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Summary Thesis

Research on the status of heavy metals in the soil-plant system in Copşa Mica - Micăsasa area

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Introduction

The research conducted in this thesis had the main objective to establish areal distribution and the contamination of soil, mainly with the elements: Pb, Zn, Cu, Cd and Fe, Mn, Ni, Co, Cr and their translocation in plants in polluted area, between Copşa Mica and Micăsasa. Our study covers an area of 1,700 hectares situated between Copşa Mica town and Micăsasa village. The area is used by local people in the most part for agriculture. The main objectives of this work are:

→ determine the concentrations of heavy metals in the soils investigated area;

→ determine the excess of the normal, alert thresholds and intervention for type of use of the land concerned;

→ establishing areals distribution of heavy metals, mainly Pb, Zn, Cu and Cd and Fe, Mn, Ni, Co and Cr relative to the predominant direction of movement of the air masses of the source of pollution;

→ establishing the degree of pollution of the soil with the elements investigated in relation to distance from the emission source;

→ establishing translocation of heavy metals in soil samples in the roots (where they were collected) and ground to the upper parts of plants;

→ determine the concentrations of metallic elements in tissue samples of plant material;

→ determine the relationship between concentrations of heavy metals in samples of plant material and concentration limits of the law.

To achieve these objectives, sampling:

 two levels of soil depth: 0-20 cm and 20-40 cm obtaining 200 soil samples.

 plant material found at every point where soil samples were collected.

Chapter I. The nature of the investigated area

I.1. Geographical location and topography

The study area is located in Sibiu County, between the Copşa Mica town and Micăsasa village, on the middle of the Târnava Mare river. Geomorphological units that borders are Blajului Plateau in the north, Amnas Plateau in the south, Cergăului Plateau in the south-west and Medias Plateau in the south-east.

I.2. The soil

In the investigated area and in adjacent soil types within classes Protisoluri, Cernisoluri, Luvisols and Antrisoluri. Soil types are presented only as strictly meet the investigated area.

Protisoils (Fluvisols gleyic) are on the floodplain corridors of Târnava Mare. Was executed a soil profile located approximately half researched area. Type of soils determinated was aluviosoil limestone-molic-gleic, drained (AS ka-mo-gc-k1). It is characterized by the presence of a horizon showed compacted (Apt) and a dark mollic horizon, well structured (I), followed by a transition horizon A / C and pass directly into the parent material that has formed, Fluval deposits consisting of silty-clayish carbonate.

Luvisoils in the study area (the south) are represented by typical Luvisols formed on various material under the good to moderate drainage. Texture in the upper horizon and below it varies from sandy loam to loam argilosă.

I.3. Aspects of climatic regime

The study area falls within the temperate continental climate with strong influences of cyclones in the North Atlantic and polar air masses from the north. The hottest month is July when the average temperature ranges between 19.2 ° C and 19.9 ° C in Sighisoara Blaj. The coldest month is January, when average monthly temperatures range between -3.5 ° C and -4.7 ° C Blaj Dumbrăveni. For the correlation of temperature with altitude Copşa Minor suggests that annual average temperatures decrease with altitude from 9.6 ° C in the valley bottom Târnavei 8.2 ° C higher in areas with greater height (Goga, 2010). Average annual rainfall ranges from 524 mm to 645 mm Blaj and Sighisoara (Bunescu, 2003).

I.3.1. The wind and the influence on the dispersion of pollutants

Measurements Meteorological Observatory pollution monitoring has four automatic monitoring stations located in Copșa Mica and Medias show that in 58% of cases (for one year) is recorded sharp movements of air masses and in 42% of pacifying prevalent cases (Goga, 2010). Of air traffic systems are mainly determined by positioning Târnavei Great Valley and its tributaries valleys. We can separate these two meanings prevailing atmospheric circulation influences on pollutant dispersion follows:

- the north-east to south-west, with a frequency of 27.3% and speeds from 0.5 to 3.5 m / s which favors the dispersion of pollutants in large areas west of the source of pollution;

- from southwest to northeast, with lower speeds and a lower frequency of 21% (on the first sector) leads to the dispersion of pollutants shorter distances, their accumulation near the source of emission (Goga, 2010).

In terms of climate and topography, location of industrial units in the area proved to be totally inadequate, leading to increased pollution because it is a lowland bounded by high hills. Such is stopped pollutant dispersion in the atmosphere also self-purification capacity is reduced due to periods manifested phenomena as fog, cloud ceiling down, calm atmosphere or thermal inversion.

Chapter II. Heavy metals, General

The term heavy metal is used to define metals and semi-metals with toxic properties, generating confusion about the correct term signifies (Duffus, 2002). Heavy metals are considered those chemicals with a density greater than 5 g/cm3 and atomic mass between 63.54 and 200.59 (Singh, 2005 Hâncu, 2008). Are considered to be toxic because they tend to bioaccumulate and may have adverse effects on the body (Caliman, 2009).

Heavy metals such as Fe, Mn, Ni, Cu, Zn, Pb, Cd, As, Hg are part of the natural components of the environment. A chemical element can have an actual and a potential contaminant of "perspective" by changing environmental conditions and hence changing its accessibility and concentration. Some of these elements play an important role in normal development of organisms, and due to the generally low content of these elements in soils and plants, and by the biological role they have, are grouped as micronutrients (Lăcătuşu, 1995). Each element participating in human nutrition expresses fully effective only in the presence of all the other elements involved in metabolic processes (Trifu, 1976).

The most common symptom for heavy metals phytotoxicity manifested by leaf chlorosis (Lăcătuşu, 2006). At the cellular level, heavy metal toxicity is manifested by changing the permeability of the plasma membrane, cell organelles structure change and influencing metabolic processes. At the physiological level, the effects of heavy metal toxicity is manifested by impaired growth, reduced photosynthesis and transpiration intensity, disrupting water regime (apples, after Dobrotă 2009, 1999 and Onac, 2005).

Although soil possess regenerative capacity, once destroyed can not restore as it was originally because it can create the same conditions that led to its formation. It can get more than a body with similar functions (Plopeanu, 2010).

Natural sources of heavy metals are generally represented by parental rocks. Anthropogenic sources are represented by human activities such as ore, various metallurgical and related industries, burning of fuels, their use in various fertilizers or pesticides for agricultural, domestic and industrial waste. Sources with the greatest potential pollutant are units metallurgy and metal smelters, they pollute a distinct group of elements, namely Pb, Cd, Cu and Zn (Alloway, 2013).

II.1. Heavy metal pollution in the Copşa Mica

SC Sometra SA was established as an economic unit between 1939-1940. Currently the only Romanian company producing zinc metal and lead mining concentrated. At the end of last refurbishment, the plant had an annual production capacity of 30,000 t 20,000 t Zn and Pb. Since 2007, unit activity was stopped temporarily and moment production activity is stopped.

Heavily polluted area is 21,875 ha of which 18,630 ha are agricultural land and 3,245 ha forests. Data on heavy metal pollution of soils of Little Copşa since 1987 are made of malice C. The area with the highest total forms of heavy metal pollution caused by Dumitru et al, (1994) had exceeded AML Pb of 3 to 30 times, 2 to 32 times the Cd, with 24-times and the 2 - 3 times the die. In 1995, Lăcătuşu et.al. determined the degree of loading / heavy metal pollution of soils in some pastures located in the neighborhood of Copşa Minor. Mobile forms of heavy metals in relation to AML showing a 3.5 times for Cd, Pb 10.5 times, while for Zn exceeded 3.9 times. In 1996, Lăcătuşu et.al., shows a severe degree of soil contamination with Cd, Pb and Zn moderately easy loading for Cu.

The concentrations of Pb, Cu, Zn or Cd in soils Copşa Mica were studied soil profiles for different types of soil based on the physical and chemical properties. Were determined values between 561-2768 $mg.kg^{-1}$ for Pb concentrations between 71.1 and 96.9 $mg.kg^{-1}$ for Cu, values of 684 $mg.kg^{-1}$ for Zn content of 18 mg. kg-1 for Cd, all in neutral pH conditions with different humus content (0.48 to 4.56%) (Damian, 2008).

The results of recent studies conducted by Vrinceanu (2010) reveal a high degree of pollution remains at alarming levels, even if the main source of pollution was stopped.

Chapter III. Working Methodology

III. Sampling and analysis of soil samples

Soil samples were collected by a network of sampling of side about 400 m sampling network was established based on topographic maps (1:25,000). Soil samples were collected from two depth ranges from 0-20 cm and 20-40 cm. We have taken a number of 200 samples, every 100 samples for each sampling level.

The samples were dried at room temperature for about 35 days, after which they were mortar and sieved to fraction of ≤ 1 mm, prior to being removed residual vegetable material (roots). Determination of the concentrations of (heavy metals) in soil samples was conducted at the National Institute of Research-Development Institute for Soil Science, Agrochemistry and Environment Protection (ICPA Bucharest) by flame atomic absorption spectrometry, the model appliance is Solaar S4.

III. Sampling, analysis of samples of plant material and interpretation of analytical

Samples were harvested plant material by the same network sampling as in the case of the ground, exactly at the place where soil samples were also taken. Proof was held in early June 2011, being awarded a number of 100 samples. For exact identification of each plant species was used an Atlas Botanic (Mourousis, 1985).

After the removal of particulate soil and dust by washing with distilled water, the samples were dried at 80 ° C in an oven, after which they were finely divided and stored in paper bags. Determination of heavy metals was carried out in the Laboratory soil-plant interrelationships, food quality (ICPA Bucharest) with flame atomic absorption spectrometry (AAS) model Solaar S4. The largest share had a crop being number 58 most of them are located in the central and western part of the investigated area.

Samples of the corn were 4 to 6 leaf stage of growth. The aerial part of the plant was harvested and N in some cases and roots. LMA will be considered as set by Order 18/2007. Were harvested wheat (13 samples), alfalfa (5 samples) and a sample of plum. For samples of wheat were harvested grains, which are crushed. These were the phenological stage of ripening grain (maturation). For these samples will be considered as those established by Ordinu LMA 975/1998. For samples of alfalfa were harvested aerial part of the plant.

Spontaneous vegetation samples (42 samples), most were of acacia (Robinia pseudacacia, 12) and field grass (Agrostis stolonifera, 8). When these samples were collected following parts of plants: trees and shrubs - leaves, canopy - the aerial part of the plant. Most samples in this category were located in the eastern part of the area studied. Interpretation of the data was performed taking into account the predominant plant species: maize and acacia.

Chapter IV. Analysis of the distribution of metallic elements in soil

IV.1 Statistical analysis of the data set for soil samples

The data set was divided into two categories namely the 0-20 cm and 20-40 cm respectively in 3 sectors away 0-3, 3-6 and 6-9 km from the source of pollution to the west. The number of samples considered for each sector is 37 for the 0-3 km, 25 km and 38 sector to sector 3-6 6-9 km. Concentrations obtained for elements of soil samples are reported in LMA established by Ordinance 756/1997. Were determined following statistical parameters: mean, median, minimum, maximum, lower and upper quartiles, coefficient of variation, standard deviation, asymmetry and flatness, and correlation coefficients.

After the average concentration each element abundance is found next to the 0-20 cm sampling: Fe> Zn> Pb> Mn> Cu> Cd> Ni> Cr> Co. For the 20-40 cm sampling, the order of abundance based on the average concentration of elements changes compared to the first level: Fe> Zn> Mn> Pb> Cu> Ni> Cr> Cd> Co.

The average concentrations of polluting elements characteristic of the area studied (Pb, Zn, Cu, and Cd) has exceeded normal values for both levels of sampling. The highest exceedances of normal and alert and intervention thresholds were obtained for samples from 0-20 cm horizon, showing, as expected, the concentration of these elements in the upper part of the soil. The highest values were recorded near the source of pollution in the 0-3 km, they will decrease with removal from the source of contamination for the other two sectors 3-6 and 6-9 km.

IV.2. Lead

Pb concentration in the study area ranges from 19.78 mg.kg^{-1} and 4532 mg.kg-1, with an average of 619.11 mg.kg^{-1} in the 0-20 cm sampling interval. The minimum value of 8.35 mg.kg^{-1} and maximum of 2706 mg.kg^{-1} and an average of 192.5 mg.kg^{-1} belong sampling interval 20-40 cm. The concentrations of these elements in the soil above the normal value, only 1% of the samples with a concentration lower than this. Most evidence that is 92% above PISS 0-20 cm horizon investigation. For sampling horizon 20-40 cm, only 6% of Pb values are below normal and 51% above PISS

Compared to the distance from the pollution source, the concentrations of this element gradually declines westward from the source of pollution. Pearson linear correlation coefficient of Pb concentrations in the distance from the source recording a negative value of -0.5 to -0.28 horizon for 0-20 cm and 20-40 cm. The analysis of distribution maps for the two depth horizons, it outlines clear areas with the highest content of lead.

IV.3. Cadmium

Limits values falling this element are 0.29 mg.kg^{-1} and 166.6 mg.kg^{-1}, where only 1% of the samples are below normal, 10% below and 21% below PISS PASS for 0-20 cm. Concentrations ranging from 0.1 mg.kg^{-1} and 152 mg.kg^{-1} with 8% of the values are below the normal range, 33% below and 37% above PISS PASS were determined 20-40 cm.

Mean content for 0-20 cm throughout the studied area is 33.1 mg.kg^{-1}, exceeding the 33.1 times normal levels in soils PASS 11 times, 6.6 times PISS, 6 , 6 times PASmpS and 3.3 PISmpS. For

20-40 cm, the mean was 14.9 $mg.kg^{-1}$, which shows an excess of normal of 14.9 times, 4.9 times PASS. PASmpS was exceeded by 2.9 times and 1.49 times PISmpS.

Cd concentrations have a correlation (r) for 0-20 negative -0.64 and -0.41 for 20-40 cm in relation to the distance from the source of pollution.

It outlines the area with the highest concentrations near the source of pollution, up to about 2.5 km, followed by a gradual decrease in concentrations, but that remains above normal, alert thresholds and intervention even near Micăsasa, located 9 km away industrial unit. The lowest values of cadmium found in the south-west of the area studied area at the confluence of the Great Valley and Valley Şeica Târnavei Minor. After contact air masses from the two valleys, atmospheric deposition conditions are created loaded with Cd in the north-west area.

Given the topography of the Târnava Mare corridors, with altitudes ranging from 287 m in the E and 268 m in the west side of the hills with heights between 550 and 430 m in the north and between 450 m and 360 m on the south, to the fact that the industrial facility operated to close the shut-off exhaust chimney low height, with the fact that most of the cool air and mist prevails time frequency, all these factors have led to the accumulation of soil concentrations of large heavy metals. Bin 250 m was built only in 1989, towards the end of industrial activity, without significantly reducing the accumulation of pollutants in the vicinity of the emission source.

When configuring the distribution of pollutants, an important role and atmospheric currents formed confluent valleys meadow Mari Târnavei like Valley Chestlerului or currents that form the valley Șeica Minor. High concentration of heavy metals in the N - NE investigated area also suggests the influence of air currents that form the valley corridors Visa, located in the SE of the area.

Chapter V. Analysis of metal elements in plant samples

V.1. Corn

Statistical analysis of the data set for the characteristic elements polluting the study area are shown to shape distributions and concentrations of these elements in plant samples of corn.

V.1.1. Lead

The average value of lead in the samples of maize was studied to 25 mg.kg-1, and extreme values were 106.4 and 7.6 mg.kg^{-1} mg.kg-1. Taking into account the values determnate lead in roots, the average is 32 mg.kg-1.

General distribution of Pb determined on samples of corn plant has a visible decrease in the content in comparison with the removal of the source of pollution to the west along with the removal of the source of pollution.

Tolerance established by Kabata Pendias in 1992, to the 10 mg.kg^{-1} dry matter exceeded the mean concentration of Pb in samples of maize by 2.5 times. For the five samples taken from the range 0-3 km maize were collected and root samples.

Transfer factor Ft = [M] p / [M] t of lead in soil samples of corn had a value of 0.2. Calculated for roots, Ft value is 0.3. Transfer factor calculation was performed using the mean concentrations of Pb's horizon 0-40 cm soil samples were selected only from points where samples were taken and corn. Corn roots concentrated in a large amount of heavy metalel ground, blocking their absorption by the rest of the plant.

V.1.2. Cadmium

The corn samples, the average value of Cd is 4.3 mg.kg-1. The range of Cd to the aerial part of maize is between 0.3 to 12 mg.kg-1. If roots are included and the average value of the samples of CD is 5.1 mg.kg-1, and the maximum value of 21.7 mg.kg-1. The general trend of Cd content in maize plants is one obvious decrease with the removal from the source of pollution.

Compared to the limit of Cd in Order 18/2007 on undesirable substances in animal feed (1 mg.kg-1), its average value exceeds 4.3 times the permissible limit. Transfer factor of the air in the soil Cd maize plant has a value of 0.7. Root samples transfer factor value of 1.6. The CD of the roots was 1.7 times higher than the levels of the routes of the plant.

Between concentration the elements determined in samples of corn and distance from the source of pollution, linear correlation coefficients were negative at -0.7 to -0.6 Pb and Cd, pointing out that increased towards the pollution source distnaţei concentrations of metallic elements in plant tissue samples of corn fall.

V.2. Acacia

Average of the four elements are determined for samples of acacia 20.4 $mg.kg^{-1}$ Pb, 117.1 $mg.kg^{-1}$ Zn, 7.3 $mg.kg^{-1}$ and 1.2 $mg.kg^{-1}$ Cd . The concentrations of these elements in the leaves of acacia are at a fairly high considering that they do not accumulate metallic elements. The main reason is the buildup of air, loaded with metallic elements in view of their leaves that most samples are placed in the vicinity of the source of pollution. The average age of acacia trees were sampled from the plant tissue of about 10-15 years.

The average concentrations of the other components specified for the harvested plant species Pb values ranging from 3.62 $mg.kg^{-1}$, 132 $mg.kg^{-1}$, for zinc from 34 to 842 $mg.kg^{-1}$, for Cu of 2 , 5 and 9.3 $mg.kg^{-1}$, and the CD of 0.2 to 119.3 $mg.kg^{-1}$.

Determined values for concentrations of heavy metals in samples of plant material shows that the species probably Copşa Mica plants are not in the category hiperacumulatoare. Plants of the Low Copşa have adapted to the conditions of heavy metal pollution, fail to develop normally even if they have accumulated high concentrations of heavy metals.

Chapter VI. Conclusions

VI.1. Conclusions on the distribution of elements analyzed for soil

Polluting elements characteristic of this zone are Pb, Zn, Cu, Cd. Depending on their average concentration in surface sampling, polluting elements follow the order Zn> Pb> Cu> Cd;

Pollution degree, determined by the number of exceedances of the normal laws of Romania, is as follows: Cd> Pb> Zn> Cu.

→ For the range 0-20 cm:

- a remote VN Cd exceeds 0-3 km west of 75.4 times, 5.9 times less (compared to the first interval distance) of 3-6 km from the source area and 13.7 times less reported 0-3 km to 6-9 km;

- Pb exceeds 54.4 times VN 0-3 km, halved at a distance of 3-6 km, and the 6-9 km is 4.2 times smaller than the first area;For the range 20-40 cm:
- Zn exced 32 times VN at 0-3 km of 8 or less for 3-6 km and less than 9.6 times the 6-9 km in relation to the first section;
- Cu exced 16,8 times the 0-3km VN, 2.4 times and 3.6 times less than for 3-6 and 6-9 km compared to the first sector;

→ Comparing a number of exceedances of VN between the two sampling interval:

- the range of 0-3 km is found that for 0-20 cm overruns value was 3.2 times higher for Pb, 2.3 times higher for Cd;
- for 3-6 km 0-20 cm compared to 20-40 cm, VN overruns were 3.4 times higher for Pb and Cd 3.1 or higher;
- for 6-9 km to the number of exceedances VN 0-20 cm was 2.8 times higher for Pb, and 1.6-fold for Cd;

→ Comparing the two sampling intervals 0-20 cm 20-40 cm for the second sampling interval from 3 km west from the source, pollution decreases.

VI.2. Conclusions on the distribution of plant material elements of the samples analyzed

→ The highest concentrations of heavy metals in corn plants were obtained for samples located approximately 5 km west from the source of pollution;

→ Concentrations of heavy metals in samples of corn drop by removing the source of pollution, the linear coefficient values corealție concentrations of heavy metals were negative;

→ The average values of the elements Pb and Cd in maize samples exceeding 2.4 times 4.2 times for Pb and Cd LMA;

→ Average concentrations determined in the roots of corn were 4 times higher for Pb and Cd 1.7 times higher as compared with the average values determined for the route;Pentru rădăcini, valoarea factorului de transfer a fost de 1,6 pentru Cd și de 0,3 pentru Pb;

→ Heavy metals in leaves of acacia had averages of 20.4 $mg.kg^{-1}$ Pb, 117.1 $mg.kg^{-1}$ Zn, 7.3 $mg.kg^{-1}$ and 1.2 $mg.kg^{-1}$ Cd;

→ For samples of plant material rcoltate the canopy, the maximum values of heavy metals were observed for Pb (240 mg.kg-1) to hawthorn for Zn (1020 mg.kg-1) and Cd (142 mg.kg -1) in leaves of poplar, and Cu (13 mg.kg-1) in samples of shepherd's purse.