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Abstract – Beringite and steel shots were mixed with the upper 20 cm of the soil. One year after addition, the extractability in calcium nitrate (0.1 M) and the plant availability of soil-Cd and -Ni were investigated. The addition of beringite (5 % w/w) and steel shots (1 % w/w) led to a lower extractability of Cd and Ni. In the most contaminated plots, the extractability of Cd and Ni after 1 year had decreased, respectively, 54 % and 53 % for beringite and 41 % and 40 % for steel shots. The metal content in different organs of maize plants (shoots, sixth leaf, ear leaf and grains), grown on the field trial, was determined. The Cd transfer from soil to plant decreased following the addition of beringite, except in the most contaminated plots. No decreased soil–plant transfer of Cd was observed after the addition of steel shots. Both the addition of beringite and steel shots led to a lower Ni transfer to the maize aerial organs and grains. No phytotoxicity or deficiency symptoms due to the additives were observed on the plants. The addition of beringite and steel shots seems promising to lower the soil–plant transfer of Ni at such metal contaminated soils. The depth of mixing and the method of application of the soil additives in the field appear to be very significant variables; additional comparative tests are needed, however. (© Inra/Elsevier, Paris.)

sewage sludge / cadmium / nickel / immobilization / soil–plant transfer

Résumé – Immobilisation à court-terme du Cd et du Ni in situ après l'apport de béringite et de grenaille d'acier dans des sols amendés par des boues urbaines. La béringite et la grenaille d'acier ont été mélangées dans les 20 premiers cm d'un sol pollué par des métaux. Un an après leurs apports, des extractions au nitrate de calcium (0,1 M) et la détermination du transfert sol-maïs pour le Cd et le Ni ont été réalisées. L'addition de béringite (5% w/w) et de grenaille d'acier (1% w/w) ont diminué l'extractibilité du Cd et du Ni. Dans les parcelles les plus polluées, l'extractibilité de Cd

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et Ni a été diminuée respectivement de 54% et 53% pour la béringite et de 41% et 40% pour la grenaille d'acier. Après une culture, les teneurs en métaux dans la 6ème feuille, la feuille de l'épi et les grains ont été déterminées. Le transfert sol-plante du Cd a diminué après l'apport de béringite (excepté sur les parcelles les plus polluées), contrairement à un apport de grenaille d'acier. L'addition de béringite et de grenaille d'acier a diminué le transfert du Ni du sol aux parties aériennes du maïs et aux grains. Aucuns symptômes de phytotoxicité ou de carence ont été observés suite à l'apport de ces amendements. L'utilisation de béringite ou de grenaille d'acier dans les sols pollués semble intéressante pour diminuer le transfert sol-maïs du Ni. La profondeur d'enfouissement et la méthode d'application de ces amendements dans les sols devront être étudiées. (© Inra/Elsevier, Paris)

boues urbaines / cadmium / nickel / immobilisation / transfert sol-plante

1. INTRODUCTION

Trace metal contaminated sites are of growing concern and there is a strong need for remediation of these sites. Remediation aims to protect humans, animals and the environment from exposure to hazards by removing the source or interrupting the pathways of pollutants [31]. Two main groups of remediation techniques can be distinguished. The first is the group of the so-called hard techniques such as solidification [3], high pressure water extraction [15] and acid leaching [27]. This group of techniques has the disadvantage that biological activity is impaired and/or the physical soil structure is destroyed. Besides, the hard techniques are quite expensive and may co-generate by-products.

The so-called soft remediation techniques form the second group. These techniques are designed to eliminate exposure and/or hazards without destroying the soil. The methods used can be subdivided into removal of the contaminants by means of phytoremediation technologies [4, 5, 21, 32] or microorganisms [7], and physicochemical in situ immobilization or inactivation.

The main goal of the immobilization technique is to render the trace metals less bioavailable. On agricultural sites the decreased plant availability will lower human and animal exposure to metals through plant-derived products. On heavily polluted bare industrial sites, a vegetation cover might be restored, preventing lateral wind erosion and reducing metal percolation to the groundwater [34].

One of the important factors determining the bioavailability of a trace metal is its mobility in soils i.e. its ability to be transferred into the soil solution. In general, plants readily take up the mobile species of trace metals that are dissolved in the soil solution. Therefore, strong trace metal immobilization seems a solution to minimize their plant uptake by consequence and also to protect the quality of products derived from plants grown on soils containing increased metal concentrations.

Treatment of soils contaminated by trace metals is classically based on the application of lime and phosphates and the addition of organic matter [17]. The addition of lime, however, does not always deliver the aimed effects on the solubility of trace metals [1]. Oliver et al. [26] found that the effect of soil pH on the Cd concentration in wheat and barley grain was very small. Excessive liming may lead to a depression in crop yield [13]. In addition, liming a Zn polluted soil was found to lower, at first, the exchangeable amount of Zn, but with time (6 months), the exchangeable amount of Zn increased [2].

Several other inorganic materials have been tested, mostly in pot experiments. Immobilization of Pb and Cd in soil by either synthetic or natural zeolites reduced the Pb, Cd, Cu and Zn contents of plant tissues [2, 10, 11, 28]. The hydrous oxides of Al, Fe and Mn are also known to enhance metal immobility in soils through specific sorption processes [9, 22, 23]. In the last few years experiments have also been carried out with two industrial products: beringite (a modified aluminosilicate) and steel shots. The addition of beringite to polluted soil samples decreased the mobility of Zn, Cd and Pb and reduced or eliminated their phytotoxicity in bean [23, 33, 35, 36]. Vangronsveld et al. [36, 37] also reported field experiments in which the addition of beringite to a site with mainly Zn/Pb/Cd pollution enabled the restoration of plant growth and biodiversity. In pot experiments, the addition of 1 % w/w of steel shots to samples of trace metal contaminated sites also decreased the plant availability of trace metals [23, 30].

Both beringite and steel shots are industrial products, large quantities are easily accessible and the costs, including soil application, are relatively low compared to hard techniques. Based on the results of beringite and steel shots on bench scale, and the promising results on an industrially Zn/Pb/Cd contaminated soil on field scale, it is important to gain information in field trials on different soil types differing in metal concentration and origin of the contamination. Therefore, these soil additives were tested in the south-west of France on a long-term sewage sludge treated experimental site with increased Cd and Ni contents. The objectives of the field study are to determine if: 1) the addition of beringite and steel shots lowers the extractability of Cd and Ni in soils; 2) there are any toxicity or deficiency symptoms due to the application of the soil additives; 3) Cd and Ni uptake by maize plants is decreased by the addition of beringite and steel shots.

2. MATERIALS AND METHODS

2.1. Sampling site and soil characteristics

A long-term sewage sludge field trial exists at the Inra Couhins experimental farm (Bordeaux, France) on an acid coarse sandy soil (Arenic Udifluvent). The experiment started in 1976 and contained five blocks with four separate plots (3 m * 6 m) in each block which received one of the following four treatments [16]: C = control with inorganic fertilizer only; FYM = farm yard manure at a loading rate of 10 t DM ha^{-1} y^{-1}; S1 = sewage sludge at a loading rate of 10 t DM ha^{-1} y^{-1}; S2 = sewage sludge at a loading rate of 100 t DM ha^{-1} 2 y^{-1}.

The experimental farm received sludge from a sewage treatment plant (Louis Fargues) in the Bordeaux conurbation. It was a solid, anaerobically digested and heat-dehydrated sludge with high Cd and Ni contents arising from effluents discharged by a battery manufacturer [38]. Every year a subsample of the sludge was analyzed for the amount of trace elements. The mean concentration (in $mg \cdot kg^{-1}$) of trace elements for the years 1976–1980 was: Cd 1 830, Cu 488, Zn 3 062, Mn 699, Ni 4 071 and Pb 722. Sludge application was stopped after 1980, because a strong phytotoxic effect on maize was observed (50 % yield decrease on S2 plots). The total sludge loading rates are therefore 50 t DM ha^{-1} (S1) and 300 t DM ha^{-1} (S2).

Two blocks of four plots of the field trial were used for testing soil additives whereas the other three blocks remained unchanged. In April 1995, 1 % by the soil weight (w/w) of steel shots (SS) was mixed with the first 20 cm of the soils in all four plots (C, FYM, S1, S2) of one block. At the same time, 5 % (w/w) of beringite (B) was mixed in the same manner in three plots (FYM, S1, S2) of another of the five blocks. As there was not enough beringite available, it was not mixed with an inorganic fertilized control (C) plot. The application rates for steel shots and beringite were based on former experiments showing that these rates were optimum in light of metal immobilization in combination with a favourable soil structure [23, 35]. The plots of the other three blocks did not receive any soil additive. The reasons for treating only two blocks are given here.

– As the contamination level at the experimental site is very heterogeneous because of its long past, it was chosen to overpass this problem by treating whole plots of 3 m * 6 m accounting for spatial variability instead of dividing each plot into very small untreated, beringite-treated and steel shots treated parts.

– Not enough of the additives was available (especially of beringite) to treat a complete supplementary block of the field trial.

Table I gives the trace element and iron composition of the soil additives steel shots and beringite. The physicochemical soil characterization of the plots that were taken under consideration in the present study are given in *table II*.

2.2. Soil sampling and preparation

Soil samples for the metal-mobility test were taken in April 1995 (just before additives were added) and in April 1996. Subsamples (± 10 kg) from the topsoil (0–20 cm) were collected with a spade at random points (n = 10) in each plot. Samples were air-dried and sieved (< 2 mm) carefully by hand, avoiding the discard of sewage sludge particles with gravel, especially in S2 samples. A nylon sieve was used. Subsamples were oven dried at 105 °C to determine dry matter.

Table I. Trace element content of steel shots and beringite.

	Steel shots (g·kg^{-1})	Beringite (g·kg^{-1})
As	0.07–0.15	
Cd	< 0.01	0.009
Co		0.098
Cr	2–5	0.95
Cu	1–3	0.12
Fe	~ 990	
Mn	6–10	1.1
Ni	0.8–1.5	0.123
Pb	0.01–0.02	0.203
Zn	0.07–0.15	0.63

2.3. Assessment of metal mobility

Cadmium and nickel mobility was assessed based on an extraction in 0.1 M $Ca(NO_3)_2$ (Merck, Suprapur) [38]. All vessels were previously washed in nitric acid (1.4 N) and rinsed with distilled water. Six replicates of 10 g of air-dried soil were shaken end-over-end in plastic flasks with 50 mL of extractant for 2 h. Extracts were filtered through ash-free paper and collected in plastic flasks. The calcium nitrate extracts were acidified with 14 N nitric acid (2 mL) to prevent metal adsorption. All solutions were kept at 7 °C until analysis. Concentrations of metals were determined by flame atomic absorption spectrophotometry (Varian Spectra A20).

2.4. Assessment of metal plant availability

Every year, maize (*Zea mays* L. cv. Inra 260) was sown in April. Agricultural practices were reported previously [38]. The assessment of the metal plant availability was based on the metal concentration of maize cultivated in the field trial. The following plant tissues were analyzed: shoots (at the stage of 24 days [24 d]), sixth leaf (40 d), ear leaf (62 d) and grain (143 d). After harvesting, all plants from each plot were put together to obtain a representative sample for the whole plot. Plant material was washed and then dried at 70 °C for at least 48 h. Thereafter, plant samples were grounded (vegetative plant parts: zirconium covered planetary grinder,

Table II. Physicochemical soil characterization of the plots at the Couhins experimental farm.[a]

	FYM			S1			S2		
Soil additive[b]	UNT	B	SS	UNT	B	SS	UNT	B	SS
Plot number	32	34	39	29	35	40	30	36	37
Clay (g·kg^{-1})	44	55	24	66	53	31	59	73	56
Silt (g·kg^{-1})	100	148	99	122	141	108	103	136	150
Sand (g·kg^{-1})	856	797	877	812	806	861	838	791	794
Organic matter (g·kg^{-1})	13.7	20.2	13.3	17.8	37.5	14.53	30.4	29.3	15.48
CEC (cmol·kg^{-1})	3.5	3.5	2.8	3.7	4.0	3.7	5.1	6.8	4.2
pH H_2O	5.9	7.4	6.3	6.5	7.7	6.6	6.7	7.3	7.0
Total metal conc. (mg·kg^{-1})[c]									
Cd	5.8 ± 0.6	3.9± 0.1	4.1 ± 0.1	38.4 ± 7.4	34.6 ± 6.4	19.6 ± 2.0	111.1 ± 17.4	121.98 ± 17.8	102.5 ± 8.3
Cu	8.7 ± 0.1	10.2 ± 1.0	24.7 ± 1.6	26.8 ± 6.1	26.4 ± 0.4	25.6 ± 0.6	50.8 ± 10.0	55.6 ± 6.9	58.2 ± 6.33
Zn	29.4 ± 2.2	34.2 ± 2.8	22.7 ± 3.1	65.5 ± 9.5	86.3 ± 7.1	47.5± 3.4	165.5 ± 21.2	200.3 ± 2.4	154.3 ± 12.4
Mn	56.5 ± 9.0	83.2 ± 12.4	222.0 ± 9.1	62.1 ± 4.2	122.9 ± 12.6	165.9 ± 2.9	94.6 ± 7.9	132.2 ± 7.1	186.1 ± 4.8
Ni	14.9 ± 0.7	12.4 ± 4.3	25.8 ± 1.9	83.9 ± 17.3	81.4 ± 17.3	51.6 ± 7.5	259.6 ± 42.3	269.0 ± 27.8	241.6 ± 20.4
Pb	49.3 ± 16.3	30.6 ± 2.9	36.1 ± 14.8	44.5 ± 12.8	47.5 ± 6.0	43.1 ± 23.7	68.1 ± 20.8	83.6 ± 7.9	67.8 ± 11.3

[a] Data refer to dry matter (105 °C) of surface soil (0–20 cm) sieved at < 2 mm; [b] UNT: untreated; B: beringite; SS: steel shots; [c] mineralization in nitric (14 N) and chlorhydric (12 N) acid followed by a hydrofluoric attack (mean value ± standard deviation, $n = 3$).

Retch PM4; grains: tungsten grinder) and then stocked in airtight containers until analysis.

2.5. Plant analysis

One gram of the plant material was wet-digested overnight in supra-pure 14 N HNO_3 (10 mL) and 30 % H_2O_2 (20 mL), which was followed by a hot digestion (120 °C for 2 h). The solution was filtered through ash-free paper and adjusted to 100 mL with distilled water. Blanks of reagents and standardized reference (Rye grass CRM 231, Community Bureau of Reference, DG XI, Commission of the European Community) samples were included in the analysis. The concentrations of Cd, Cu and Ni were determined by either flame or electrothermic atomic absorption spectrometry, depending on the concentration. The concentrations of Zn, Mn, Mg, Ca, P and K were determined by inductively coupled plasma emission (Varian liberty 200).

3. RESULTS AND DISCUSSION

3.1. Physicochemical soil parameters

Compared to the FYM application, the application of sewage sludge from 1976 until 1980 led to a strong increase in the total soil content of all six metals under investigation and especially of Ni and Cd (*table II*). The strongest increases were found in plots that received the highest load of sewage sludge (S2). The application of sewage sludge also changed the physical soil characteristics: the pH and the CEC slightly increased. There were still some sewage sludge particles left in the S1 and S2 plots, leading to high standard errors of the total metal concentration. Comparison of the metal concentration in the different plots shows that the experimental site became rather heterogeneous after 20 years.

Comparing the metal content in the plots S1 and S2 to the European Union upper limits (i.e. [in $mg \cdot kg^{-1}$] Cd: 3, Cu: 140, Zn: 300, Ni: 75 and Pb: 300) [8] for soils that have been applied with sewage sludge, it can be concluded that the Cd and Ni concentrations are still well in excess. Problems related to the high contents of these two metals might be expected, and further research will focus therefore mainly on Cd and Ni.

The pH of the plots that received beringite and steel shots was higher than the pH of the untreated plots (*table II*). This is not surprising since on the basis of former experiments we already had quite strong evidence that the addition of steel shots and beringite would cause an increase of pH, with the effect of beringite being more pronounced [23, 24, 37]. The addition of steel shots caused a strong increase of the Mn concentration, due to the high Mn content of steel shots (*table I*).

3.2. Metal mobility

Figure 1 shows the extractable amount of Ni and Cd as a function of the total Ni and Cd content of the soil. The year 1995 presents the metal mobility just before the addition of steel shots and beringite, whereas 1996 presents the mobility 1 year later.

In the case of all three soil treatments (FYM, S1 and S2) the addition of beringite led to a decrease of extractable Ni (84, 82 and 53 %, respectively). The addition of steel shots decreased the Ni extractability in the S1 and S2 plot with 53 and 40 %, respectively. Both beringite and steel shots lowered the extractability of Cd in the different plots. The decreased Cd extractabilities in the plots FYM, S1 and S2 are 88, 56 and 41 %, respectively, when beringite was added and 58, 56 and 41 %, respectively, when steel shots were added. From these data it can be concluded that 1 year after application, both beringite and steel shots are able to lower the extractable amount of Ni and Cd, with the effect of the addition of beringite being more pronounced. These immobilizing capacities of beringite and steel shots are consistent with the results of a number of pot experiments that have been carried out during the last few years [23, 24]. Furthermore, the effect of B and SS on the Cd and Ni extractability seems to increase with an increasing total metal content of the plots. The only exception is the effect of steel shots on Ni in the FYM plot. The slightly

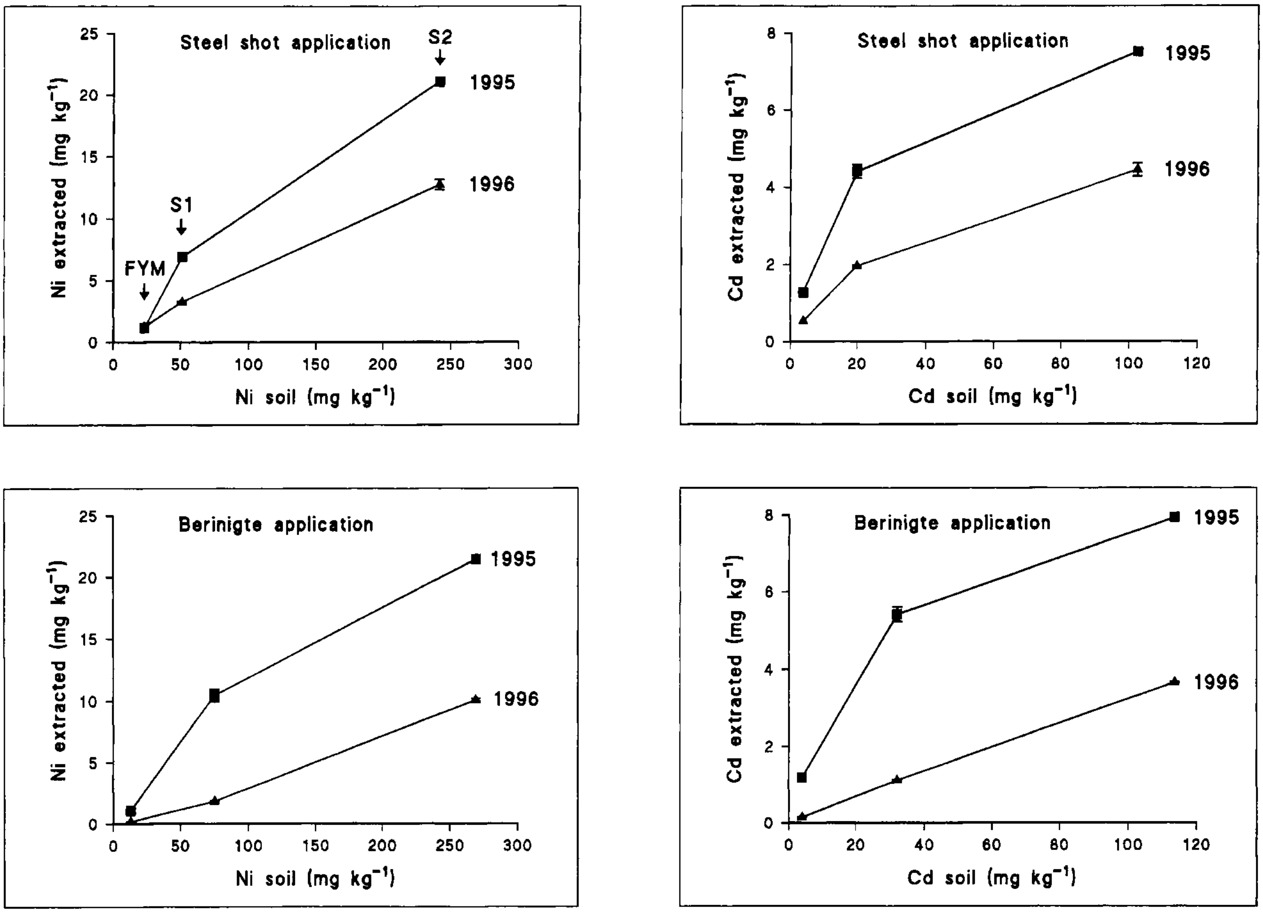

Figure 1. Ni and Cd extracted with $Ca(NO_3)_2$ just before and 1 year after the addition of beringite and steel shots. FYM: farm yard manure 10 t DM ha^{-1} y^{-1}; S1: sewage sludge 10 t DM ha^{-1} y^{-1}; S2: sewage sludge 100 t DM ha^{-1} 2 y^{-1}.

increased Ni extractability may be due to the Ni present in the steel shots (*table I*).

The high metal immobilizing capacity of beringite is based on chemical precipitation, ion exchange and crystal growth. The combination of these three sorption mechanisms may explain its high metal sorption capacity [6]. The strong alkalinity of the product perhaps leads to metal immobilization as well. In a sandy soil from Belgium, it has been shown that beringite leads to co-precipitation of metals such as Zn with silicates [14]. For steel shots, iron oxide formation is a plausible process; iron oxide particles sampled in steel shots treated soils were identified as lepidocrocite, maghemite and magnetite [30]. Metal immobilization may take place through the processes of co-precipitation with or sorption on the newly formed iron oxides. However, Manceau et al. [19] stated that the principal active compound of the steel shots might be the Mn present in this material. By means of extended X-ray absorption fine structure spectroscopy, it was shown that phyllomanganates are formed when steel shots are added to the soil. Phyllomanganates are known for their strong Zn and Pb immobilizing properties and might possibly immobilize other metals as well [14, 20].

3.3. Plant yield

The grain yields during the period 1984–1994 and in 1996 are listed in *table III*. For the untreated plots, the grain yield in 1996 was numerically below the average yield of the period 1984–1994. On the untreated S1 plot, the yield was below the minimum value of the preceding period. The 1996 grain yield on the beringite and steel shots plots are below the average of the preceding period, except for the maize of the S2 plot that received steel shots. The yields fall, however, in the range of values obtained for the period 1984–1994. It can therefore be concluded that the addition of beringite and steel shots had no negative impact on the grain yield.

Another important parameter is the uptake of major nutrients. It is known, for example, that P is strongly retained in soils by hydrous oxides of iron and aluminium [29]. Even though there seems to be a slightly decreased P uptake after the addition of beringite and steel shots (data not shown), the P content ([in $mg \cdot kg^{-1}$] sixth leaf 3.2–4.4; ear leaf 3.1–3.7; grains 3.1–3.3) is above the minimum critical value (2.5 $mg \cdot kg^{-1}$) reported by Halliday and Trenkel [12]. The values of the N and K content of plants grown on the field trial were above the critical values as well. The addition of beringite and steel shots did not lead to deficiency of major nutrients.

3.4. Metal uptake by maize plants

In a first approach, the metal content of the maize plants 1 year after the addition of the soil additives was compared to the average metal content of plants grown on the same plot during the 10-year period before the addition of the soil additives (*table IV*). For this 10-year period, mean values and standard errors are given. The results indicate that there is a high inter-annual variance which is quite typical for studies carried out in the field. However, no trend is visible in time (e.g. no increase or decrease in concentration with the years; data not shown). Beringite and steel shots are known for their capacity to imobilize a wide range of metals and some antagonisms such as Zn/Cd uptake by plants exist. Therefore, in addition to Cd and Ni, Zn, Cu, Mn and Fe are included in *table IV* as well.

Table III. Maize grain yield ($t \cdot ha^{-1}$ dry weight).

Soil treatment		84–94	96
Untreated	FYM	7.2 ± 1.1	5.9
	S1	6.5 ± 0.7	5.2
	S2	6.6 ± 0.7	6.2
Beringite (5 % w/w)	FYM	7.2 ± 0.9	6.8
	S1	6.6 ± 0.9	6.5
	S2	6.0 ± 0.6	5.4
Steel shots (1 % w/w)	FYM	7.0 ± 0.9	5.8
	S1	6.8 ± 0.8	5.5
	S2	7.1 ± 0.7	7.2

The inter-annual variance is too high to base final conclusions on this data. However, some trends can be observed. All the data in *table IV* that are given in **bold** characters represent data from 1996 which are lower than the minimum value (data not shown) obtained during the period 1984–1994 on the same plot. If the 1996 metal content of plants grown in the beringite and steel shots treated plots is below the minimum value of the 1984–1994 period and the 1996 metal content of plants on the untreated plot fall in the 1984–1994 range, we might consider that the lower metal content is most probably due to the addition of beringite and steel shots. For Ni, we find this situation in both S1 and S2 plots with beringite and steel shot applications. Therefore, both beringite and steel shots appeared to be able to lower the Ni transfer from the soil to the aerial maize plant parts.

The Cd content of the sixth leaf of plants grown on S1 plots with the addition of steel shots determined in 1996 is lower than the lowest 1984–1994 content. This suggests that steel shots have the potential to reduce the Cd uptake by maize. Even though the Zn contents in the sixth leaf and ear leaf of maize grown on the steel shots treated plots are below the mean value of 1984–1994, they still fall

Table IV. Mineral composition maize tissues (mean values ± standard deviation, $n = 3$).

Element		Year	Untreated			Beringite addition (in 1996)			Steel shots addition (in 1996)		
			FYM	S1	S2	FYM	S1	S2	FYM	S1	S2
Ni	6th leaf	84–94	1.1 ± 0.8	4.7 ± 1.9	11.6 ± 4.0	1.1 ± 0.6	3.9 ± 1.6	8.1 ± 2.7	1.1 ± 0.9	2.5 ± 0.9	9.6 ± 3.2
($mg \cdot kg^{-1}$)		96	1.2	4.0	5.9	0.8	**1.9**[a]	**6.0**	0.6	**1.3**	**3.7**
	ear leaf	84–94	0.6 ± 0.2	1.7 ± 0.8	3.4 ± 0.7	0.6 ± 0.2	1.8 ± 0.4	3.3 ± 0.7	0.5 ± 0.3	1.2 ± 0.2	3.7 ± 0.9
		96	1.0	1.9	2.4	0.5	**0.8**	**1.9**	0.5	**0.7**	**1.3**
	grain	84–94	1.0 ± 0.3	1.9 ± 0.6	3.6 ± 0.8	0.9 ± 0.2	2.3 ± 1.1	4.1 ± 1.8	0.6 ± 0.2	1.7 ± 1.1	3.8 ± 2.8
		96	**0.5**	1.7	2.8	**0.6**	1.3	**1.9**	0.6	1.0	2.2
Cd	6th leaf	84–94	21.4 ± 10.2	65.6 ± 13.0	72.1 ± 9.4	17.1 ± 7.4	58.2 ± 14.4	73.2 ± 11.2	13.9 ± 5.21	55.1 ± 12.5	82.5 ± 17.1
($mg \cdot kg^{-1}$)		96	28.1	63.6	71.0	7.7	44.5	72.9	8.3	**29.7**	82.3
	ear leaf	84–94	7.2 ± 3.4	30.1 ± 9.7	29.8 ± 10.6	6.1 ± 2.5	26.1 ± 6.6	31.7 ± 7.0	5.2 ± 2.1	25.1 ± 6.9	37.0 ± 8.7
		96	16.2	31.7	26.7	3.1	15.7	31.5	3.8	15.2	34.9
	grain	84–94	0.2 ± 0.1	0.5 ± 0.1	0.6 ± 0.2	0.2 ± 0.0	0.4 ± 0.1	0.6 ± 0.2	0.1 ± 0.0	0.4 ± 0.1	0.6 ± 0.2
		96	0.2	0.3	**0.4**	0.1	**0.2**	**0.4**	**0.07**	0.5	0.8
Zn	6th leaf	84–94	53.1 ± 18.2	59.1 ± 16.3	65.1 ± 13.1	38.5 ± 12.0	59.5 ± 18.6	68.5 ± 13.2	38.7 ± 9.5	64.7 ± 15.6	69.4 ± 14.2
($mg \cdot kg^{-1}$)		96	39.4	37.0	57.7	25.1	57.1	72.0	26.7	41.2	48.7
	ear leaf	84–94	45.3 ± 9.3	47.3 ± 8.7	49.7 ± 8.2	35.3 ± 5.8	48.4 ± 7.7	54.0 ± 11.5	38.2 ± 4.6	56.4 ± 11.4	54.5 ± 5.9
		96	41.7	39.5	46.2	32.5	46.3	60.1	32.4	44.3	47.8
	grain	84–94	27.8 ± 1.6	28.8 ± 2.3	28.2 ± 3.0	25.9 ± 3.3	29.0 ± 3.0	29.6 ± 2.5	26.5 ± 3.0	30.1 ± 2.6	28.7 ± 1.6
		96	27.6	28.8	26.0	24.8	27.5	29.8	26.2	28.1	27.4
Cu	6th leaf	84–94	9.9 ± 1.2	12.5 ± 1.5	15.6 ± 2.2	9.7 ± 0.9	11.8 ± 1.0	16.7 ± 5.2	9.7 ± 1.2	12.0 ± 2.8	16.6 ± 2.4
($mg \cdot kg^{-1}$)		96	8.4	1.08	15.7	9.8	13.8	19.5	9.2	10.7	17.2
	ear leaf	84–94	8.8 ± 1.8	11.4 ± 1.0	12.3 ± 1.2	8.7 ± 0.8	11.0 ± 1.3	13.6 ± 4.1	8.7 ± 1.3	10.9 ± 3.2	13.5 ± 1.3
		96	11.7	**7.6**	**9.4**	9.8	12.3	22.8	11.6	23.5	**11.3**
	grain	84–94	1.1 ± 0.7	1.4 ± 0.7	2.0 ± 0.3	1.2 ± 0.6	1.3 ± 0.6	2.4 ± 1.2	1.3 ± 0.8	1.1 ± 0.7	2.4 ± 0.5
		96	1.6	2.0	2.2	1.4	1.7	1.8	1.7	2.0	2.2
Mn	6th leaf	84–94	66.7 ± 15.0	36.8 ± 9.5	31.1 ± 6.4	70.8 ± 19.1	33.5 ± 12.4	26.7 ± 2.9	68.1 ± 11.0	41.0 ± 13.2	32.8 ± 2.6
($mg \cdot kg^{-1}$)		96	**32.0**	22.8	29.3	**29.3**	37.1	33.4	**50.5**	46.3	51.6
	ear leaf	84–94	62.0 ± 15.7	30.2 ± 9.3	21.1 ± 3.6	64.5 ± 14.3	28.0 ± 7.4	18.8 ± 3.2	62.9 ± 11.3	37.2 ± 11.3	23.4 ± 3.1
		96	**22.6**	**17.6**	15.2	**13**	**15**	**15**	**35.5**	30.1	30.1
	grain	84–94	6.1 ± 2.2	2.1 ± 1.0	1.4 ± 1.4	5.2 ± 1.3	2 ± 0.9	1.4 ± 1.2	6.0 ± 0.9	2.4 ± 0.7	1.4 ± 0.8
		96	**2**	**0.6**	**0.01**	**1.4**	**0.6**	**0.03**	**3.8**	**1.8**	**0.6**
Fe	6th leaf	84–94	167.7 ± 30.5	148.8 ± 31.1	137.6 ± 26.5	159.2 ± 22.2	132.6 ± 21.5	130.7 ± 20.7	163.7 ± 25.6	139.2 ± 22.1	149.8 ± 46.6
($mg \cdot kg^{-1}$)		96	**110**	117	105	160.5	123.5	129.1	178.3	144.2	132.8
	ear leaf	84–94	130.0 ± 23.7	117.6 ± 17.7	106.6 ± 18.5	133.4 ± 18.5	117.2 ± 20.2	108.3 ± 15.4	132.3 ± 19.5	121.7 ± 19.5	116.5 ± 23.7
		96	**84**	**87**	**78**	**103.8**	107.6	97.2	120.2	111.9	101.8
	grain	84–94	29.5 ± 11.8	28.5 ± 7.1	23.7 ± 6.4	25.5 ± 7.7	28.0 ± 13.8	24.5 ± 4.5	26.0 ± 5.1	26.1 ± 8.7	25.1 ± 4.5
		96	21.8	**21**	18.1	19.9	21.3	22.2	23.8	22.1	22.8

[a] Values in bold type are those that are lower than the minimum value in the 1984–1994 period.

in the range of values obtained for those years. Concerning Cu, there is only a decreased uptake on the untreated plots. For Mn there is an overall decrease in uptake. Even if the total Mn content of the soils strongly increased after the addition of steel shots, the Mn contents of the plant tissues fall in or below the range for 1984–1994. The iron content is only decreased in maize grown on the untreated plots. The addition of steel shots, an iron-bearing material (*table I*), did not result in an increased Fe uptake.

In a second approach, we compared the Cd and Ni contents of plants grown in 1996 on plots with the original treatment (FYM, S1 and S2), with and without the addition of beringite and steel shots. To do so, we compared only those plots whose soils contained similar total amounts of Cd and Ni (*table II*). The FYM plot that received steel shots had a twofold higher total Ni content than the untreated and beringite-treated plot. Even if the plots are not absolutely comparable, the FYM steel shots plot has been included. Shoots, sixth leaf and ear leaf are the plant tissues under study.

For all three soil treatments, the addition of beringite and steel shots led to a lower Ni content in the maize shoots (*figure 2*). Concerning the sixth leaf and ear leaf, the addition of beringite resulted in a lower Ni content in plants grown on the S1 plot. The standard errors obtained for the plants of the FYM and S2 plots are too high to make a conclusion about the efficiency of beringite to lower the Ni content. The addition of steel shots to the S2 plot led, however, to a lower Ni content in the leaves. Particularly striking are the results of the FYM plots with steel shots addition. Although the total Ni content of this plot is twice as high as on the untreated FYM plot, the Ni content in the maize organs is lower. These results are in agreement with those obtained in the first approach; the addition of beringite and steel shots leads to a lower Ni mobility and therefore a lower Ni uptake.

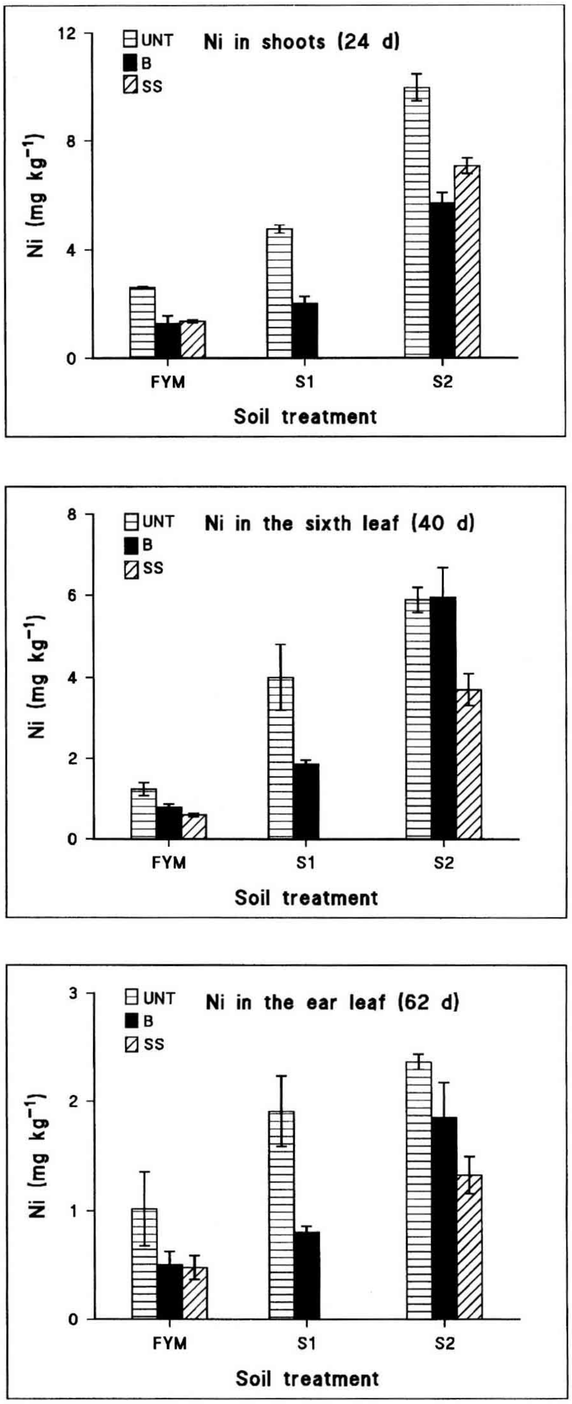

Figure 2. Ni content (mg·kg^{-1} DM) in the shoots, sixth leaf and ear leaf of maize (*Zea mays* L.) grown on plots with and without the addition of soil additives. UNT: untreated; B: beringite; SS: steel shots. FYM: farm yard manure 10 t DM ha^{-1} y^{-1}; S1: sewage sludge 10 t DM ha^{-1} y^{-1}; S2: sewage sludge 100 t DM ha^{-1} 2 y^{-1}.

The addition of beringite resulted in a lower Cd content in the shoots and leaves of plants grown on the S1 plots (*figure 3*). The Cd content in shoots, sixth leaf and ear leaf after beringite addition decreased with 55, 30 and 50 %, respectively.

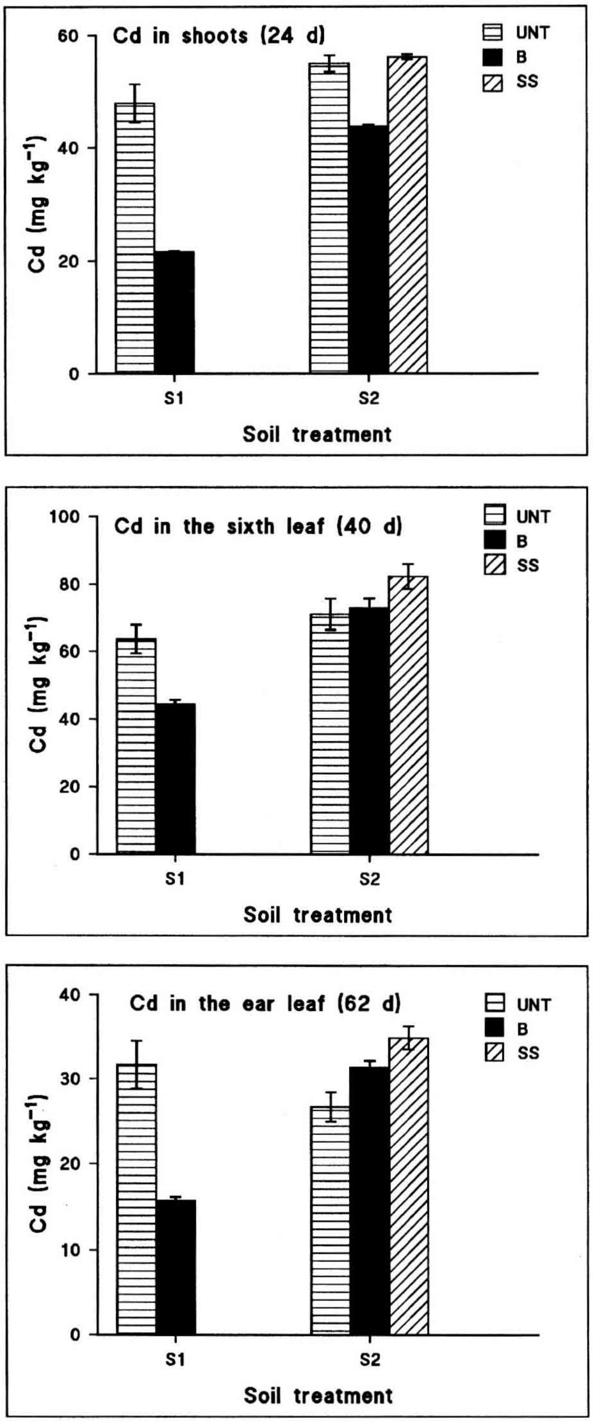

Figure 3. Cd content (mg·kg^{-1} DM) in the shoots, sixth leaf and ear leaf of maize (*Zea mays* L.) grown in plots with and without the addition of soil additives. UNT: untreated; B: beringite; SS: steel shots; S1: sewage sludge 10 t DM ha^{-1} y^{-1}; S2: sewage sludge 100 t DM ha^{-1} 2 y^{-1}.

Comparison of these values with those found for Ni in the same plots (57, 53 and 58 %, respectively) suggests that beringite seems to have a slightly stronger immobilizing influence on Ni than on Cd. In maize grown on the S2 plots, generally no decrease of Cd content was found after the addition of beringite and steel shots. The only exception is a slightly decreased Cd content in the shoots (earliest stage) after beringite addition. The addition of steel shots did not result in a decreased Cd uptake, although it led to a decreased Ni uptake (*figure 2*). This suggets that in our study, steel shots should be more effective in reducing the soil–plant transfer of Ni than of Cd.

The results obtained in studies on bench scale where steel shots decreased the transfer of Cd from soils to young plants and the results at short term of the field experiment seem somewhat conflicting. Several factors may be responsible for this. First, mixing steel shots with topsoil is less efficient at the field scale. Aggregates of iron oxides were frequently formed in the field plots while this does not appear in pots. Additionally, other possible explanations can be given for the fact that there is no decrease in Cd content in the shoots and leaves on the S2 plot. Even if the extractability of Cd decreases following the treatment with soil additives (*figure 1*), the Cd concentration in soil solution may still be high enough to ensure a high Cd uptake. The additives were added to the top layer of the soil (20 cm), but depending on the soil texture at different depths of the soil profile, the roots can also explore deeper soil layers [25]. At the experimental site it has been observed that the rooting system of the maize plants extends to a depth of more than 20 cm. Although migration of the additives from the topsoil to the deeper layers was visible, they might not have been migrated in the whole rooting soil like in pot experiments. Furthermore, there were still some particles of the sewage sludge visible in the soil samples of the plots which received the high dose (S2). If these particles are present in the rhizosphere, Cd might be released as a result of either the acidification or mineralization induced by the plant root activity, and Cd uptake can take place immediately after. In a similar respect, maize roots have been shown to colonize preferentially the maize stalk residues from the previous crop which contain a high Cd content and are not completely mineralized from October to April. A last hypothesis is that the lower available Ni content results in a better root functioning as Ni accumulates mainly in the roots [18]. This improved root functioning might lead to a higher Cd uptake.

4. CONCLUSION

The extractability and availability of Ni and Cd depended on the sewage sludge loading rate. The higher Ni and Cd contents resulted in an increased transfer of these metals from soil to plant, even though sludge application was terminated in 1980. To decrease this transfer, specific additives that lower the mobility and availability of these metals for plants can be supplied to the soil.

The addition of beringite and steel shots appeared to be both effective in the short term in decreasing the Ni extractability. This was reflected in the plant uptake as the addition of both steel shots (1 % w/w) and beringite (5 % w/w) to polluted plots mostly resulted in a reduced Ni uptake by maize plants. Both additives, therefore, are useful tools to lower risks related to Ni transfer from soil to plant. In the case of Cd, both soil additives led to a lower extractability. In the less polluted plots, beringite was effective in lowering the Cd content in maize shoots and leaves. However, in the most polluted plots, steel shots and beringite treatment did not result in reduction of the Cd content of maize. The Cd supply from the soil is still high enough to reach a maximum Cd content in maize tissues. From previous literature and the present study, it can be concluded that beringite is a promising additive for the remediation of Cd-contaminated soils. However, its effectiveness appears to be dependent on the pollution level or source and probably also on the spreading of the contaminants through the soil profile. The profits of beringite on decreased Cd transfer might therefore be site-specific. Based on the present study, steel shots does not seem to decrease the Cd uptake by plants. This result in the short term is contradictory with those found on bench scale, but several explanations such as heterogeneous mixing and a different behaviour of root systems at the field scale are possible.

Beringite and steel shots treatment did not lead to any deficiency or toxicity problems for the maize plants.

Based on the results obtained in this field study, it is recommended to perform further (long-term) experiments on the addition of steel shots and beringite in the field. In future experiments, it might be considered to mix beringite and steel shots with the whole rooting zone instead of just with the 20-cm topsoil layer. Moreover, the addition of the additives could be fractionated in several applications. In the present field trial, the formation of iron congregates probably due to the addition of all the steel shots at one time was observed.

Steel shots and beringite should also be tested for other metals, plant species and soil types before concluding on their effectiveness for remediating trace metal polluted soils. In light of the European project PHYTOREHAB in which this study takes part, other field trials have started in Finland, Belgium and Portugal. On the plots of the field trial reported in this study, in April 1997 potato plants were planted in order to follow up the treated plots and investigate the effects of the soil additives on another plant species. In 1998, maize will be grown again to evaluate the long-term (3 years) effects and sustainability of the immobilization technique.

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