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Letter to Editor

Spatial Distribution of Copper in Arable Soils and in Non-Consumable Crops (Flax, Oil-Seed Rape) Cultivated Near a Copper Smelter

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Abstract

In the years 1995 and 1996 a study was conducted to investigate the heavy metal contamination of soil and crops (flax and oil-seed rape) in the vicinity of the "Glogow Copper Smelter" in Poland. The concentration of copper, as the main soil pollutant, ranges from background amounts to levels higher than admissible limits. The patterns of copper spatial distribution observed in the vicinity of the smelter is, to a large degree, accounted for by dominant wind direction and distance from the smelter. The area of elevated total soil Cu content, i.e. above 100 mg/kg soil, spreads up to 5.4 km in the NE and 4.9 km in the SE directions but only up to 2.9 km in the NW and 3.9 km in the SW directions from the emitters and covers 3,750 ha. Copper concentrations in capsules of both crops exceeded those in the other plant organs. Hence, the capsules can be the place of copper hyperaccumulation and could be used as bioindicators of Cu spatial distribution. It was also found that the area contaminated by copper as defined by the threshold value of 100 mg/kg soil Cu is about 50% larger than that determined by the threshold value of 15 mg Cu/kg DW in rape capsules.

Keywords: copper smelter, contamination, spatial distribution, soil, flax, oil-seed rape.

Introduction

Heavy metal accumulation in agricultural soil due to atmospheric fallout from ore smelters is known to have an adverse effect on the quality of agricultural land. Plant uptake of heavy metals from soil may result in yield reduction, an unacceptable deterioration of its quality and may be harmful to the human population [1, 8, 9, 11, 13, 15, 16, 18, 20].

The "Glogow" Copper Works began production in 1971 and it emits into the atmosphere primarily dusts and gases of which the dominant are sulphur, nitrogen and carbon oxides. Dusts emitted into the atmosphere contain molecules of such metals as: Cu, Pb, Zn, As, Ag, Cd. The highest values of dust emission were recorded in 1974-1979. In the middle of the '90s the emission of copper was much lower than before but still amounted to 270 kg daily [3]. Hence, the main problem of sound management of agriculture soils threatened by copper smelter emissions is to make a reliable description of the size of the contaminated area. It was assumed that biological monitoring based on the accumulation of heavy metals in crop organs can be an additional source of data referring to their spatial distribution.

The objective of the investigation conducted during the 1995, 1996 growing seasons was:

(i) to identify crop organs accumulating particularly high amounts of Cu in their tissues, and

(ii) to map the pollutant (copper) spatial distribution, in the area threatened by the emission from the copper smelter located near Glogow, Poland.

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Materials and Methods

The material studied were soil and plant samples collected randomly at different distances from the copper smelter at Giogow, within a radius of 10 kilometres. Arable soils of the area studied are potentially fertile. The content of plant nutrients such as available phosphorus, potassium and magnesium was high during the study. The slightly acid and neutral soils made about 70% of the soils studied. In the two subsequent years 1994 and 1995 soil samples in the number of 166 were analysed for total content of Cu. The samples were taken from the Ap horizons of agricultural soils. The part of the land lying in the close vicinity of the copper plant, referred to as the "sanitary belt", was excluded from investigation. Each sample was composed of 50 subsamples taken from an area of 20 m^2. The soil samples were air-dried, sieved through a lmm-mesh sieve and stored in plastic bags before use. Total contents of the metals were determined by the attack of a ground sample with aqua-regia [17].

The plant data are limited only to one year of study for each crop, i.e. to flax (n=68) cultivated in 1994 and to oil-seed rape (n=47) cultivated in 1995. The plant samples were harvested at the time of maturity from an area of 0.5 m^2 (in four replications). Then samples were threshed and divided into subsamples of grain, chaff (i.e. capsules) and straw. Roots were carefully washed out of soil particles. The subsamples were dry-ashed at 540°C and dissolved in diluted aqua regia solution [14]. The amount of copper in plant organs as well as in soil was determined by the AAS flame method.

The relationship between total metal contents in the soil and/or plant and the distance from the copper smelter were assessed by means of a simple regression. Heavy metal concentrations in soils and oil-seed rape capsules were mapped with respect to the distance from the smelter using a computer simulating program (Corel DRAW! 6).

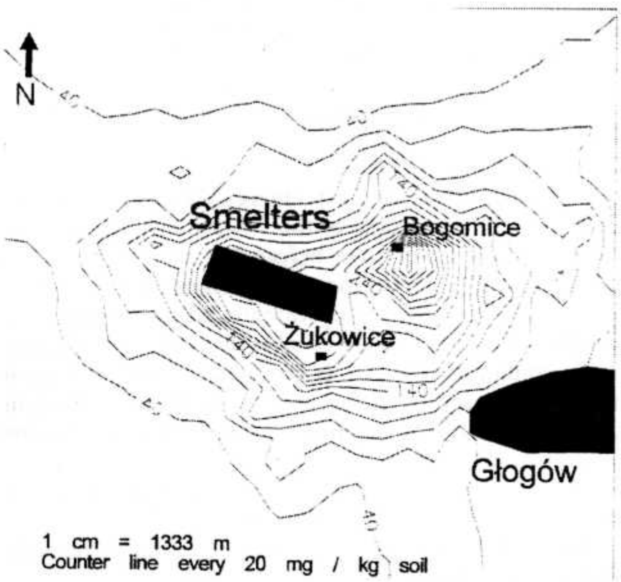

Fig. 1. Spatial distribution around the Copper Smelter Giogow of total copper (mg/kg soil).

Results and Discussion

The total content of copper (as the most important pollutant) in soils adjacent to the Giogow Copper Works (extending up to 10 km from plant chimneys) ranged from about 26 to 330 mg/kg soil. As shown in Figure 1 the copper content in arable soils reveals a clearly zonal distribution in the area under investigation. The zone in which copper concentrations exceeded the admissible level of 100 mg Cu/kg soil, spread from the emitters of the copper plants NE to a distance of 5.4 km, while SE to 4.9 km. In the NW-W wind direction the zone spreads only to a distance of 3.9 km and SW-S of 2.9 km. The data on copper concentration distribution proved a decreasing Cu content in the soil with the distance from the smelter, as shown in Fig. 2 (a, b, c, d) according to the multiplicative regression model. The observed decrease of the total soil copper concentration with the distance from smelters corroborated the thesis on the character of heavy metal deposition around point emitters [11,15,16, 18]. However, individual measurements for each gradient were highly variable, as has been shown by the R^2 coefficients. In terms of reliability a better description of the contaminated area was obtained in the SW and NW than to the NE and SE directions from the source of Cu emission. The results presented are compatible with the wind-rose for the examined area where southwestern and western winds are dominant. A significant effect of the calm air in the area studied has also been established, which can be responsible for changes in the Cu concentration up to 21.9%. So the calm air and predominance of winds of lower than 2 m • s^{-1} velocity probably favoured deposition of dusts in a vicinity close to exposure the Copper Works. Concentrations of copper in this zone exceeded several times the levels admissible according to Polish standards, reaching in the "hot spots" about 9,800 mg/kg of Cu [16]. This highly contaminated area covers about 3,000 ha and has been already excluded from agricultural production and afforested. It should be stressed that the data presented refer mostly to arable soils lying outside the "sanitary belt".

Heavy metal concentrations in natural vegetation or in crops differ, depending on a number of factors such as emission rate, atmospheric transport and deposition, and plant uptake, which all show year-to-year variations. Furthermore, the annual distribution of precipitation and variations in crop growth rate may additionally increase this variability [3, 9]. Therefore, we decided to restrict our evaluation to one year of study for each crop.

Bioavailability is the key to understanding the behaviour of copper in the soil [5, 6, 21]. Bioavailable metal can be defined as the form of metal that can be absorbed by biota, i.e. in our case by crops. The evaluation of crop organs as bioindicators is based on the following assumptions:

1. Crops are able to take up soluble Cu compounds from dust particles, which setle on the foliage, but they can also take up Cu salts from the soil solution. Hence, plant Cu reflects both the current and past pollutant fal lout, respectively.
2. The indicator plant organ should be harvested eas ily and with high accuracy, i.e., roots generally are ex cluded as a monitoring plant organ.

Copper content in the crops studied was highly variable with respect to the distance from a smelter. On average flax plants, independent of the organ, were able to concentrate higher amounts of copper (Table 1). This phenomenon could be explained by plant anatomical characteristics such as surface waxing and the presence of hair and also variability in structure and shape, which affects the ability of individual plant species to take up airborne particles [2, 19, 21]. In addition, processes of heavy metals uptake are strongly governed by soil and plant factors, such as organic matter content and pH [5, 7, 10].

The observed results reveal high variability in copper concentrations among organs of both crops, i.e., indicating their different accumulation capabilities:

Flax: capsules > seeds = roots > stems,

oil-seed rape: capsules > stems = seeds > roots.

In oil-seed rape organs (even in the capsules) the average Cu concentration did not exceed the phytotoxic threshold value of 15 mg/kg dry matter. In flax, its concentration only in the capsules was higher that this value. Differences in the copper concentrations in crop organs can be explained by deposition of heavy metals from atmospheric fallout during plant growth or by their uptake directly from the soil solution. However, the methodology assumed does not permit identification of the most important route of copper accumulation in capsules. On the one hand, the very short time of capsules exposure to atmospheric fallout of dusts (less than 2 month), suggests another route of copper accumulation in plant tissues. On the other hand, even a two-month exposure of this specific organ to atmospheric fallout could significantly increase the copper concentration. This viewpoint is confirmed by the data obtained in the control micro-plot experiment conducted simultaneously on the same soils, but under controlled conditions, i.e. without atmospheric Cu fallout. It was observed that the capsules of field grown oil-seed rape contained twice higher amounts of copper: 16.4 versus 8.8 mg Cu/kg DW for the plants grown on micro-plots located 150 kg north of the studied area. For the flax this relationship was 10.8 versus 3.5 mg/kg DW [6].

The size of the contaminated area was determined on the basis of the concentrations of Cu in the soil and plant samples collected at random at different distances from the source of emission. The results obtained on the basis of soil analysis were correlated with the concentration of Cu in plant tissues (Table 2). The best-fit regression models describing these relationships for capsules of both crops were found and the following equations describing the relationships between soil and plant copper contents were derived:

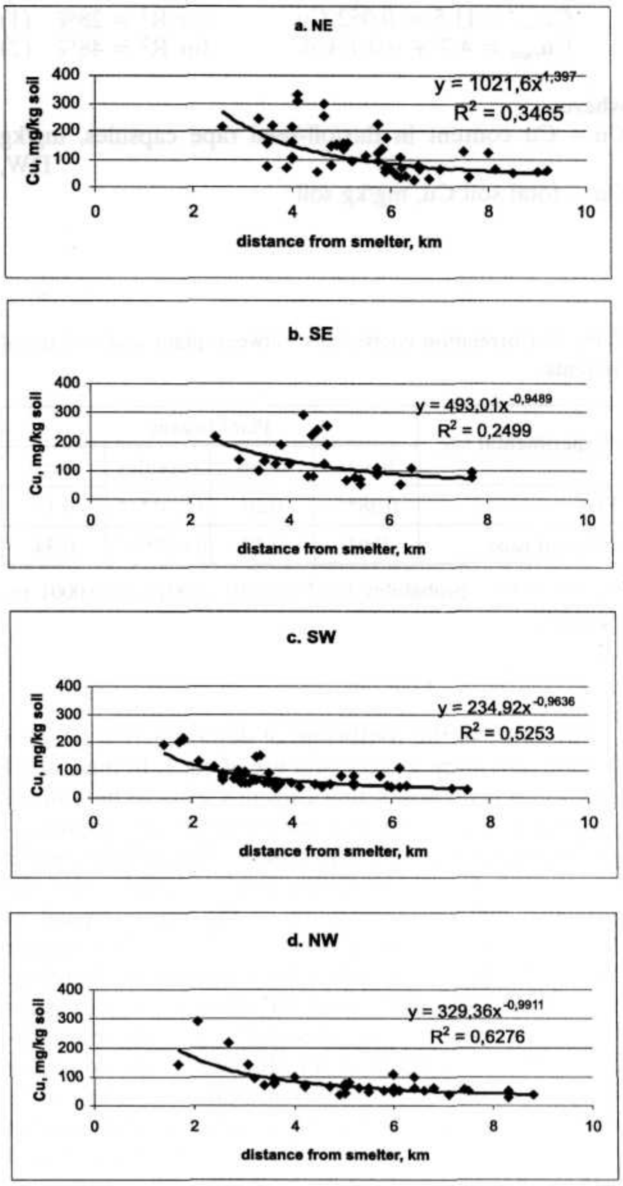

Fig. 2. relationships between total soil Cu and distance from smelter on the prevailing wind directions.

Table 1. Statistical characteristics of copper distribution among flax and oil-seed rape organs, mg/kg DW.

Statistical parameters	Flax, n = 68 plant organs				Oil-seed rape, n = 47 plant organs			
	roots	stems	capsules	seeds	roots	stems	capsules	seeds
Average	11.1	9.0	16.4	11.3	3.6	4.5	10.5	4.3
SD*	8.3	5.9	6.7	4.8	0.8	1.1	3.6	1.0
CV**, %	74.5	64.7	40.9	42.5	31.3	24.4	34.0	22.5

* standard deviation, ** – coefficient of variation

$Cu_{flax} = 11.5 + 0.052\ Cu_r$, for $R^2 = 28\%$ (1)
$Cu_{rape} = 4.7 + 0.056\ Cu_r$ for $R^2 = 48\%$ (2)

where:
Cu - Cu content in flax/oil-seed rape capsules, mg/kg DW,

Cu_r - total soil Cu, mg/kg soil.

Table 2. Correlation coefficients between plant and soil metal contents.

Experimental site	Plant organs			
	Roots	stems	capsules	seeds
Flax	0.38**	0.20	0.53****	0.15
Oil-seed rape	0.03	0.27	0.69*****	0.34

, *, **** – probability levels at 0.01; 0.001 and 0.0001 respectively

The value of the coefficient of determination (R^2) for flax does not allow a successful use of eq. 1. In the case of rape, there is no doubt that capsules seem to be a much better bioindicator organ of the environment contamination by copper that flax. The observed linear relationship between the Cu concentration in the capsules and the respective metal concentration in the soil is typical of plants having indicator strategy (Fig. 3) [12]. In this type of plant the passive metals uptake dominates, therefore the internal concentrations of the metal can reflect external metal concentrations. Another important index describing the availability of an element in the soil-plant system is the metal concentration ratio in these two components. As shown in Figure 4, this ratio plotted against soil copper concentration gives a hyporbolic-shaped curve, which is supposed to be typical of essential elements, i.e. in our case copper [4]. The shape of the curves means that copper was taken up from soil by oil-seed rape at a different rate. At low soil Cu concentrations its uptake was relatively high, but at high soil metal concentrations it was several times lower. This phenomenon stresses again the importance of soil contamination with Cu as the main source of plant content of copper.

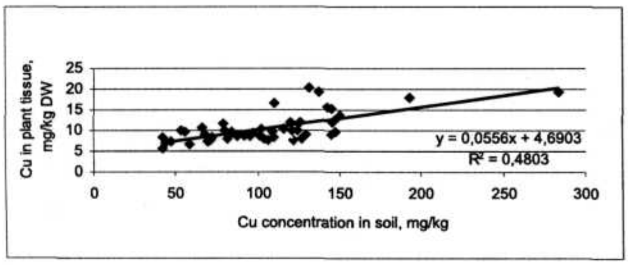

Fig. 3. Relationship between copper concentration in the soil and its concentration in oil-seed rape capsules.

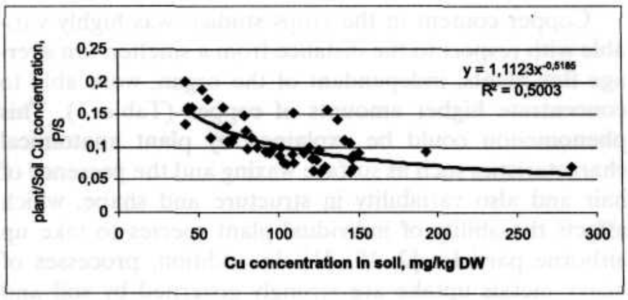

Fig. 4. Relationship between copper concentration in the soil and its plant/soil concentration ratio.

An approximate assessment of the size of the area contaminated by copper emitted by the Copper Works has been made on the basis of the concentrations of Cu determined in the soil and in the crops. In the second case only Cu concentrations in the capsules of oil-seed rape were used. The calculation procedure is presented below: 1° Soil Cu

As is presented in the Figure 1, the area contaminated by Cu covers about 3 750 ha;. 2° Capsules Cu

Cu_{ca} as independent value and d - distance from the emitters

$$d = 2.71\ Cu_{ca}^{-0,62} \text{ where } R^2 = 38\% \quad (3)$$

The size of the contaminated area has been calculated on the basis of some data referring to:

a. 3.5 mg/kg (average content of Cu in plants grown outside the contaminated area) [6]. d = 6.96 km -» 152.11 km^2; this area reflects the elevated level of plant Cu content.

b. 15 mg/kg DM (critical plant Cu concentration) d = 2.83 km -> 25.15 km^2; this area reflects the polluted level of plant Cu content.

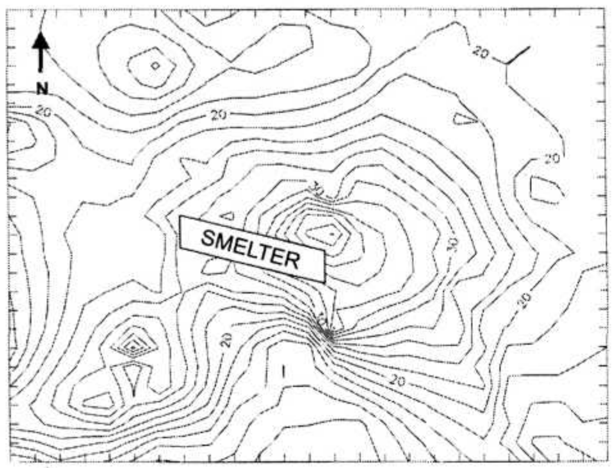

Fig. 5. Spatial distribution around the Copper Smelter Glogow of winter oil-seed rape capsules Cu (mg/kg DW).

Fig. 5 shows the spatial distribution of copper concentration in the vicinity of the smelter assessed by means of its concentration in oil-seed rape capsules. The obtained results, in spite of lower numbers of plant samples, are surprising, because the acreage polluted by copper as defined by the threshold value of 100 mg/kg soil Cu has been found to be about 50% larger than that determined by the threshold value of 15 mg/kg dry matter of rape capsules. Therefore, it could be concluded, that plants can serve as bioindicators and the concentration of heavy metals in their organs can be used for mapping a relative level of pollution by heavy metals throughout a given area.

Conclusions

1. A multiplicative regression model fitted best spatial variability of copper concentrations in arable soils with respect to the distance from the source of emission.
2. The content of copper in responsive crops organs such as capsules of flax or oil-seed rape could be used as reliable indicators of environmental contamination.
3. Using threshold values of soil and plant Cu concentration it is possible to make a reliable estimation of an area contaminated by this metal.

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