Acta Agrophysica, 2001, 56, 189-198

THE RATIONAL CULTIVATION OF CHEMICALLY CONTAMINATED SOILS NEAR THE COPPER SMELTER

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Abstract. Investigations were carried out on contaminated soils (Phaeozems and Cambisols) occurring in the neighbourhood of a copper smelter plant. They developed from loess silt sediments. In the above-mentioned soils basic physical and chemical properties as well as the total concentration Cu, Pb and Zn and sulphur were determined. Additionally, field experiments with some varieties of willow trees were conducted on these soils. Both concentrations of Cu, Pb, Zn and S as well as plant yields from a 4-year experiment were determined in the collected plant material (leaves, shoots and roots). The highest concentrations of the analysed heavy metals were found in leaves and shoots, i.e. plant parts of practical importance. Plant yields were very high both with regards to their quality and quantity. *Salix americana* seams to be the most recommendable variety.

Keywords: copper, lead, contaminated soils, willow, Phaeozems, Cambisols.

INTRODUCTION

Soil contamination with toxic elements is observed in neighbourhoods of many industrial enterprises. Exceptionally high levels of toxic substances are found in soils situated in zones of sanitary protection adjacent to non-ferrous smelteries. The degree of contamination and the accompanying chemical degradation of such soils build up with passage of time and depend on both the distance from the source of emission of smeltery dusts and gases as well as the frequency and direction of winds.

The negative effect of industrial pollution on the increase of heavy metals and sulphur content in adjacent soils is well recognised. Much less is known about methods of re-gradation of soils, which would allow restoration of the disturbed biological balance and result in their reinstatement to agricultural or forestry use. This was one of the main objectives of investigations which are presented in this study.

OBJECT AND METHODOLOGY OF INVESTIGATIONS

The analysis comprised an area of approximately 40-50 ha situated on the east of the "Legnica" Copper Smelter. This study presents results obtained only from one experimental object with the area about 7 ha.

The selected area is situated between two hills forming an elongated valley with a watercourse flowing in its middle. The hills were covered with brown soils (Cambisols), while at the foot of their rather steep slopes, brown soils (Cambisols) occurred changing into humus soils. Black earths (Phaeozems) were found in the lowest places.

Major soil properties were determined using methods commonly accepted in Polish soil science. Heavy metals (Cu, Pb, Zn) were determined after soil digestion with HF and $HClO_4$ according to Jackson [6] with atom absorption spectrophotometry (AAS). Total sulphur content was determined in the extract by the nephelometric method according to Chandhy and Cornfield [4]. Cu, Zn and Pb in plant material were determined directly using the AAS method after wet sample mineralisation (HNO_3 and $HClO_4$), while total sulphur concentration was assayed nephelometrically according to Butters and Chenery [3].

RESULTS AND DISCUSSION

On the basis of seven soil profiles, it can be assed that the parent material of the analysed soils was made up of deluvial silt sediment. With respect to soil texture, they can be classified as silty loams (SiL) moderately deep or deep underlayed by clays (C).

The reaction of the examined soils was fairly uniform (Tab. 1). From the point of view of exchange acidity (pH_{KCl}), the analysed soils belong to slightly acid or neutral soils.

The content of organic carbon in surface layers ranged from 1.22 to 2.88%. Because of their deluvial character, Corg. was present in the majority of soils, even in deeper soil horizons. The C:N ratios calculated on the basis of carbon and nitrogen, fluctuated in surface horizons from 8-12, which can indicate strong biological activity of the examined soils.

The content of humus in t/ha is a good parameter illustrating its considerable quantities in these soils. Organic matter rich in exceptional quantities of humus found in these soils resulted from a considerable depth – occasionally extending

Table 1. Reaction and organic matter
Tabela 1. Odczyn i materia organiczna

Horizon	pH		C org.	N tot.	C:N	Humus	
	H_2O	1M KCl	%			%	t/ha
A	6,5-7,7	5,5-6,9	1,22-2,88	0,14-0,29	8-12,5	2,10-4,96	53-210
C	6,0-7,0	5,3-7,0	0,24-0,38			0,41-0,66	

The humus content in t/ha is a good parameter illustrating its considerable quantities in these soils. Organic matter rich in exceptional quantities of humus found in these soils resulted from a considerable depth – occasionally extending from 60-90 cm – of A horizons abounding in this most precious, biogenic soil substance.

One of the measures of chemical contamination of soils with heavy metals is determine their total concentration. The highest quantities of copper, lead and zinc were determined in humus horizons (Tab. 2). It can, therefore, be stated that the general assumption about increased accumulation of heavy metals in surface soil layers was confirmed.

Table 2. Total content of heavy metals and sulphur
Tabela 2. Całkowita zawartość metali ciężkich i siarki

Horizon	Cu	Pb	Zn	S
	mg/kg			
A	160-1070	240-570	45-170	450-2150
C	16-100	60-180	12-88	310-1060

Quantities of heavy metals in soil profiles were found to decrease with depth. Apart from smaller content of organic matter, this could be caused by poor mobility caused by a relatively high pH of the analysed soils. This relationship was confirmed by experiments carried out by many researchers [5, 12, 14].

In general, it can be stated that quantities of Cu and Pb in polluted soils were several times higher in comparison with total amounts of these elements found in soils which are not contaminated with industrial emissions.

The content of sulphur in soils of the examined object was high, although it exhibited considerable variation (Tab. 2). The quantities of sulphur in surface soil layers were 10 times higher than in uncontaminated soils more distant from pollution sources which were analysed by Kowaliński *et al.* [10].

Because of high accumulation of heavy metals, the discussed soils are completely unsuitable for agricultural cultivation. Therefore, attempts were made to utilise them for production of willow, which is a plant characterised by considerable capabilities to adapt to various environments [2, 15]. Several varieties were selected to be tested in the performed experiment to increase chances of finding those, which would do well in those difficult site conditions.

In order to verify the assumed hypothesis, ten varieties of commercial willow (*Salix*) were planted on two experimental areas established on the investigated soils. In this article we discusse the results obtained for the best cropping varieties (Tab. 3-6).

Table 3. Total content of heavy metals and sulphur in willow (mean values content for four years)
Tabela 3. Całkowita zawartość metali ciężkich i siarki w wierzbie (średnia zawartość z 4 lat)

Variety	Cu			Pb		
	mg/kg					
	leaves	shoots	roots	leaves	shoots	roots
Piaskówka	539,8	29,5	59,5	97,0	43,0	63,5
Odra	376,5	25,0	66,3	90,0	27,5	55,0
Amerykanka	378,8	28,8	98,3	98,5	30,5	57,0
Kottenheider	378,3	27,3	57,8	97,0	26,5	82,0
Królewska	446,3	26,3	61,5	124,5	26,0	84,5
mean values	423,9	27,4	68,7	101,4	30,7	68,4
Variety	**Zn**			**S**		
	mg/kg			%		
	leaves	shoots	roots	leaves	shoots	roots
Piaskówka	451,0	98,00	76,8	1,07	0,16	0,28
Odra	489,5	101,8	87,5	1,06	0,16	0,24
Amerykanka	239,5	67,5	77,8	0,95	0,20	0,32
Kottenheider	358,5	72,5	62,8	0,93	0,11	0,18
Królewska	203,5	59,0	62,8	1,04	0,13	0,18
mean values	348,4	79,8	73,5	1,01	0,15	0,24

Table 4. Total content of heavy metals and sulphur in the willow leaves (Nowy Tomyśl)

Tabela 4. Całkowita zawartośc metali ciężkich i siarki w liściach wierzby (Nowy Tomyśl)

Variety	Cu	Pb	Zn	S
	mg/kg			%
Piaskówka	39,00	6,20	145,00	0,96
Odra	16,00	4,70	150,00	1,07
Amerykanka	16,00	5,50	97,00	0,81
Kottenheider	11,00	3,90	245,00	1,15
Królewska	8,00	3,40	33,00	0,90
mean values	18,00	4,70	135,00	0,98

Table 5. Indexes of contamination in the willow leaves

Tabela 5. Wskaźniki skażenia w liściach wierzby

Heavy metals	In leaves of some varieties	In agricultural plants from contaminated regions of Poland [8]
Cu	13,7 – 65,1 29,6	10 – 21
Pb	15,1 – 42,4 24,0	2,4 – 134,0
Zn	1,0 – 6,0 3,2	1,4 – 165,0

Table 6. Percentage of acceptance of cuttings and productivity and quantity of the willow crop

Tabela 6. Procentowe przyjęcie zrzezów oraz produktywność i jakość plonów wierzby

Variety	1st year		2nd year			3rd year			4th year		
	Acceptance of cuttings		t/ha	Ist class	IInd class	t/ha	Ist class	IInd class	t/ha	Ist class	IInd class
	%	t/ha		%			%			%	
Piaskówka	90,1	3,2	18,2	59	41	19,1	78	22	18,4	76	24
Odra	94,1	3,9	16,3	61	39	20,1	71	29	17,5	69	31
Amerykanka	91,0	2,3	17,5	67	33	17,0	83	17	22,6	79	21
Kottenheider	94,5	3,2	29,4	62	38	27,2	70	30	26,8	71	29
Królewska	94,0	6,7	19,4	57	43	17,3	78	22	17,8	74	26
mean values	92,7	3,9	20,2	61	39	20,1	76	24	20,6	74	26

The degree of contamination of environment can be assessed quite accurately by determining the content of heavy metals and sulphur in the biomass of plants growing in that area. That is why the authors determined quantities of these elements in leaves as well as in shoots and roots.

The highest quantities of copper were determined in leaves (Tab. 3), while shoots were found to contain the smallest amounts of this element. The quantities of Cu in roots were 6-8 times lower than in leaves but 2-3 times higher than in shoots. The high amounts of Cu in leaves can be attributed to its absorption from both the soil and directly from dusts and atmospheric precipitation.

Higher Cu accumulation in roots than in shoots can be treated as normal since with the increase of copper concentration in soil solution, roots contain higher quantities of this metal [9]. This can be the result of biological barriers confining copper transport which is caused by a stronger binding of this metal by negatively charged pectin substances found in cell walls of root primary bark [1]. The highest content of copper in roots of *Salix Americana* should be attributed to its shallow and flat root system, i.e. in the soil layer most contaminated with this element.

In comparison with the composition of leaves derived from non-contaminated mucky soils (Gleysols) from the region of Nowy Tomyśl (Tab. 4), leaves of willow trees growing in the neighbourhood of the copper smeltery accumulated, on average, 30 time more of this metal (Tab. 5) .

Assuming the mean copper concentrations in crop plants do not, as a rule, exceed toxic levels, i.e. 20 mg/kg, or even 30-100 mg/kg [8], visible disturbances in root development of willow trees should be expected. However, no symptoms of leaf chlorosis or necrosis were found and growth and development of willow trees were not inhibited.

Similar regularities occurred in lead concentrations. The highest quantities of this heavy metal were also observed in leaves (Tab. 3). This should be attributed mainly to the deposition on their surfaces of dusts rich in this element emitted from the smeltery. This is confirmed by studies conducted by Lagerwerff [11] indicating that more than 40% of lead found in over ground plant parts is of "other than root" origin.

Calculated indices of leaf contamination with this metal averaged approximately 24 and were within the interval 15-42 (Tab. 5). Therefore, the examined plants could be treated as highly tolerant to considerable lead concentrations. It is undoubtedly associated with strong binding of this element by cell membranes which reduces its mobility and possible toxicity [14].

In the case of zinc, the highest accumulation of this metal in leaves was also confirmed (Tab. 3). Concentration of this metal in shoots and roots were 4-6 times smaller. When compared with leaves of plants growing near Nowy Tomyśl, leaves of willow varieties growing in the sanitary protection zone of the copper smeltery accumulated 3 times more of this element (Tab. 5). It can, therefore, be said that the current emission of zinc does not pose a serious influence to the development of willow trees, the more so as the upper toxicity limit of this metal in plants was determined at the level of 300-400 mg/kg dry matter [7]. This was also confirmed by the absence of chlorosis or reduced rate of leaf growth of willows – basic symptoms indicating zinc toxicity.

Sulphur concentration in leaves of willow growing on contaminated soils was similar to the quantities of this element determined in identical willow varieties growing near Nowy Tomyśl (Tab. 3 and 4). It can, therefore, be concluded that willow trees belong to the group of plants, which can accumulate much sulphur.

Sulphur quantities found in shoots and roots were similar to concentrations of this element found in many crop plants originating from both areas situated close to copper smelters and growing in other regions of our country [13, 16]. Therefore, it can be said that, at present, sulphur emissions do not pose a serious threat to growth and development of willow trees on the examined object.

Table 6 presents synthetic results of four years of experiments concerning breeding-practical parameters for 5 varieties of willow trees.

Harvests collected from first-year plantations could not be used as production raw material, therefore, their commercial value, i.e. share of shoots in the 1st and 2nd quality class, was not estimated. First-year cuttings are treated only as the so-called tending thinnings. An important parameter in the first year of plantation utilisation is the estimation of the percentage of cuttings, which take root. Values of this parameter for the examined varieties were very high which was an unexpected, albeit welcome, effect as it is well known that plants in their first stadium of development are most sensitive to the toxic influence of heavy metals. The obtained weights of shoots can be treated as average.

Yields obtained in the second year of plantation utilisation were very high, exceeding the yield of shoot biomass obtained on two-year willow production plantations of identical varieties growing on non-contaminated sites in other parts of the country. The value of the harvested raw material was also high since shoots of the 1st class (with very few biological forks) were dominant.

Yields of willow raw material in successive vegetation periods (3rd and 4th) were similar to those recorded in the previous year but their quality was found much higher (Tab. 6).

On the basis of the performed evaluation of the obtained raw material, it can be concluded that concentrations of heavy metals found in the examined soils did not result in a reduction of shoot technological value. It was similar to traits of raw material derived from non-contaminated areas.

CONCLUSIONS

1. The obtained results indicate that, in the examined sanitary protection zone adjacent to "Legnica" Copper Smelter, it is not only the wet areas of humic deluvial soils and proper black earths (Phaeozems) that are suitable for willow cultivation. This plant can also be grown on large areas of local hill slopes which are covered by brown deluvial soils and brown soils (Cambisols) with strong symptoms of water erosion.
2. Lowerd areas should be used for cultivation of *Salix Americana* whose shoots supply the best quality raw material for industry. Their high technological quality is valuable in plaiting industry.
3. Alongside Salix Americana, plantations with *Salix arenaria* or *Salix Kottenheider* should be planted on hill slopes, especially at higher altitudes, as they are characterised by wider ecological amplitude.

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RACJONALNE ZAGOSPODAROWANIE GLEB CHEMICZNIE SKAŻONYCH W SĄSIEDZTWIE HUTY MIEDZI

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Streszczenie. Badaniami objęto gleby (czarne ziemie i gleby brunatnoziemne) skażone miedzią i ołowiem, usytuowane w sąsiedztwie Huty Miedzi Legnica. Powstały one z utworów pyłowych typu lessowego. Charakteryzują się stosunkowo wysoką zawartością materii organicznej

(2-4%) oraz odczynem lekko kwaśnym lub zbliżonym do obojętnego. W poziomach wierzchnich stwierdzono wysoką zawartość miedzi (160-1070 mg/kg) oraz ołowiu (210-570 mg/kg). Założono 4-letnie doświadczenie polowe z kilkoma odmianami wierzby (wikliny). Uzyskane plony tzw. prętów (pędów) przekraczały zdecydowanie ilości surowca uzyskiwanego w innych rejonach Polski. Największe ilości miedzi i ołowiu stwierdzono w liściach (średnio ok. 420 mg/kg Cu i ok. 100 mg/kg Pb). Najmniejszą koncentracją tych metali charakteryzowały się pędy (ok. 27 mg/kg Cu i ok. 30 mg/kg Pb), a więc części mające praktyczne wykorzystanie. Odmianą szczególnie zalecaną do uprawy na tych glebach okazała się *Salix americana*. Udanie plonowały także odmiany *Salix arenaria* Piaskówka oraz *Salix* Kottenheider.

Słowa kluczowe: miedź, ołów, skażone gleby, czarne ziemie, gleby brunatnoziemne.