EFFECTS OF LONG-TERM INDUSTRIAL POLLUTION ON
HEAVY METALS ACCUMULATION IN SOILS AND MAIZE
CROPS ON TÂRNAVA MARE RIVER BOTTOMLAND

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Heavy metals contents in soil and maize plants were examined to quantify the influence of
long-term industrial pollution on soils and maize crops on Târnava Mare River
bottomland. An objective of this paper is to evaluate the relationship between the distance
from polluter and the accumulation of cadmium, lead and zinc in soil. Also, the study was
carried out in order to estimate the statistical dependency between heavy metals contents
in maize plants and distance from pollution source. A network of 59 sampling points
located in Târnava Mare River bottomland was used. Soil and plants samples taken from
each sampling point were analyzed to determine the content of heavy metals (Cd, Pb and
Zn). Relationships between heavy metals contents in soil and maize plants and distance
from pollution source were estimated by means of power or exponential regression
functions. The values of correlation coefficient indicate good correlations between
considered variables as follows: for cadmium (rsoil = −0.950; rleaves = −0.859; rstalk =
−0.826; rgrain = −0.466); for lead (rsoil = −0.932; rleaves = −0.858; rstalk = −0.728; rgrains =
−0.402); for zinc (rsoil = −0.937; rleaves = −0.857; rstalk = −0.654; rgrains = −0.417).

Key words: heavy metals, regression curves, soil, maize, bottomland, Târnava Mare.

INTRODUCTION

Chemical compounds coming to ecosystem from various human activities are
accumulated in soil and water reservoirs. That is the way the soil may be regarded
as a long-term reservoir of environment contaminants from which these compounds
enter the terrestrial food chains and/or underground water. Soil pollution with
heavy metals near pollution sources is a constant process having toxic effect on
plants and on soil microorganisms (Peciulyte and Dirginciute-Volodkiene, 2009).

The contribution of metals to environmental pollution from industrial,
agricultural and mining processes besides automobile emission, has been the main
subject of many studies and research in recent years. Atmospheric emissions from
industrial establishments are one of the major sources of environmental pollution
(Addo et al., 2012).
The main environmental damages in the area Copşa Mică (Romania) are caused by ore processing. Copşa Mică, situated on the Târnava Mare River, the most polluted area in the Sibiu County, was classified as an environmental disaster area. The S.C. Sometra S.A., a non-ferrous metallurgical factory, was the main industry responsible by the pollution. The emissions coming from the other economic agents from industrial platform of Mediaș city (S.C. Emailul, S.C. Vitrometan, S.C. Geromed) is add to pollution in this area (Suciu et al., 2008).

The main objective of the present study was to evaluate the influence of long-term pollution caused by emissions from non-ferrous metallurgical factory in the area Copşa Mică. The study focuses mainly on the accumulation of heavy metals (Cd, Pb and Zn) in soils and maize crops on Târnava Mare bottomland.

MATERIALS AND METHODS

The study of heavy metals accumulation in soil and maize crops was achieved using a sampling network (59 sampling points) located on Târnava Mare River (Fig. 1). At each soil sampling point, the plant samples were collected from maize crops at full maturity.

Soil samples taken from soil top layer (0-40 cm depth) were air-dried at room temperature and then ground to pass through a 0.2 mm sieve. Soil samples were digested with acid mixture in the microwave digestion system using PTFE digestion vessel with pressure and temperature feedback control. The maize plants were separated into three parts (leaves, stalks and grains), were dried in an oven at 60°C for 48 h, until
constant weight was reached, grounded and then were digested with nitric acid in a microwave digestion system. The metal content was measured using a flame atomic absorption spectrometer in hydrochloric solution resulted by acid digestion of samples.

Power and exponential regression functions were used to describe the statistical relationships between metal content in soil/plant and distance from the polluter (SC Sometra SA). The exponential and power regression functions use linear regression on log-transformed data.

RESULTS AND DISCUSSIONS

The results of study carried out in Târnava Mare River bottomland allowed establishing stochastic relationships between the cadmium, lead and zinc contents in soil, as dependent variables, and the distance from the pollution source, as independent variable (Fig.2).

The data on cadmium concentration distribution proved a decreasing of cadmium content in soil with the distance from pollution source according with the regression equation represented in Fig.2. The area where cadmium concentrations in soil exceeded the intervention threshold (IT) for sensitive land use (IT – 5 mg/kg) is extended up to 8.38 km West from pollution source. The trend of variation estimated with a power regression function indicates that the values of total cadmium content in 0-40 cm layer decrease below the alert threshold (AT) at distances higher then 12.56 km West from the polluter.

For all sampling points the values of total lead content exceeded the alert threshold (AT – 50 mg/kg). For the entire studied area, lead proved to be the limiting factor for the agricultural use of land.

The trend of variation estimated with a power regression function indicates that the values of total zinc content in soil (0-40 cm layer) decrease below the intervention threshold (IT – 600 mg/kg) at distances higher than 6.74 km West, but remain above alert threshold (AT – 300 mg/kg) to about 12.86 km West from pollution source (see Fig.2).

According to a semi-log graph (Fig.3), the maize grains accumulated high amounts of metals. The values of metal contents in grains were correlated with the distance from the source by means of a power regression equation. For cadmium, the value of linear correlation coefficient corresponding to linear form of the regression equation was very highly significantly different from zero ($r = -0.466^{***}$), indicating a good correlation between the cadmium content in grains and the distance from the pollution source. The maximum allowable value for cadmium in food (MALFD - 0.2 mg/kg) was exceeded for the grains of maize plants grown on soils located up to 2.44 km west from the pollution source.

According with these empirical models used to estimate the cadmium, lead or zinc accumulation in maize grains, the values of metal content in grains for all samples are bellow to the maximum allowable limit for each metal in fodder.

All grains samples had higher concentrations of lead and zinc than maximum allowable limit in food, indicating that the grains were contaminated with these metals and may not be suitable for human consumption.
Metals accumulated in grain are mainly transported from the leaves via phloem (Bi et al., 2009). The grains surface was unlikely contaminated by airborne/soil particle because all the grains were wrapped by the husks when sampling. Therefore, the metal accumulation in the maize grains refers to that of tissue absorption instead of surface adsorption.

The heavy metals accumulation in maize stalks can be described very well using a power function, with the distance from source as independent variable (Fig.4). In maize leaves the contents of heavy metals determined are presented in Fig.5.

\[
\text{Cd}_{0-40} = \frac{73.233 \cdot D_{\text{km}}^{1.2627}}{D_{\text{km}}^{1-0.2627}}
\]

\[
\lg(\text{Cd}_{0-40}) = 1.8647 - 1.2627 \cdot \lg(D_{\text{km}}) \\
r = -0.950^{***} \quad (n = 59)
\]

\[
\text{Pb}_{0-40} = \frac{1719 \cdot D_{\text{km}}^{1-0.2627}}{D_{\text{km}}^{1-0.2627}}
\]

\[
\lg(\text{Pb}_{0-40}) = 2.3353 - 1.0248 \cdot \lg(D_{\text{km}}) \\
r = -0.932^{***} \quad (n = 59)
\]

\[
\text{Zn}_{0-40} = \frac{4645.8 \cdot D_{\text{km}}^{1-0.728}}{D_{\text{km}}^{1-0.728}}
\]

\[
\lg(\text{Zn}_{0-40}) = 3.6671 - 1.0728 \cdot \lg(D_{\text{km}}) \\
r = -0.937^{***} \quad (n = 59)
\]

Fig. 2. Total cadmium, lead and zinc contents in soil as function of the distance from pollution source – S.C. SOMETRA S.A. (Copşa Mică, 2007, 0–40 cm layer).
Heavy metals accumulation in soils and maize crops

**Fig. 3.** Cadmium, lead and zinc contents in maize grains as function of the distance from pollution source – S.C. SOMETRA S.A. (Copşa Mică, 2007).
Fig. 4. Cadmium, lead and zinc contents in maize stalk as function of the distance from pollution source – S.C. SOMETRA S.A. (Copșa Mică, 2007).
Heavy metals accumulation in soils and maize crops

MALFR - Maximum Allowable Limit for Fodder

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**Cd** in maize leaves (mg/kg)

\[ Cd_{\text{leaves}} = 47.119 e^{-0.1427 D_{\text{km}}} \]

\[ \lg(Cd_{\text{leaves}}) = 1.6732 - 0.062 D_{\text{km}} \]

\[ r = -0.859^{***} \quad (n = 59) \]

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**Pb** in maize leaves (mg/kg)

\[ Pb_{\text{leaves}} = 1520.3 e^{-0.1521 D_{\text{km}}} \]

\[ \lg(Pb_{\text{leaves}}) = 3.1819 - 0.0661 D_{\text{km}} \]

\[ r = -0.858^{***} \quad (n = 59) \]

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**Zn** in maize leaves (mg/kg)

\[ Zn_{\text{leaves}} = 2763.7 e^{-0.1451 D_{\text{km}}} \]

\[ \lg(Zn_{\text{leaves}}) = 3.4415 - 0.063 D_{\text{km}} \]

\[ r = -0.857^{***} \quad (n = 59) \]

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MALFR (1 mg/kg)

MALFR (10 mg/kg)

MALFR (250 mg/kg)

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Fig. 5. Cadmium, lead and zinc contents in maize leaves as function of the distance from pollution source – S.C. SOMETRA S.A. (Copşa Mică, 2007).
The results revealed that the maximum allowable limit for cadmium in fodder (MALFR – 1 mg/kg) was exceeded for stalks of maize plants grown on soils located up to 5.9 km from source. The values of cadmium content in stalks are well correlated with distance from source by means of a power function. The linear correlation coefficient obtained is very highly significantly different from zero (r = -0.826***), indicating a strong dependency between these two variables. The lead contents in maize stalks decreased below maximum allowable limits for cadmium in fodder at distances higher than 5 km from pollution source. All stalk samples in this study had concentrations of Zn lower than maximum allowable limit in food indicating that there are no restrictions for animal consumption (see Fig. 4).

The results of our study showed that the highest metal contents were found in maize leaves. The cadmium, lead and zinc contents obtained for maize leaves exceeded the maximum allowable limit for fodder for all 59 sampling points (see Fig. 5). Part of metals quantified in maize leaves come from dust loaded with heavy metals from pollution source.

CONCLUSIONS

1. It could be concluded that the empirical models presented in this paper can be used to describe a relative level of pollution with heavy metals through a given area.
2. High contents of cadmium, lead and zinc in maize grains harvested from crops within studied area (up to 15 km from pollution source) could pose a possible health risk to regular consumers. Also, the aerial parts of maize plant are not suitable for animal consumption due to high contents of these heavy metals.
3. Using threshold values of food and fodder metal concentration it is possible to make a reliable estimation of contaminated area from Târnava Mare River bottomland.

REFERENCES