the time taken for the transfer of Ba from roots to shoots was very short compared with the age of the trees. Barium was also observed in wheat, although most was concentrated in the stalks and leaves rather than in the grain [44].

The increase in Ba uptake by maize grain (level maximum 0.09 mg Ba per plant) after the application of 127.5 t ha^{-1} of sewage sludge in a period of 9 consecutive years is not likely to pose any threat to human health, because average daily intake of Ba is estimated at around 0.5–0.6 mg Ba kg^{-1} d^{-1}, and the intake of 70 μg Ba kg^{-1} BW is considered harmless [29,45].

Barium may accumulate in different parts of plants [35]. In this work, the percentage of the Ba accumulated in the tissues of the maize plants was higher in leaves and straw (Fig. 6). Accumulation of Ba in wheat plants also mostly occurred in the stalks and leaves rather than in the grain [44]. Nevertheless, due to the paucity of information on the levels of Ba in maize plants it is difficult to evaluate the results.

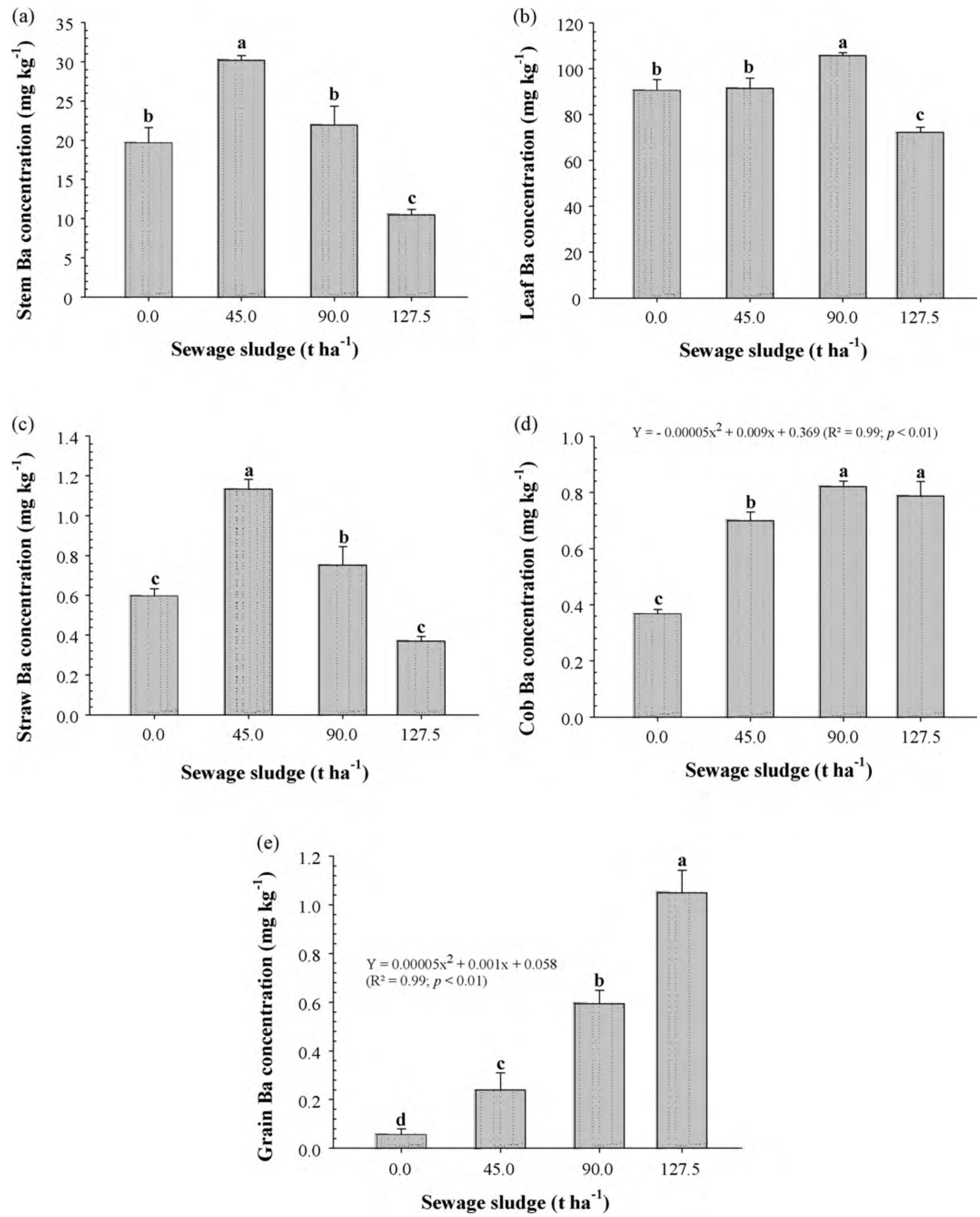

Fig. 4. Barium concentration in different parts of maize plants under varying sewage sludge rates applied for nine consecutive years. Means followed by the same letters are not significantly different by the Tukey's test at $p < 0.05$. Bars represent the standard error of the mean.

3.5. Barium uptake correlation

Correlation was conducted between total recoverable Ba or total Ba in soil and the Ba accumulated in maize plants parts (Table 5). Total recoverable Ba significantly correlated only with Ba accumulated in cob and grain, whereas there was a positive significant correlation between total Ba and Ba accumulated in all the parts of maize plant. The close correlations between levels of Ba in soil and their accumulation in plants were expected, since annual additions of sewage sludge increased available Ba concentration in soil. In this study, no correlation was found ($r = 0.77$, $t = 1.72^{NS}$) between Ba uptake and the yield of maize plants.

Table 5
Correlation coefficients of Pearson's (r) and respective statistical significances by t test, obtained between total recoverable Ba or total Ba and Ba uptake by maize plants grown in a Typic Eutrorthox soil treated with increasing rates of sewage sludge for 9 consecutive years.

Maize plant Ba uptake (mg plant^{-1})	Total recoverable Ba	Total Ba
	mg kg^{-1} (oven dry basis)	
Stem	-0.32^{NS}	-0.62^{**}
Leaf	-0.22^{NS}	-0.50^{*}
Husk	-0.07^{NS}	-0.47^{*}
Cob	0.77^{**}	0.58^{**}
Grain	0.78^{**}	0.87^{**}
Shoot[a]	-0.23^{NS}	-0.56^{**}

[a] Sum of all aerial plant parts.
*Significant at $p < 0.05$.
**Significant at $p < 0.01$.
NS, not significant.

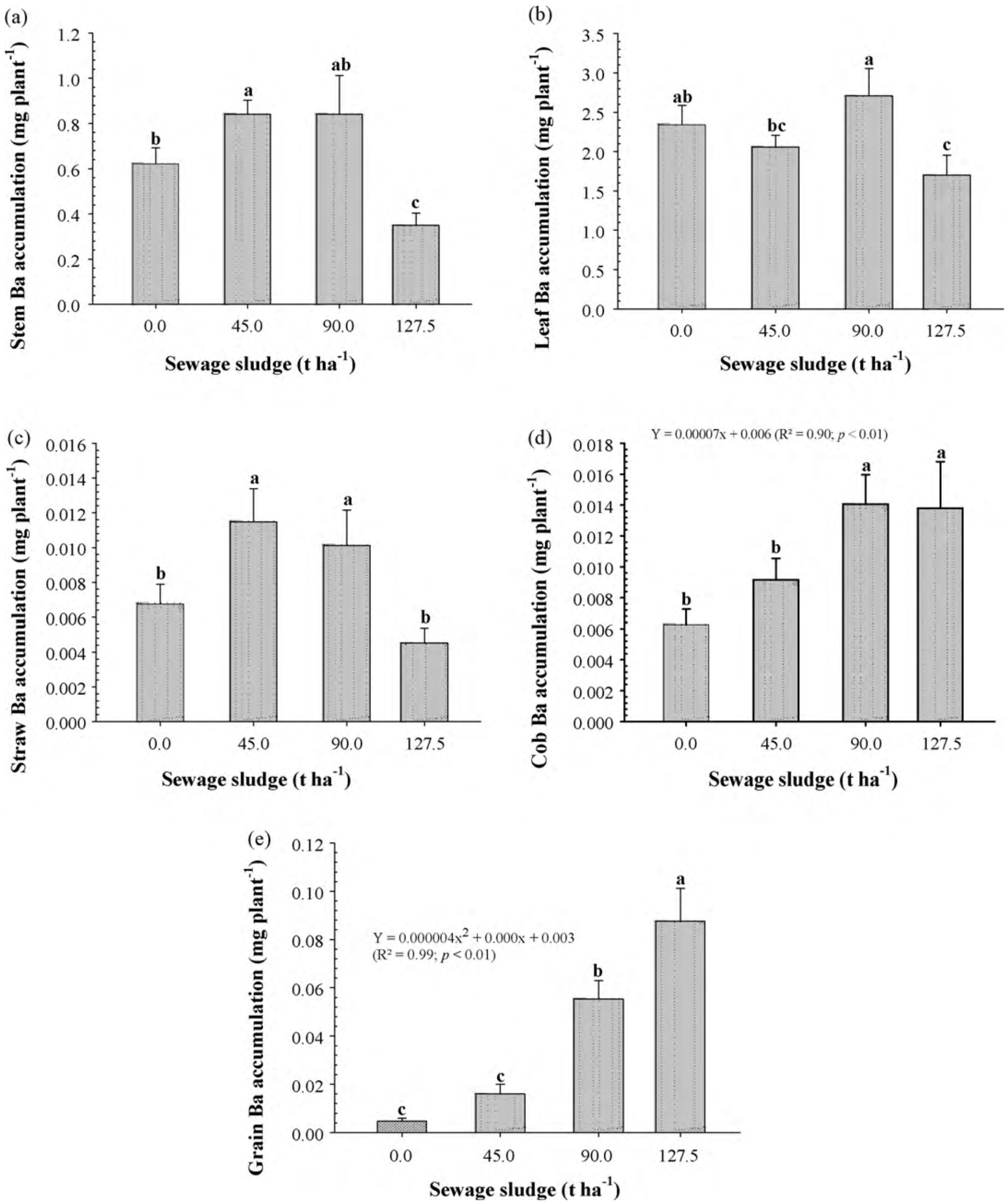

Fig. 5. Barium accumulation in different parts of maize plants under varying sewage sludge rates applied for nine consecutive years. Means followed by the same letters are not significantly different by the Tukey's test at $p < 0.05$. Bars represent the standard error of the mean.

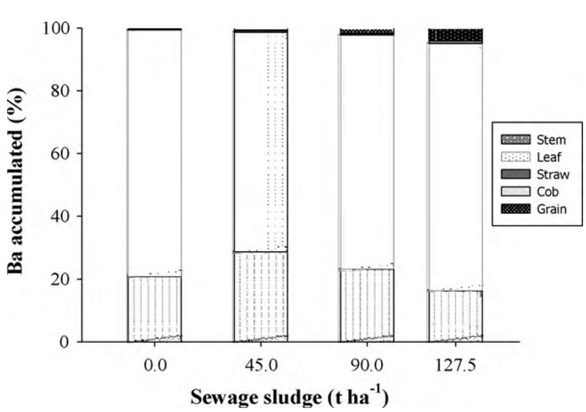

Fig. 6. Distribution of Ba accumulated in parts of maize plant cropped on a soil treated with sewage sludge for nine consecutive years. All the data are means of five replications.

4. Conclusion

Sewage sludge through the accumulated rates applied for nine consecutive years increased soil Ba concentration as estimated by Jackson's method (total Ba) or the USEPA‘s method 3050B (total recoverable Ba). The accumulated contents of Ba in the cob and grain were raised by successive applications of sewage sludge. However, Ba concentration in maize grain does not exceed the critical levels for human consumption. Therefore, sewage sludge is a valuable resource for agriculture if it can be used properly, but cautions need to be exercised as the concentration of Ba in grain increased linearly or exponentially with sewage sludge application rate. Sewage sludge and mineral fertilizers had similar effects on dry matter and grain yield. Further studies on the effects of sewage sludge application on Ba uptake by crop plants would be useful to better characterize the environmental fate of Ba and define the importance of food chain accumulation as a source of human exposure.

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