Original Research

Impact of Ecochemical Soil Conditions on Selected Heavy Metals Content in Garden Allotment Vegetables

Elżbieta Jolanta Bielińska[1]*, Agnieszka Mocek-Płóciniak[2]**

[1]Institute of Soil Science and Environmental Development, Lublin University of Life Sciences, Leszczyńskiego 7, 20-069 Lublin, Poland
[2]Department of General and Environmental Microbiology, Poznan University of Life Sciences, Szydłowska 50, 60-656 Poznań, Poland

Received: 30 March 2010
Accepted: 12 April 2010

Abstract

The objective of our study was to investigate the activity of selected soil enzymes (dehydrogenases, phosphatases, urease, and protease), as well as cadmium and lead concentrations, in soils and vegetables from gardening allotments in areas exposed to industrial contamination and from areas of similar physiographic conditions but that were not exposed to the direct impact of industrial emissions. Investigations comprised eight gardening allotments situated in the area of Upper Silesia (Miasteczko Śląskie, Zabrze) and in cities in eastern Poland (Lublin, Stalowa Wola). Strong correlations were demonstrated between cadmium and lead concentrations in the soil and root systems of analyzed plants (red beet, carrot, parsley). The observed high inactivation of the examined enzymes in soils exposed to strong anthropogenic influence (the area of Upper Silesia) confirms that soil environment contamination with Cd and Pb reached levels that threaten living organisms.

Keywords: soil, vegetables, heavy metals, enzymatic activity

Introduction

Higher plants are capable of accumulating heavy metals without any toxic symptoms to such levels that can be hazardous for human health. This is particularly dangerous in industrial regions, i.e. in an environment exposed to constant pressure of toxic factors [1]. The availability of chemical elements to plants as well as the dynamics of their uptake from soil are influenced by environmental factors, both of natural and anthropogenic nature. These factors include: soil-climatic conditions (concentrations of mineral and organic colloids, temperature, soil moisture, oxygenation, and pH, among others) and the applied agrotechnical practices. These factors modify the intensity of uptake and transport of chemical elements that are connected with changes in the intensity of biochemical processes affecting their availability for plants [2, 3].

In Poland, in accordance with Article 9 of the Bill adopted in 2001 concerning health conditions of food and nutrition [JL 2001 No. 63, Item 634 with later amendments], regulations were implemented that specify maximum levels of chemical and biological contamination that may be found in food articles. Legal regulations currently in force in the case of heavy metals include limits on lead and cadmium concentrations in plant material intended for consumption [4].

*e-mail: elzbieta.bielinska@up.lublin.pl
**e-mail: agam-p@up.poznan.pl

One of the good markers of changes taking place in the soil environment under the influence of natural and anthropogenic factors is the activity of enzymes responsible for transformations of its constituents [5-7]. Changes in soil enzymatic activities are among the earliest signals indicating changes in the intensity of environmental life processes that result from the fact that many chemical compounds assume a toxic or mutagenic character following metabolic transformations occurring in living organisms [8].

The objective of the performed investigations was to examine the activity of the selected soil enzymes and cadmium and lead concentrations in soils and plants derived from gardening allotments situated in areas exposed to strong pressure resulting from industrial contaminations, and from areas of similar physiographic conditions but that were not directly exposed to industrial emissions. Investigations in this field will make it possible to assess the extent of negative impact of industrial contamination on soil ecosystems and potential hazards caused by the consumption of plants cultivated in given soil conditions.

Material and Methods

The experiments comprised eight gardening allotments situated in the region of Upper Silesia (Miasteczko Śląskie, Zabrze) and towns in eastern Poland (Lublin, Stalowa Wola). The study involved simultaneous investigations of gardening allotments located in areas exposed to strong pressures of industrial contamination, as well as those situated in similar physiographic conditions but not subjected to direct exposure to industrial emissions:

a) potentially high anthropogenic influence (gardening allotments situated near industrial plants – Lublin – 1; Miasteczko Śląskie – 1; Stalowa Wola – 1; Zabrze – 1;
b) potentially low anthropogenic effect (gardening allotments situated in municipal suburbs – Lublin – 2; Miasteczko Śląskie – 2; Stalowa Wola – 2; Zabrze – 2.

In each of eight selected areas of gardening allotments, one representative allotment was chosen. The performed soil analyses revealed that sandy loam (SL) occurred on the examined objects.

In June 2008, soil samples from humus horizons as well as roots of plants (red beet, carrot, parsley) cultivated in those conditions were collected. The analyzed soil and plant samples were means from 5 samples collected from each of the experimental gardens. In soil samples, activities of the following enzymes were determined: dehydrogenases [9], phosphatases [10], urease [11], protease [12], pH in 1 mol·dm^{-3} KCl [ISO 10390], organic carbon [ISO 14235], and total nitrogen [ISO 13878].

The total cadmium and lead concentrations in soils and plants were determined by emission spectrometry with the assistance of a Leeman Labs PS 950 apparatus with ICP excitation in argon. Soil and plant samples were wet-mineralized in a mixture of concentrated acids: $HCl+HNO_3$ (3:1) – soil and HNO_3+HClO_4 (1:3) – plants [13]. All assays were performed in three repetitions.

Table 1. Soil reaction, organic carbon and total nitrogen contents, C:N ratio of investigated soils.

City/Town	No.	pH_{KCl}	C (g·kg^{-1})	N (g·kg^{-1})	C:N
Lublin	1	7.1	1.96	0.16	12.2
	2	6.4	1.68	0.17	9.8
Stalowa Wola	1	7.2	1.94	0.15	12.9
	2	6.6	1.67	0.18	9.2
Miasteczko Śląskie	1	6.8	3.50	0.23	15.2
	2	6.2	2.92	0.24	12.1
Zabrze	1	7.0	2.75	0.19	14.4
	2	6.5	1.92	0.21	9.1

The significance of differences between individual values of enzymatic assays was estimated by Tukey test at significance level $p<0.05$. In addition, the authors calculated coefficients of simple correlation between the content of heavy metals in soils and plants, as well as between enzymatic activity of soils and heavy metals.

Results and Discussion

Generally speaking, soils of gardening allotments situated in urban suburbs were characterized by a slightly acid reaction, while soils from industrial regions exhibited neutral reaction (Table 1). Soil alkalisation close to industrial plants is associated mainly with the fallout of alkaline dusts [6].

The organic carbon content in soils derived from the industrialized regions of Upper Silesia (Miasteczko Śląskie, Zabrze) was clearly higher than in the soils from the areas of eastern Poland (Lublin, Stalowa Wola) characterized by smaller intensity of anthropogenic impact (Table 1). The factor modifying the $C_{org.}$ concentrations in soils derived from industrialized regions is the quantity of this constituent which reaches soils with dry or wet fallout (among others, emissions derived from industrial enterprises and means of transport). The value of the C:N ratio in soils derived from gardens situated close to industrial enterprises following increased supply to the soil environment of C of anthropogenic origin was higher than in soils from urban suburbs (Table 1).

Considerable variability was determined in cadmium and lead contents (Table 2), which were associated with the degree of soil exposure to industrial contamination [14]. Estimating the extent of soil contamination with cadmium and lead in accordance with the criteria recommended by Kabata-Pendias et al. [15], it can be said that the examined soils were characterized by varying accumulation of these elements indicating five classes of their concentrations (Table 3): natural content (level 0), elevated content (level 1, mild contamination (level ll), moderate contamination

Table 2. Content of heavy metals in soils and plants in mg·kg^{-1} d.m.

Town/City	No.	Metal	Soil	Plant		
				Red-beet	Carrot	Parsley
Lublin	1	Cd	3.0	0.07	0.04	0.06
		Pb	63.8	0.69	1.23	0.53
	2	Cd	0.4	0.05	0.02	0.05
		Pb	42.6	0.19	0.26	0.15
Stalowa Wola	1	Cd	3.3	0.07	0.04	0.08
		Pb	47.4	0.71	1.02	0.55
	2	Cd	0.5	0.06	0.03	0.06
		Pb	25.1	0.12	0.19	0.03
Miasteczko Śląskie	1	Cd	88.9	2.34	1.82	2.27
		Pb	1,936.8	2.34	2.85	2.02
	2	Cd	7.6	1.12	0.68	1.13
		Pb	351.2	0.52	0.67	0.43
Zabrze	1	Cd	4.3	1.22	0.74	1.19
		Pb	180.7	0.94	1.23	0.69
	2	Cd	3.6	0.08	0.06	0.09
		Pb	110.0	0.36	0.44	0.32

(level lll), strong contamination (level lV), and very strong contamination (level V). Soils derived from the region of Upper Silesia were found to be most contaminated with these chemical elements and the pollution was so high that it ruled out field cultivations and the growing of vegetables [15].

The content of the examined heavy metals in soils derived from the gardening allotments situated in industrial regions was several times higher than in soils derived from suburbs (Table 2). This testifies to the point pressure of the anthropogenic factor. It is important to emphasise an extremely high Cd concentration in the soil of a gardening allotment situated close to a zinc and lead smelter in Miasteczko Śląskie (Miasteczko Śląskie 1) of up to 88.9 mg·kg^{-1}, as well as of Pb (1,936.8 mg·kg^{-1}).

The content of cadmium and lead in the analyzed plants differed depending on the extent of soil contamination with these elements (Table 2). The amount of Cd and Pb in the examined vegetable samples fluctuated within a wide range of values, from 0.02-0.08 mg·kg^{-1} d.m. and 0.15-0.55 mg·kg^{-1} d.m. (Lublin, Stalowa Wola) to 0.09-2.34 mg·kg^{-1} d.m and 0.32-2.85 mg·kg^{-1} d.m. (Miasteczko Śląskie, Zabrze), respectively. Acceptable content levels of these metals were found to be exceeded in vegetable samples derived from Upper Silesia (Miasteczko Śląskie, Zabrze) [JL. 2001, No. 9]. The performed investigations confirmed the existence of strong correlations between cadmium and lead concentrations in the soil-root system of the analyzed plants and the

Table 3. Soil contamination classes by Kabata-Pendias et al. [15].

Town/City	No.	Cd	Pb
Lublin	1	I	0
	2	0	0
Stalowa Wola	1	I	0
	2	0	0
Miasteczko Śląskie	1	V	III
	2	IV	II
Zabrze	1	III	II
	2	II	II

0, I, II, III, IV, V – soil contamination classes.

Table 4. Correlation coefficients between the content of heavy metals in soils and plants.

Heavy metals	Red-beet	Carrot	Parsley
Cd	0.76*	0.72*	0.74*
Pb	0.65*	0.60*	0.62*

*significant at p=0.05

Table 5. Enzymatic activity of soils.

Town/City	No.	Adh	AF	AU	AP
Lublin	1	0.92b	36.15c	10.29c	2.63b
	2	3.45d	86.24d	20.11d	7.12d
Stalowa Wola	1	0.78b	31.89b	5.83b	3.05b
	2	3.09d	78.53d	18.30d	7.89d
Miasteczko Śląskie	1	0.32a	10.67a	2.38a	1.34a
	2	2.43c	43.09c	12.45c	3.41b
Zabrze	1	0.54a	16.34a	5.16b	1.77a
	2	2.27c	40.21c	12.57c	4.26c

DhA – dehydrogenases in cm^3 $H_2 \cdot kg^{-1} \cdot d^{-1}$,
PhA – phosphatase in mmol $PNP \cdot kg^{-1} \cdot h^{-1}$,
UA – urease in mg $N\text{-}NH_4^+ \cdot kg^{-1} \cdot h^{-1}$,
PA – protease in mg $tyrosine \cdot kg^{-1} \cdot h^{-1}$;
values in the column followed by the same letter do not differ significantly at $p < 0.05$, *t*-test.

Table 6. Correlation coefficients between enzymatic activity of soil and heavy metals.

Heavy metals	Dehydrogenases	Phosphatases	Urease	Protease
Cd	n.i.	n.i.	n.i.	n.i.
Pb	-0.64*	-0.70*	-0.60*	-0.62*

*significant at p = 0.05, n.i. = non-significant.

highest values of correlation coefficients were recorded in the case of cadmium (Table 4). Similar relationships were also reported by other researchers [16-19].

From among the analyzed vegetables, the highest quantities of cadmium were found to accumulate in red beet and parsley (Table 2). The same sequence of cadmium accumulation in vegetables was reported by Leszczyńska [20] and Jagiełło et al. [21]. In the case of lead concentrations in roots of the examined vegetables, the sequence was as follows: carrot > red beet > parsley (Table 2), which is in keeping with data presented by Jagiełło et al. [21]. A different sequence of lead accumulation was reported by Jasiewicz [22] (red beet > parsley > carrot) and still different – by Leszczyńska [20] (parsley > red beet > carrot). The quantity of a given element absorbed by a plant depends on its concentration in the soil solution, environmental factors, properties of the element itself, and its hydrolytic capability, as well as on the plant developmental phase determining the change of the chemical composition of its own ecological niche and, consequently, the intensity of biochemical processes [1, 4, 15, 23]. Live activities of microorganisms are stimulated by products of photosynthesis secreted by roots into soil [24]. Different populations of one species may exert differing influence on the activity of enzymes catalyzing the activation of soil constituents, including those that are ecologically unfavourable [5].

The obtained research results revealed high inactivation of the examined enzymes in the case of areas exposed to strong pressures from industrial contamination (Table 5). Soils derived from Upper Silesia (Miasteczko Śląskie, Zabrze) were characterized by the smallest enzymatic activity. The activity of all the analyzed enzymes in the soils derived from the gardening allotments situated in regions not exposed to direct industrial emissions was a couple of times higher in comparison with the gardening allotment situated in the industrial zone.

On the basis of the correlation analysis, an inverse linear relationship was demonstrated between the soil lead concentration and the activity of the examined enzymes (Table 6), although such regularity was absent in the case of cadmium. It is interesting that the soil derived from the gardening allotment situated in the outskirts of Miasteczko Śląskie, despite significant cadmium contamination (7.6 $mg \cdot kg^{-1}$), was characterized by relatively high enzymatic activity (Table 5). The obtained results encourage cautiousness with regard to the evaluation of the significance of the heavy metal content toxicity levels in soils for living organisms assessed on the basis of enzymatic activity.

Of all the examined enzymes, the activity of phosphatases turned out to be the most sensitive indicator of the contamination of the examined soils with lead, as indicated by the value of the correlation coefficient between the activity of this group of enzymes and soil Pb content (Table 5).

Numerous data from the literature on this subject [7, 25-27] corroborate the special sensitivity of phosphatases to soil environment contamination with heavy metals. The toxic impact of metal ions on enzyme structure as well as their influence on changes in the soil pH environment results both in the reduction in numbers of enzyme-secreting organisms as well as in the weakening of enzyme activity [27].

No significant correlation was observed in the discussed investigations between the activity of the analyzed enzymes and the content of organic carbon in soils. This can be attributed to low proportions of humus substances in the total content of organic matter of urban soils [28] and consequently, limited access of easily available C determining the development of soil bacteria producing enzymes.

Conclusions

1. Soil and plant cadmium and lead concentrations, as well as the activity of the examined soil enzymes, showed considerable variability depending on the intensity of exerted anthropogenic pressure.
2. Soils of the examined gardening allotments situated in Upper Silesia were characterized by Cd content indicating II[nd] to V[th] degree and, in the case of Pb, – from II[nd] to III[rd] degree of contamination, ruling out any gardening cultivation in this region.
3. A close correlation was demonstrated to exist between cadmium and lead content in the soil-roots system of the analyzed plants.
4. From among the analyzed vegetables, the highest cadmium quantities were accumulated by red beet and parsley, and in the case of lead content in the roots of the examined vegetables the sequence was as follows: carrot > red beet > parsley. Standards of acceptable concentration of these metals were exceeded in vegetable samples derived from the region of Upper Silesia.
5. High inactivation of the examined enzymes in soils exposed to strong anthropogenic influence (area of Upper Silesia) indicates that the contamination of the soil environment by Cd and Pb reached levels that threaten living organisms.
6. In the case of soils of the gardening allotments situated in industrial zones, the content of the examined heavy metals was several times higher and the activity of enzymes several times smaller than in soils derived from allotments situated in urban suburbs. This indicates a point impact of the anthropogenic pressure factor.
7. A negative correlation was observed between the lead content in soils and the activates of the investigated soil enzymes. Such regularity was not observed in the case of cadmium, which appears to indicate the need to amend standards of soil heavy metal content acceptability with regard to their toxicity expressed in enzymatic activity.

References

1. BADORA A. Mobile forms of selected metals in soils and some aspects of their immobilisation, Rozprawy Naukowe AR w Lublinie, **225**, **1999** [In Polish].
2. BIELIŃSKA E.J., PRANAGAL J. Enzymatic activity of soil contaminated with triazine herbicides, Polish J. of Environ. Stud., **16**, (2), 295, **2007**.
3. STANISŁAWSKA-GLUBIAK E., KORZENIOWSKA J. Evaluation of plant nutritional status; Oddział Krakowski Polskiego Towarzystwa Inżynierii Ekologicznej, Kraków – Warszawa – Wrocław, **2007** [In Polish].
4. WIŚNIOWSKA-KIELIAN B., LIPIŃSKI W. Evaluation of plant chemical composition; Oddział Krakowski Polskiego Towarzystwa Inżynierii Ekologicznej, Krajowa Stacja Chemiczno-Rolnicza, Kraków-Warszawa-Wrocław, **2007** [In Polish].
5. KIELISZEWSKA-ROKICKA B. Soil enzymes and their significance in investigations of soil microbiological activity, Microorganisms of soil environment; Red. H. Dahm, A. Pokojska-Burdziej, UMK Toruń, pp. 37-47, **2001** [In Polish].
6. BIELIŃSKA E.J. Soil enzyme activity in the rhizosphere of dandelion as an indicator of urban soils ecochemical status; Journal of Research and Applications in Agricultural Engineering, **52**, (3), 10, **2007** [In Polish].
7. MOCEK-PŁÓCINIAK A. Interrelationships between biological and chemical soil contamination indicators; Maszyn. Pr. dokt. Kat. Mikrobiol. UP, Poznań, 148, **2006** [In Polish].
8. HÜBNER H. Ecological biomonitoring of the Man; Ecology and its delations with different disciplines of science; Red. A. Kurnatowska, Wydawnictwo Naukowe PWN, Warszawa-Łódź, 321, **2002** [In Polish]..
9. THALMANN A. Method of determination of dehydrogenase activity in soil with Triphenyltetrazoliumchlorid (TTC), Landwirtsch. Forsch. **21**, 249, **1968**.
10. TABATABAI M.A., BREMNER J.M. Use of p-nitrophenol phosphate for assay of soil phosphatase activity, Soil Biology and Biochemistry, **1**, 301, **1969**.
11. ZANTUA M.I., BEMNER J.M. Comparison of methods of assaying urease activity in soil, Soil Biology and Biochemistry, **7**, 291, **1975**.
12. LADD N., BUTLER J.H.A. Short-term assays of soil proteolytic enzyme activities using proteins and dipeptide derivatives as substrates, Soil Biology and Biochemistry, **4**, 19, **1972**.
13. OSTROWSKA A., GAWLIŃSKI S., SZCZUBIAŁKA Z. Methods of analysis and assessment of soil and plant properties; IOŚ, Warszawa, **1991** [In Polish].
14. SZYCZEWSKI P., SIEPAK J., NIEDZIELSKI P., SOBCZYŃSKI T. Research on heavy metals in Poland, Invited Review, Polish J. Environ. Stud. **18**, (5), 755, **2009**.
15. KABATA-PENDIAS A., MOTOWICKA-TERELAK T., PIOTROWSKA M., TERELAK H., WITEK T. Evaluation of soil and plant contamination with heavy metals and sulphur; General recommendations for agriculture; IUNG Puławy **35**, 5, **1993** [In Polish].
16. GWOREK B., MOCEK A. Turnover of chemical elements in nature; Inst. Ochr. Środ., Warszawa, **I, 2000** [In Polish].
17. BARAN S., WÓJCIKOWSKA-KAPUSTA A., OLESZCZUK P., ŻUKOWSKA G. Content of selected heavy metals in soils and red beet of varying influence of anthropo-pressure; Journal of Elementology **10**, (3), **II**, 683, **2005** [In Polish].

18. JANKIEWICZ B., PTASZYŃSKI B., WIECZOREK M. Spectrophotometric determination of cadmium (II) in soil of Allotment gardens in Łódź, Polish J. of Environ. Stud., **9**, (2), 83, **2000**.
19. JANKIEWICZ B., PTASZYŃSKI B., WIECZOREK M. Spectrophotometric determination of lead in the soil of allotment gardens in Łódź, Polish J. of Environ. Stud., **10**, (2), 123, **2001**.
20. LESZCZYŃSKA T. Comparison of the content of selected heavy metals in vegetables derived from shops with ecological food products and from market places: Bromat. Chem. Toksykol, **2**, 191, **1999** [In Polish].
21. JAGIEŁŁO A., BOŻYM M., WACŁAWEK W. Concentration of Cd, Cu, Pb, Zn and N-NO_3 in anatomical parts of vegetables derived from gardening allotments in Brzeg (Opole Voivodeship); Rocz. Glebozn. **54**, (4), 83, **2003** [In Polish].
22. JASIEWICZ Cz. Lead in vegetables from gardening allotments; Aura **12**, 16, **1991** [In Polish].
23. KOBUS J. Biological processes and soil fertility development; Zesz. Probl. Post. Nauk Rol. **421a**, 209, **1995** [In Polish].
24. ROSSEL D., TARRADELLAS J., BITTON G., MOREL J.L. Use of enzymes in soil ecotoxicology: a case for dehydrogenase and hydrolytic enzymes, In: J. Tarradellas, G. Bitton, D. Rossel (Ed.), Soil ecotoxicology. CRC Lewis Publishers, Boca Raton-New York-London-Toyo, pp. 179-205, **1997**.
25. BIELIŃSKA E.J., DOMŻAŁ H. Enzymatic activity of the soil as an indicator of environment contamination, Acta Agrophysica **56**, 60, **2001**.
26. SHINDO H., HUANG Q.Y. Comparison of the influence of Cu, Zn, and Cd on the activity and kinetics of free and immobilized acid phosphatase, Soil Science and Plant Nutrition **47**, (4), 767, **2001**.
27. NOWAK J., SZYMCZAK J., SŁOBODZIAN T. An attempt to determine 50% toxicity rates of different heavy metals for soil phosphatases; Zesz. Probl. Post. Nauk Roln. **492**, 241, **2003** [In Polish].
28. CZARNOWSKA K. Soils and plants in urban environment; Zesz. Probl. Post. Nauk Roln. **418**, 11, **1995** [In Polish].