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EFFECT OF ZEOLITE-BEARING ROCKS UPON INACTIVATION OF CADMIUM IN SOILS

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INTRODUCTION

The fate of trace elements that accumulate in soils in an uncontrolled way is to a large extent conditioned by physical and chemical properties of both soils and the elements themselves. Cadmium has been shown to be most rapidly mobilized in an experiment aimed at determining the behaviour of heavy metals (Cu, Pb, Zn and Cd) introduced into arable soils of diverse origin [Dudka 1989; Piotrowska 1985].

Despite that cadmium is not needed for the plant growth, it is exceptionally easily taken up by both root systems and leaves. Generally, plants are capable of taking up cadmium proportionally to its concentrations in the soil [Gworek 1993; Piotrowska 1985]. Human and animals ingest cadmium mostly together contaminated food and accumulate it in kidneys and liver in particular, though it was found that cadmium may be to a some extent excreted. Because of its mobility in the food chain, cadmium has been allocated to the category of potentially highly threatening elements.

The present work was aimed at determining the possibility of using a natural zeolite-bearing rock to immobilize cadmium in the soil, i.e. to reduce cadmium quantities which enter the food chain. The effect of cadmium inactivation in soils was evaluated by comparing its content in plants grown with the zeolite additive with those in control plants.

MATERIALS AND METHODS

In order to establish the extent of cadmium inactivation by zeolite additive, a three-year long pot experiment was carried out in a glasshouse in four replicates. Soil material for laboratory tests was sampled from upper horizons (0–20 cm) of anthropogenic soils of the Upper Silesia Industrial Region, from the municipalities of Szopienice and Jaworzno. Both areas lie within the impact of large industrial agglomerations and, locally, are also influenced by waste dumps.

TABLE 1. Basic chemical properties of soil material

Locality	pH		Hh	Ca	Mg	K	Na	C	N	Cd
	H_2O	KCl	[me / 100 g]					[%]		[mg/kg]
Szopienice	6.6	6.2	2.10	48.78	6.80	0.64	1.52	4.05	0.28	43.04
Jaworzno	5.5	5.0	1.95	7.93	2.08	0.74	3.88	1.67	1.14	4.74
Chylice	6.0	5.8	2.00	8.10	1.10	0.80	1.94	1.04	0.54	0.82

Additionally, tests with simulated cadmium contamination were performed using topsoil taken from the study field of the Warsaw Agricultural University in Chylice. To this soil, 20 mg Cd per kg soil dry weight in the form of $Cd(NO_3)_2$ were added. Basic chemical properties of the soils are given in Table 1. The soils have been classified to the respective soil texture groups: soils from Szopienice and Jaworzno – heavily loamy sand, and those from Chylice – light loam.

The amounts of soils taken for the experiment corresponded to 1.5 kg soil of dry weight. Before filling in the pots, macroelements were added to the soil in the quantities recommended by the agrotechnical requirements of plants under cultivation. At the same time zeolite-bearing rock was added as pellets of 1–3 mm in diameter at the rate of 2% of the soil weight. The rock is in 90% built of clinoptilolite [$(K, Na, 1/2Ca)_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 8H_2O$]. Anthropogenic and artificially contaminated soils without any addition of natural zeolite-bearing rock were used as reference.

Oat of var. Dragon, beetroot of var. Red Ball and perennial ryegrass (*Lolium perenne*) were sown directly to the pots. Two-week old seedlings of lettuce of var. Wonder of Volburg were also used in the experiment. During the growing season all plants were watered daily with redistilled water up to 60% of the maximum field water capacity. Foliar dressings of nitrogen at the rate of 0.1 g N/kg soil dry weight were given to lettuce during the third week of growth while to oat and ryegrass during the tillering phase. Three crops of lettuce were grown successively in the same pots. After 6 weeks all plants were cut. Plant material, except for oat straw, grains and glumes, was washed with tap water and, subsequently, rinsed with redistilled water. Washed material was then dried at 60° C, ground and ashed in a muffle furnace at 480°C. The ash thus obtained was dissolved in 20% HCl.

Soil samples were sieved through 1 mm sieve and ashed at 480°C, then digested in 20% HCl for 30 min. Cadmium content in plant and soil mineralisates was determined directly by AAS technique.

RESULTS

The effect of zeolite-bearing rock upon cadmium content in plants cultivated on anthropogenic soils is presented in Table 2. Leaves and roots of successive lettuce crops grown on the soil from Szopienice contained, respectively, from 21.4 to 39.3 mg/kg of d.w. and from 34.3 to 74.2 mg/kg d.w. Whereas in the successive crops of lettuce grown on the soil from Jaworzno, the respective quantities amounted from 3.9 to 4.9 mg/kg d.w. Considerably higher cadmium content in the reference lettuce grown on the soil from Szopienice relative to that of the reference lettuce from Jaworzno results from higher soil cadmium levels in Szopienice.

TABLE 2. Mean (±SD) cadmium content [mg/kg of d. w.] in leaves and roots (n = 12) of plants cultivated on anthropogenic soils with and without zeolite additive

Plants part	Combination	Szopienice			Jaworzno		
		Control	ZN	WO%	Control	ZN	WO%
Lettuce							
Leaves	I	49.3±8.3	24.7±3.4	49.8	4.6±1.8	2.9±0.9	35.9
	II	38.8±6.9	28.1±3.2	27.3	4.9±1.2	1.0±0.6	78.9
	III	21.4±2.4	10.3±2.7	48.2	3.9±1.3	1.0±0.4	73.1
Roots	I	34.3±4.2	27.2±3.0	20.6	6.3±1.4	3.3±1.1	47.8
	II	74.2±5.7	30.9±6.2	41.6	8.0±2.1	3.9±0.8	50.9
	III	47.2±4.2	19.2±2.7	59.1	5.4±1.9	2.3±0.9	57.4
Ryegrass							
Harvest	I	11.3±1.2	6.3±1.0	44.2	4.3±0.9	3.7±0.9	13.9
	II	6.2±0.9	4.3±0.8	30.6	2.8±0.3	1.2±0.04	57.1
	III	8.6±1.0	4.2±0.6	51.1	3.0±0.7	2.0±0.06	33.3
Roots		37.3±2.1	18.2±2.3	51.2	20.3±2.3	16.2±1.9	20.2
Oat							
Straw		9.6±1.3	3.6±0.7	62.5	2.6±0.6	0.9±0.04	
Grain		–	–	–	0.9±0.06	0.4±0.02	
Glumes		10.7±2.1	2.7±0.6	74.8	1.7±0.1	1.0±0.06	
Roots		34.2±3.6	13,4±2,4	60.8	6.3±1.3	2.2±0.09	
Beet							
Leaves		37.4±3.4	20.3±4.0	45.7	8.7±1.6	5.6±1.2	
Roots		29.8±2.0	18.2±3.7	38.9	6.2±1.2	5.0±1.9	

Control – no additive of zeolite-bearing rock; ZN – treatment with zeolite additive; WO – percent reduction of cadium relative to the control.

Zeolite-rock addition reduced cadmium content in leaves of lettuce grown on the soil from Szopienice by 27.3–49.8% and in roots by 20.6–59.1%, whereas in the lettuce grown on the soil from Jaworzno these reductions ranged, respectively, from 35.9–78.9% and 47.8–57.4%. As far as leaves are concerned, the highest percent reduction in cadmium content induced by the zeolite additive was observed in the first crop of lettuce grown on the soil from Szopienice, while in the lettuce on the soil from Jaworzno – in the second crop. In the roots the highest reduction in cadmium content was found in III crop of lettuce grown on soils from both Szopienice and Jaworzno.

The advantage of using natural zeolites for a partial removal of excess cadmium from the trophic chain was also corroborated by the results of analyses of the three harvests of grass. In the grass grown on the anthropogenic soils, the reduction in cadmium content in the leaves was from 3.9 to 57.1%, while in the roots - from 21.2 to 51.2% (Table 2).

The experiments with oat have shown that plants grown in the presence of natural zeolite additives contain less cadmium not only in vegetative organs but also in the generative ones relative to the control plants. This was evidenced by the amounts of cadmium in grain of oat cultivated on the anthropogenic soil from Jaworzno with and without the zeolite additive. On the other hand, it was impossible to assess the zeolite effect on soils from Szopienice due to the fact that oat eared but no grains were developed. In general, the reduction in cadmium content, regardless the treatment, amounted to: in oat grain – 55.5%, in straw – 62.5% and 65.3%, in glumes – 41.2% and 74.8% and in roots – 60.8% and 65.3% relative to the control (Table 2). It was also found that the amounts of cadmium in beetroot leaves and roots decreased when the plants were grown on soils with zeolites in comparison with the control, regardless the degree of soil contamination. This reduction was 35.6% and 45.7% in the leaves and 19.4% and 38.9% in the roots.

The results of tests with simulated cadmium contamination of soils are given in Table 3. The percent reduction of cadmium content due to zeolite additive in plants cultivated on artificially contaminated soils was generally higher than in those cultivated under comparable regimes on anthropogenic soils. The decrease in cadmium content in leaves of successive lettuce crops amounted from 62.3 to 81.4% while in roots – from 53 to 72.3%. The addition of 20 mg Cd per kg of soil dry weight, in an easily soluble form, did not affect the process of grain setting in oat. The decrease in cadmium content in the respective parts of oat cultivated on soils with the natural zeolite additive, as compared to the control, amounted to: in straw – 46.9%, in grain – 43,8%, in glumes – 52.2% and in roots – 61.5%. Similar decrease in cadmium uptake was found in beetroots cultivated with zeolite

TABLE 3. Mean (±SD) cadmium content [mg/kg of d. w.] in leaves and roots of lettuce cultivated on soils artificially contaminated with and without zeolite additive

Parts of plants	Combination	Control	ZN	WO%
Lettuce				
Leaves	I	32.9±2.7	12.4±1.4	62.3
	II	58.1±3.4	10.8±2.0	81.4
	III	58.1±3.1	11.3±1.7	80.5
Roots	I	80.1±5.7	37.6±2.4	53.0
	II	133.4±5.2	34.7±2.3	73.9
	III	122.9±3.4	34.0±3.0	72.3
Reygrass				
Harvest	I	10.4±2.4	4.3±0.9	58.6
	II	8.4±2.1	3.8±1.2	54.8
	III	25.3±3.2	5.2±1.1	79.4
Roots		80.0±5.6	39.2±3.4	51.0
Oats				
Straw		33.2±2.8	17.6±1.9	46.9
Grain		13.0±3.0	7.3±1.4	43.8
Glumes		24.3±4.3	11.6±0.9	52.2
Roots		97.0±8.2	37.3±2.7	61.5
Beet				
Leaves		146.0±12.3	58.4±3.4	60.0
Roots		40.0±6.7	21.7±2.2	45.7

Denotations as in Table 2.

TABLE 4. Mean (n=12) cadmium content [mg/kg of d. w.] in anthropogenic soils after completing the experiment

Treatment		Locality	
		Szopenice	Jaworzno
Control	S	42.4	4.0
	T	42.3	4.1
	O	41.9	3.9
	B	41.3	3.8
Natural zeolite additive	S	36.9	3.1
	T	36.2	3.0
	O	34.3	2.8
	B	34.3	2.7
Reduction of Cd to control	S	13.0	22.5
	T	14.4	26.8
	O	18.1	28.2
	B	16.9	28.9

Denotations: S – treatment with lettuce, T – treatment with reygrass, O – treatment with oat, B – treatment with beetroot

additive, the contents of cadmium being reduced, respectively, in leaves by 60% and in roots by 45.7%. A decrease was found in the soil Cd content after completing the experiment with the highest reduction coefficient for soils from Jaworzno (Table 4). In general, the greatest reductions in cadmium content in soils with the zeolite additive were observed in the treatments with oat and beetroot and, subsequently, in those with ryegrass and lettuce. The magnitude order of coefficients of Cd content reduction for respective plants cultivated on soils from Szopienice was as follows: 18.1, 16.9, 14.4 and 13.0% while that for Jaworzno soils – 28.2, 28.9, 26.8 and 22.5%.

DISCUSSION

The results of analyses of mono- and dicotyledonous plants grown on both anthropogenic and artificially contaminated soils have shown that cadmium accumulation was the highest in plant roots, smaller in the vegetative plant parts and, it was the smallest, in the generative ones. The above results point out to the existence of biological barriers in plants which reduce the transport of excess cadmium to the generative organs. The action of the above barriers consists in binding heavy metals by proteins and in depositing the compounds thus established within intracellular spaces or in the cells [Gworek 1993; Kabata-Pendias, Pendias 1993; Piotrowska 1985]. The results of a many-year-long study corroborate the fact that the highest contents of cadmium are to be found in the second crop of lettuce grown on anthropogenic soils [Gworek 1993]. Moreover, studies by other authors have shown that cadmium content in grain increases with the increase in the level of soil Cd [Gambuś 1993; Gworek 1993; Piotrowska 1985]. It was assumed that the migration of cadmium to the above ground plant parts occurs in the phase of grain development [Dudka 1989].

The results of previous studies have shown that there is a possibility of decreasing the excess cadmium in the trophic chain within the system: soil - plant - animal - man by adding the natural zeolite-bearing rock. The addition of zeolite to the Cd contaminated soils contributed significantly to decreasing cadmium levels in plants relative to the control. The decreased uptake of cadmium by plants is conditioned by the soil sorption capacity and ion exchange possibilities of zeolites [Borowiak et al. 1983; Brogowski 1987; Czupyrna et al. 1986; Gworek 1992a,b].

In the above respect, the sorption capacity of zeolites may be superior to that of the soil humus [Breck 1974]. Owing to their specific intracrystalline structure, the above minerals behave as a sort of sieves at the molecular level though their action in the soil is restricted to sorption of ions and molecules less than 1 nm in diameter [Borowiak et al. 1983].

On the basis of this study it was found that the introduction of natural zeolites to soils contaminated with cadmium resulted in a more profound decrease in cadmium content in the above ground parts than in the roots. It was also demonstrated that there is a possibility for diminishing the amounts of cadmium in the generative organs of plants. This is proven by a 43.8 and 55.5% decrease in Cd content in oat grain [Čeliščev and Čeliščeva 1981] performed an experiment on the effect of simulated Cd contamination and diverse additives of natural rock containing clinoptilolite upon the plant growth. In the experiment a decrease in Cd content was found in the green mass sampled at diverse stages of oat development and, especially, in its grain. In the latter the decrease was as much as 70%. An earlier study with the use of synthetic zeolites enabled to attain a similar or even better effects that resulted from a higher sorption capacity of the synthetic zeolites.

The analysis of cadmium content in soils after 6 months of soil conditioning with natural zeolite-bearing rock pointed out to a decrease from 13.0 to 18.1% in cadmium level for the soil from Szopienice and from 22.5 to 28.9% for the soil from Jaworzno (Table 4). One of the reasons of the higher decrease in the case of soils from Jaworzno may be their lower pH. Generally, more mobile cadmium forms are to be found in the environments having lower pH, since under those conditions cadmium may be easily entering the processes of sorption and ion exchange.

CONCLUSIONS

The study performed allows the following conclusions:

1. The introduction of zeolite-bearing rock into the cadmium contaminated soil, in the amount of two per cent of soil dry weight resulted in 19.4-81.4% decrease in the Cd level in plants grown on the soil. Considering generative organs of plants the reduction was 43.8 and 55.5%.
2. In general, a higher drop in cadmium content in plants as a consequence of the application of natural zeolites, was found in regimes with simulated Cd contamination as compared to the plants cultivated on the polluted soils.
3. After a lapse of 6 months, the addition of natural zeolite-bearing rock to the polluted soils from Szopienice resulted in a decrease in the soil Cd content by

13.0 to 18.1% while in the case of Jaworzno – this decrease was contained within the limits 22.5–28.9%.

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WPŁYW ZEOLITÓW SKAŁOTWÓRCZYCH NA UNIERUCHOMIENIE KADMU W GLEBACH

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STRESZCZENIE

W doświadczeniach wazonowych badano wpływ naturalnej skały zeolitonośnej na zmniejszenie pobierania kadmu przez rośliny uprawiane na glebach zanieczyszczonych. Zastosowana do doświadczeń skała zeolitonośna zawiera około 90% klinoptilolitu. Wprowadzenie do gleb wymienionej skały w ilości 2% wagowych w stosunku do suchej masy gleby spowodowało obniżenie zawartości kadmu w roślinach na niej uprawianych w granicach 19.4–81.4% w porównaniu z roślinami kontrolnymi (sałata, rajgras, owies, buraki). Działanie naturalnych zeolitów w glebie antropogenicznej przez 6 miesięcy spowodowało spadek ilości kadmu w glebie. Spadek ten wahał się od 13.0 do 28.9% w zależności od pH gleby.

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