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# HUMAN HEALTH RISK ASSOCIATED WITH THE TRANSFER OF HEAVY METALS INTO THE TROPHIC CHAIN BY CATTLE GRAZING ON THE AREA IN THE VICINITY OF THE TAILING PONDS IN THE EAST OF BAIA MARE CITY, ROMANIA

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**ABSTRACT.** In order to assess the potential human health risk associated with the transfer of heavy metals from contaminated soil to the trophic chain, several studies were conducted regarding the contaminants known to be associated to the non-ferrous ores processing industry in Eastern Baia Mare: Cu, Mn, Zn, Pb, Cd, Cr and Ni. The transfer of heavy metals into the trophic chain has the following order: from soil to vegetation: Zn>Cd>Cu>Mn>Pb>Cr>Ni and from vegetation to milk: Zn>Cu>Cd>Pb>Ni>Cr>Mn, respectively.

Based on the human risk index (HRI) calculated for each element, it was demonstrated that the ingestion of milk from the cows grassed on the contaminated area does not pose a significant risk for human health.

***Keywords:*** *milk, heavy metals, food chain, human health risk*

## INTRODUCTION

The presence of heavy metals in the soil and their accumulation in vegetables represents a major risk for human safety [1]. In order to evaluate the risk degree associated with the concentration of heavy metals in vegetables and their transfer into the human organism, a lot of research has been carried out [2-7]. Soils in the vicinity of mining exploitations and tailings ponds are usually characterized by high concentrations of heavy metals, such as Pb, Cd, Zn, Cu, Cr, Ni, Mo [8-9].

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The studies carried out by Zhuang et al. (2009) [10] regarding the accumulation and transfer of heavy metals from a certain mining area into the trophic chain (plants-insects - chicken) demonstrated an increase in the bioaccumulation rate for Zn and Cu as compared with the bioaccumulation of Pb and Cd.

The study carried out by Póti et al, (2012) [11] regarding the transfer of heavy metals, such as Pb, Cd and Cr in sheep milk showed that the maximum threshold allowed in the European legislation for Pb and Cd was exceeded.

Other researches on the transfer of heavy metals (Cu, Zn, Cd, Cr, Ni and Pb) from grass into cow milk, carried out by Gougoulias et al., (2014) [12] demonstrated the highest bioaccumulation for Ni, Cu and Zn.

Temiz and Soylu, (2012) [13], studied the transfer of heavy metals: Cu, Fe, Zn, Cr, Ni, Cd and Pb from vegetation into milk, considering the summer and winter season, and the results showed that Cu, Pb and Cd had the highest transfer rate during summer. The results obtained by Ogundiran et al., (2012) [14] regarding the bioaccumulation of Pb, Cd, Cu and Zn in cow milk indicated a high transfer of lead into the milk of the cows fed with grass from a heavy metals contaminated site.

Studies carried out by Akbar Jan et al., (2011) [5], on the age and gender categories, regarding the transfer of heavy metals from milk to the blood of inhabitants from a polluted area, revealed high transfer of Cu, Zn and Mn. The highest concentrations of heavy metals were accumulated by the elderly male population.

This paper intends to emphasize the risks associated with the ingestion of milk contaminated with heavy metals analyzing their transfer from the soil polluted by metallurgic and mining activities into the trophic chain. The obtained results and observations may represent a reference source for other researches on health risks associated to the ingestion of food contaminated with heavy metals.

## The study area

In order to assess the health risk associated with heavy metals from mining waste deposits, the grazing land located south of the „Iaz Central" tailings pond was chosen, situated at approximately 3 km East of Baia Mare city and less than 1 km North-East of Satu Nou de Sus (Figure 1). The study area is situated in the close vicinity of the tailings pond and it is used as a grazing ground for the cows in Satu Nou de Sus, therefore representing a risk source for the trophic chain. Furthermore, while tearing the grass, the cows also ingest a part of the soil, and in this case, the soil represents the source with the highest concentration in heavy metals.

In Satu Nou de Sus village there are approximately 360 milk cows, of which 70% are Romanian Piebald and 30% Holstein cow breeds. Most of these cows graze 120 – 150 days/year on the grazing ground situated in the vicinity of the mining waste deposit.

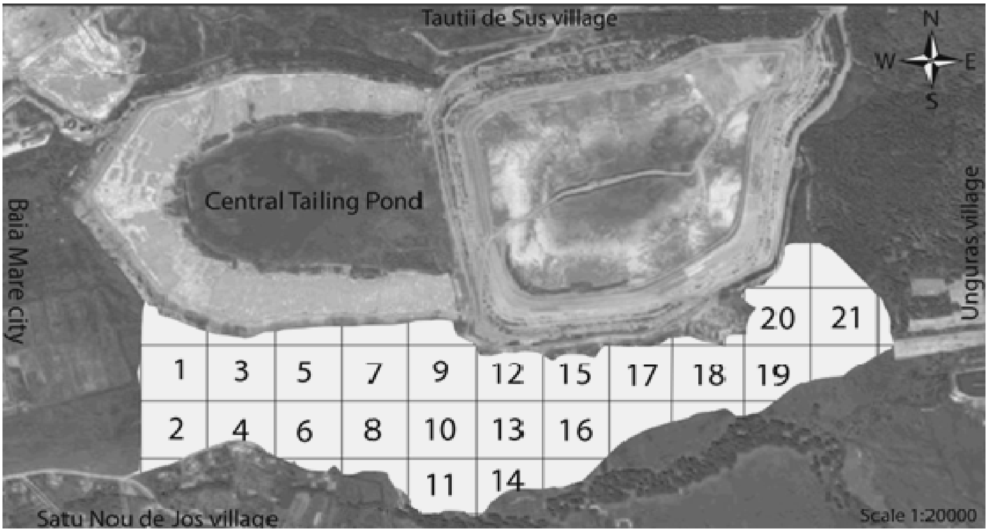


**Figure 1.** The map of the study area

This tailings pond contains more than 10 million tonnes mining tailings, produced during 25 years of processing activity of complex and gold ores coming from the mines of Şuior, Cavnic, Herja and Turţ [15-16].

Major pollution sources of the studied area were also SC Cuprom SA metallurgic plant and the Central Flotation Plant Baia Mare, due to the predominant wind directions, from West to East and South-West to North-East [17].

## RESULTS AND DISCUSSION

The soil elements in the study area are included in the Luvisol class, white luvisol type, on a clay layer, with Ao-Ea-EB-Bt profile, characterized by good drainage [18].

21 soil samples from 0-20 cm depth and 21 grass samples were sampled from the investigated area. pH reaction, humus and total nitrogen content, metal in pseudo-total and bioavailable (in DTPA extraction) forms were determined for the soil samples. The heavy metals were determined for the grass sample, as well. The elements for primary statistics are presented in table 1.

**Table 1.** Primary statistical elements for the characterization of soil and vegetation

| Indicators | Order 756/1997 [20] | | | Mean | Median | Minimum | Maximum | Standard Error | Standard Deviation | Confidence level (95.0%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | N | A | I | | | | | | | |
| pH, pH units | - | - | - | 5.622 | 5.630 | 5.170 | 6.200 | 0.071 | 0.324 | 0.148 |
| Humus, % | - | - | - | 1.397 | 1.420 | 1.080 | 1.680 | 0.036 | 0.165 | 0.075 |
| N total, % | - | - | - | 1.08 | 1.06 | 0.91 | 1.32 | 0.03 | 0.12 | 0.05 |
| Cu T, mg $kg^{-1}$ d.w. | 20 | 100 | 200 | 35.03 | 32.00 | 16.70 | 52.60 | 2.42 | 11.10 | 5.05 |
| Cu DTPA, mg $kg^{-1}$ d.w. | - | - | - | 4.389 | 4.100 | 2.110 | 7.190 | 0.349 | 1.598 | 0.728 |
| Cu Grass, mg $kg^{-1}$ d.w. | - | - | - | 1.153 | 1.130 | 0.403 | 2.030 | 0.096 | 0.440 | 0.200 |
| MnT, mg $kg^{-1}$ d.w. | 900 | 1500 | 2500 | 1118 | 1096 | 677 | 1465 | 46.0 | 209 | 95 |
| Mn DTPA, mg $kg^{-1}$ d.w. | - | - | - | 142.1 | 131.0 | 86.0 | 206.0 | 6.2 | 28.6 | 13.0 |
| Mn Grass, mg $kg^{-1}$ d.w. | - | - | - | 20.9 | 20.00 | 12.00 | 41.00 | 1.27 | 5.83 | 2.66 |
| Pb T, mg $kg^{-1}$ d.w. | 20 | 20 | 100 | 46.2 | 39.60 | 16.30 | 105.6 | 5.72 | 26.21 | 11.93 |
| Pb DTPA, mg $kg^{-1}$ d.w | - | - | - | 12.2 | 9.11 | 3.38 | 30.80 | 1.86 | 8.51 | 3.87 |
| Pb Grass, mg $kg^{-1}$ d.w. | - | - | - | 1.683 | 1.220 | 0.641 | 4.420 | 0.240 | 1.098 | 0.500 |
| ZnT, mg $kg^{-1}$ d.w. | 100 | 300 | 600 | 312.9 | 296.0 | 180.0 | 595.0 | 23.64 | 180.0 | 49.31 |
| Zn DTPA, mg $kg^{-1}$ d.w. | - | - | - | 90.9 | 91.50 | 46.40 | 145.0 | 5.56 | 25.47 | 11.59 |
| Zn Grass, mg $kg^{-1}$ d.w. | - | - | - | 26.2 | 26.60 | 13.30 | 44.70 | 1.82 | 8.34 | 3.80 |
| CdT, mg $kg^{-1}$ d.w. | 1 | 3 | 5 | 1.187 | 1.06 | 0.656 | 2.868 | 0.1005 | 0.4608 | 0.209 |
| Cd DTPA, mg $kg^{-1}$ d.w. | - | - | - | 0.417 | 0.281 | 0.164 | 1.620 | 0.076 | 0.350 | 0.159 |
| Cd Grass, mg $kg^{-1}$ d.w. | - | - | - | 0.111 | 0.088 | 0.043 | 0.358 | 0.017 | 0.0790 | 0.036 |
| Cr T, mg $kg^{-1}$ d.w. | 30 | 100 | 300 | 77.11 | 76.40 | 36.40 | 129.2 | 6.02 | 27.59 | 12.56 |
| Cr DTPA, mg $kg^{-1}$ d.w. | - | - | - | 13.04 | 7.98 | 2.90 | 129.2 | 5.83 | 26.74 | 12.17 |
| Cr Grass, mg $kg^{-1}$ d.w. | - | - | - | 0.790 | 0.769 | 0.476 | 1.28 | 0.047 | 0.2186 | 0.099 |
| Ni T, mg $kg^{-1}$ d.w. | 20 | 75 | 150 | 40.1 | 36.80 | 24.10 | 70.10 | 2.90 | 13.27 | 6.04 |

| Indicators | Order 756/1997 [20] | | | Mean | Median | Minimum | Maximum | Standard Error | Standard Deviation | Confidence level (95.0%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | N | A | I | | | | | | | |
| Ni DTPA, mg $kg^{-1}$ d.w. | - | - | - | 7.06 | 3.85 | 1.92 | 38.8 | 2.287 | 10.48 | 4.772 |
| Ni Grass, mg $kg^{-1}$ d.w. | - | - | - | 0.595 | 0.311 | 0.223 | 3.17 | 0.179 | 0.822 | 0.374 |
| Note: N- normal value of the metal; A – alert threshold value; I– intervention threshold value; d.w. -dry weight; M - T - the total form of the metal; M - DTPA- the bioavailable form of metal after its extraction in DTPA; M - Grass - the total form of metal in vegetation | | | | | | | | | | |

According to those mentioned above, one may say that the pH reaction of the soil in the investigated area falls in the moderate acid range with a very low humus content and low level of assurance with potential accessible nitrogen [19].

Furthermore, the mean concentrations of the pseudo-total form of the metals of interest exceed the normal value in the Order 756/1997 [20], cadmium by at least 1.2 times and zinc by maximum 3.1 times.

Principal factor analysis (PCA) with Pearson correlation (n) identifies significant positive correlations between the soil pH reaction and most metallic elements (Cd, Cr, Cu, Mn, Pb) in soil and vegetation (Figure 2), thus demonstrating their common source. Strong negative correlations (Figure 2) have been identified between the total available nitrogen and the studied metallic elements.

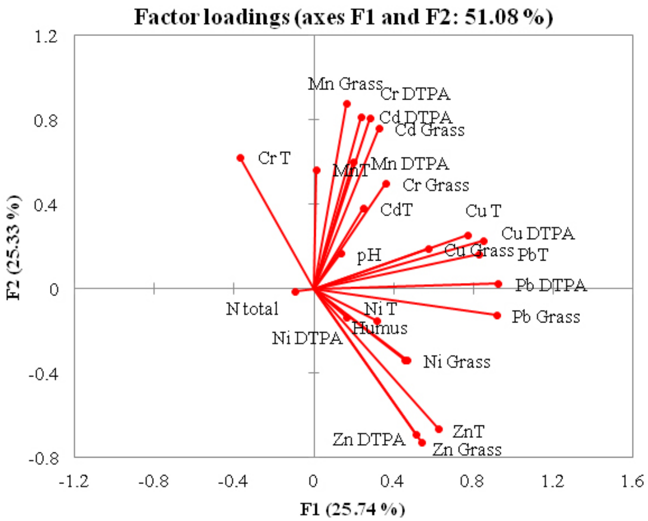


**Figure 2.** Principal factor analysis with Pearson correlation (n)

In order to assess the soil pollution level, the soil pollution index ($PI_i$) for each metal was calculated (eq. 2) [1].

$$PI_i = \frac{C_i}{S_i} \tag{2}$$

This demonstrates the highest value for zinc, followed by chromium, lead, nickel, copper, manganese and cadmium (Figure 3).

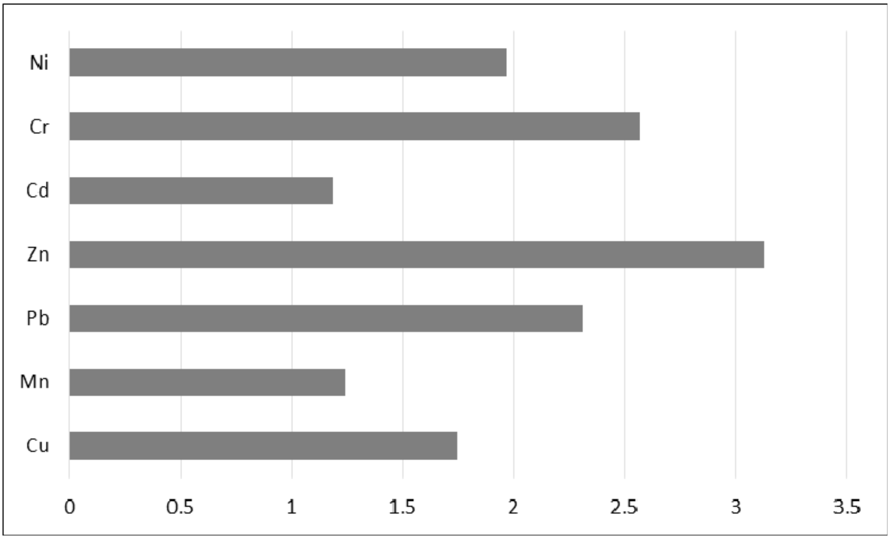


**Figure 3.** The pollution index for the soils in the grazing ground

According to studies carried out by Hu et al. (2013) [21], Yang et al. (2013) [22], Cheng (2007) [23], the Nemerow global pollution index for the investigated area ($PI_N$) was calculated using the equations 2-4 [1, 21 - 23]

$$P_{ave} = \frac{1}{7} \sum_{i=1}^{n} PI_i \tag{3}$$

$$PI_N = \sqrt{\frac{PI_{ave}^2 + PI_{i\max}^2}{2}} \tag{4}$$

where

$PI_i$ – pollution index for each metal;
$C_i$ – determined concentration of metals in soil;
$S_i$ – metal concentration, considered normal values in soils, according to the current Romanian legislation (Order 756/1997);

$PI_{ave}$ –the mean pollution index;
$PI_{imax}$ – the maximum pollution index of the 7 studied metals (in this case, Zn=3.129);
$PI_N$ – the Nemerow global pollution index.

For the studied area, the value of the Nemerow pollution index of 2.998 shows a moderate to severe pollution of the soils with heavy metals [22].

The European regulation no. 1881/2006 provides 0.020 mg $kg^{-1}$ (wet weight) as maximum allowed limit for Pb in raw milk. Thus, the determined concentrations for all 10 raw milk samples, exceed the maximum allowed limit at least by 1.65 times and at most by 3.80 times. Identically, in all mentioned studies, the lead concentration was exceeded. For Cu, Mn, Zn, Cd and Ni the determined values were between the limits reported in several studies [24-27] (table 2).

**Table 2.** Heavy metals in raw cow milk

| Metal | The present study mg $l^{-1}$ | Enb et al., (2009) [24], mg $kg^{-1}$ | Ogabiela et al, (2011) [25] mg $l^{-1}$ | Bilandžić et al., (2011) [26] µg $l^{-1}$ | Rahini, (2013) [27] mg $l^{-1}$ |
|---|---|---|---|---|---|
| Cu | 0.086 - 0.211 | 0.108 - 0.194 | 0.252 - 0.214 | 1.0 – 20.0 | nr |
| Mn | 0.057 - 0.130 | 0.040 - 0.084 | 0.179 - 0.219 | nr | nr |
| Pb | 0.033 - 0.076 | 0.040 - 0.960 | 0.550 - 0.710 | 1.0 - 476 | 1.84 – 20.7 |
| Zn | 3.086 - 4.117 | 3.001 - 3.940 | 3.239 - 5.521 | nr | nr |
| Cd | 0.0021-0.0053 | 0.070 - 0.112 | 0.163 - 0.099 | 1.0 – 20.0 | 0.28 –3.43 |
| Cr | 0.039 -0.085 | 0.028 - 0.066 | 1.757 - 1.568 | nr | nr |
| Ni | 0.0018-0.0062 | 0.002 - 0.009 | nr | nr | nr |
| Note: nr – not reported | | | | | |

According to equation (5) proposed by Khan et al., (2008) [1] and Cui et al., (2005) [28], they calculated the transfer factors (Ft) of the investigated metals from soil to vegetation and from vegetation to milk.

$$Ft = \frac{C_{grass(milk)}}{C_{bioavailablefromsoil(grass)}} \tag{5}$$

The transfer factors are sub-unitary, the highest values being recorded at the transfer from the pseudo-total form to bio-available form in soil and at the transfer from vegetation to milk (Figure 4).

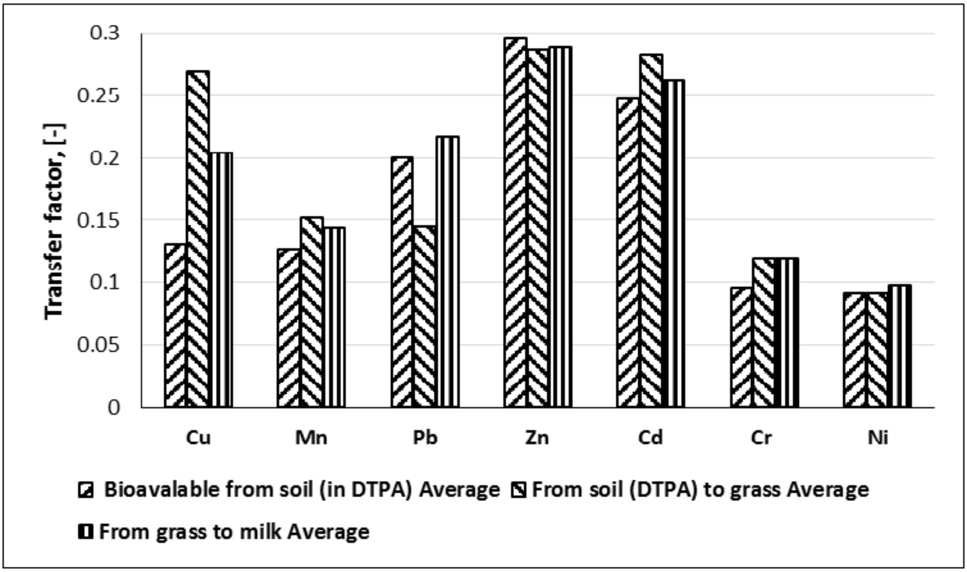


**Figure 4.** Mean values of the transfer factor for metals in soil-vegetation-milk

As shown in the graphic in Figure 5, the transfer factor of mean concentrations of heavy metals from soil to plant and from plant to milk, has the highest value for zinc, cadmium and copper, and the lowest value for nickel, chromium and manganese. In the case of lead, there is a significant difference between the values of the transfer factor from soil to grass and from grass to milk. The same situation is for copper, the difference demonstrating the higher transfer from soil to grass. One must notice that the identified transfer factor for zinc has almost identical values for each analyzed segment (0.296, 0.286 and 0.288), according to the results obtained by Kabata-Pendias, (2001) [29], and Kabata-Pendias and Mukherjee, (2007) [30].

The transfer of metallic elements allowed the establishing of the order of transfer from soil to vegetation: Zn>Cd>Cu>Mn>Pb>Cr>Ni and from vegetation to milk: Zn>Cu>Cd>Pb>Ni>Cr>Mn, in accordance with the studies carried out by Miclean et al., (2013) [31], Şenilă et al. (2012) [32].

The risks associated to human ingestion of milk from the cows that graze in the vicinity of the tailings pond were determined by calculating the Daily Oral Intake of Heavy Metals (DIM) through milk and the human risk index (HRI).

The determination of Daily Oral Intake of Heavy Metals (DIM) (equation 6) was done using the formula proposed by Khan et al. (2008) [1], considering that an adult with an average body weight of 65 kg intakes 1 litre milk/day.

$$DIM = \frac{C_{metal} \times D_{food\,intake}}{B_{average\ weight}} \tag{6}$$

where:

$C_{metal}$ - the heavy metal concentration in milk (mg·l$^{-1}$),
$D_{food\ intake}$ - the daily intake of milk (l);
$B_{average\ weight}$ - the average human body weight (kg).

The human risk index (HRI) was calculated for each studied metal, as the ratio between the Daily Oral Intake of Heavy Metals (DIM) and the oral reference dose (RfD) (eq. 7) [1].

$$HRI = \frac{DIM}{RfD} \tag{7}$$

The reference doses for heavy metals Cu, Mn, Pb, Zn, Cd, Cr, Ni were taken from the Integrated Risk Information System [33], except for lead, which is not brought under regulation (table 1).

The human risk index (HRI), the Daily Oral Intake of Heavy Metals (DIM) and the oral reference dose (RfD) are presented in table 3.

**Table 3.** Average values for metal concentrations in milk, DIM and HRI

| Metal | RfD (mg kg$^{-1}$-day) [33] | Mean±std (mg l$^{-1}$) | DIM (mg kg$^{-1}$) | HRI |
|---|---|---|---|---|
| Cu | $4\times10^{-2}$ | 0.141±0.014 | 0.002 | 0.054 |
| Mn | $1.4\times10^{-1}$ | 0.089±0.007 | 0.001 | 0.010 |
| Pb | - | 0.051±0.004 | 0.001 | - |
| Zn | $3\times10^{-1}$ | 3.702±0.097 | 0.057 | 0.190 |
| Cd | $1\times10^{-3}$ | 0.003±0.0004 | 0.000 | 0.051 |
| Cr | $5\times10^{-3}$ | 0.057±0.0044 | 0.001 | 0.176 |
| Ni | $2\times10^{-2}$ | 0.004±0.0004 | 0.000 | 0.003 |
| std – standard deviation | | | | |

Even if the limit value for Pb in raw milk, provided by the Regulation no. 1881/2006, is exceeded by 2.55 times in our study, the risk associated to the Pb presence in the ingested milk could not be determined because no reference dose was regulated for this metal [33], so far.

Because HRI has sub-unitary values [1, 3], one may say that the ingestion of milk coming from the cows that graze in the vicinity of the Central tailing pond does not pose a significant risk for human health.

## CONCLUSIONS

In the Eastern part of Baia Mare city, there are grazing grounds in the close vicinity of mining waste tailing ponds, in an anthropic modified area, with acidic soil reaction and poor in nitrogen and humus. Thus, the sustainable development of this area requires the elaboration of a strategy for soil quality improvement, which will use the natural resources of the area.

The transfer of heavy metals from the soil of an industrial area, with mining characteristics from the Baia Mare area, has the following order: from soil to vegetation: Zn>Cd>Cu>Mn>Pb>Cr>Ni, and from vegetation to milk: Zn>Cu>Cd>Pb>Ni>Cr>Mn.

Although the presence of metallic elements in their pseudo-total form is abundant, the values of transfer factors for the studied elements are sub-unitary.

In order to assess the level of trophic risk, the pollution index, as well as the transfer factor from soil to vegetation for each studied metal were taken into account.

The human risk index is sub-unitary and has the following order: Zn>Cr> Cu>Cd>Mn>Ni. The risk associated to lead was not determined, because there is no reference dose established. Without taking into account the sub-unitary values, the highest health risk may be associated to zinc and cadmium.

In order to assess the human health risk associated to the presence of heavy metals in the milk of cows grazing on a contaminated area, the human risk index (HRI) was calculated. The sub-unitary value obtained for the risk index demonstrates that there is no significant risk for human health, due to milk intake.

## EXPERIMENTAL SECTION

### Sampling, processing and sample analysis

In order to identify the health risk associated to milk ingestion (fresh and/or processed) from the cows that graze on the grazing ground situated in the close vicinity of the ”Iaz Central” mining waste tailings pond, several studies regarding the contaminants known to be associated to non-ferrous ore processing industry were performed: copper, manganese, zinc, lead, cadmium, chromium and nickel. Their concentrations were analyzed in all the levels of the trophic chain; soil (the pseudo-total and bioavailable form), grazed grass vegetation and milk. For soils, elementary physical – chemical characteristics were also determined (pH reaction, hummus content and total nitrogen).

The 21 ha of the grazing land were divided into 21 squares, each with a total area of 1 ha. Soils were sampled 60 days after grazing period began, from a depth of 0 – 20 cm, following the grass sampling, by cutting grass with a Teflon knife. The final soil sample was obtained by gathering 5 samples from each square, 0.5 kg each. Each soil and grass sample was sampled in polyethylene bags, according to standard STAS 7184/1-1984 [34] and Figure 1.

The milk samples were taken from 10 cows which grazed on the investigated area. Every morning and evening milking, an amount of 500 ml milk was sampled from every cow and put in labelled glass bottles. Then the samples were mixed to obtain a homogenous milk sample which was subjected to laboratory analyses. Every indicator, from every sample, was analyzed in 3 replicates and the mean values were calculated.

Soil samples were prepared for physical-chemical analyses according to the requirements in ISO 11464:2006 [35]; the foreign objects were removed, the soil was dried at room temperature, for 1 week. After drying, soil samples were grinded and sieved out through the 200 µm polyethylene sieve; from each sample, the pH, humus, total nitrogen and metals – the pseudo-total form [36] and DTPA extractible form [37] were determined.

The grass samples were moved entirely in Petri dishes and dried in an oven, at 105 °C, to reach the constant mass, afterwards being grinded.

The milk samples were cold preserved (2-4 °C) and analyzed within 24 hours since sampling.

In order to determine the pseudo-total forms of metals from soil, vegetation and milk samples were mineralized in a microwave oven, in Teflon capsules, in acidic medium (aqua regia for soil - 21 ml HCl 12M+7 ml $HNO_3$ 15.8M and 7 ml $HNO_3$ 15.8M +1 ml $H_2O_2$ 30 % - for vegetation and milk samples), for 20 minutes at 160 °C and 800 W. The wet residues were decanted, after filtration, in 100 ml flasks and $HNO_3$ 0.5M was added [36].

The bioavailable metallic fractions in the soil were determined by extraction in a buffer solution (at pH = 7.3 ± 0.2) of diethylene triamine pentaacetic acid (DTPA), at a temperature of (20 ± 2) $^{o}$C in specific shaking conditions and at a ratio between soil: extraction solution of 1:2 (m/v) [37].

The atomic absorption spectrometry analysis (Perkin Elmer A Analyst 700, with flame and graphite atomization techniques) of interest metals was performed according to the following conditions: on calibrating pilot with a correlation factor of $R^2 \geq 0.990$, developed through the least squares method, from reference materials with NIST traces (Merck producer) and with internal conditions of assuring the quality of results (control diagrams, quantification limit checking, repeatability and recovery check, by using a certified reference material).

The soil pH reaction was electrochemically determined, by using a WTW pH meter, InoLab 730, with Sentix probe – metrologically calibrated and verified, in aqueous solution, in m/v 1:2.5 ratio [38].

The humus content was determined through calculus, after determining the organic carbon, by using the method provided by the Romanian standard [39].

The total nitrogen was determined through the Kjeldahl method [40], by distillation in alkaline environment of the previous mineralized samples with a strong acid and the absorption of ammonia discharged in a solution of boric acid with a mix colour indicator, using a digestion system and with automatic distillation unit, ProNitro-Selecta type.

## REFERENCES

[1]. S. Khan, Q. Cao, Y.M. Zheng, Y.Z. Huang, Y.G. Zhu, *Environmental Pollution,* **2008**, *152*, 686.
[2]. G. Dziubanek, A. Piekut, M. Rusin, R. Baranowska, I. Hajok, *Ecotoxicology and Environmental Safety*, **2015**, *118*, 183.
[3]. K. Khan, H. Khan, Y. Lu, I. Ihsanullah, S. Khan, N.S. Shah, I. Shamshad, A. Maryam, J. Nawab, *Ecotoxicology and Environmental Safety*, **2014**, *108*, 224.
[4]. X. Liu, Q. Song, Y Tang, W. Li, J. Xu, J. Wu, F. Wang, P.C. Brookes, *Science of the Total Environment*, **2013**, *463*, 530.
[5]. F. Akbar Jan, M. Ishaq, S. Khan, M. Shakirullah, S.M. Asim, I., Ahmad, F. Mabood, *Journal of Environmental Sciences*, **2011,** *23*, 2069.
[6]. S. Khan, R. Farooq, S. Shahbaz, M.A. Khan, M. Sadique, *World Applied Sciences*, **2009**, 6, 1602.
[7]. N. Sridhara Chary, C.T. Kamala, D. Samuel Suman Raj, *Ecotoxicology and Environmental Safety*, **2008**, *69*, 513.
[8]. L.M. Cai, Z.C. Xu, J.Y. Qi, Z.Z. Feng, T.S., Xiang, *Chemosphere*, **2015**, *127*, 127.
[9]. D. Xu, P. Zhou, J. Zhan, Y. Gao, C. Dou, Q. Sun, *Ecotoxicology and Environmental Safety*, **2013**, *90*, 103.
[10]. P. Zhuang, H. Zou, W. Shu, *Journal of Environmental Sciences*, **2009**, *21*, 849.
[11]. P. Póti, F. Pajor, A. Bodnár, L. Bárdos, *Journal of Microbiology, Biotechnology and Food Sciences*, **2012**, *2*, 389.
[12]. N. Gougoulias, S. Leontopoulos, Ch., Makridis, *Emirates Journal of Food and Agriculture*, **2014**, *26*, 828.
[13]. H. Temiz, and A. Soylu, *International Journal of Dairy Technology*, **2012**, *65*, 516.

[14]. M.B. Ogundiran, D.T. Ogundele, P.G. Afolayan, O. Osibanjo, *International Journal of Environmental Research*, **2012**, *6*, 695.
[15]. I. Smical, I. Bud, S. Duma, *Revista Minelor*, Petroșani, **2015**, *21*, 2.
[16]. Romaltyn Mining Ltd., (2012), Site Report, http://romaltyn.ro/assets/Raport_de_amplasament_Romaltyn.pdf
[17]. National Meteorological and Hydrological Institute (NMHI), (2012), Meteorological data, hydrological and water management needs for Aurul evacuation-sizing system, Baia Mare, Bucharest (in Romanian).
[18]. Soil and Agrochemical Studies Office (SASO) of Baia Mare, (2015), Data on climatic conditions and pedogenetical in eastern Baia Mare (in Romanian).
[19]. N. Florea, V. Balaceanu, C. Rauta, A. Canarache, et. al., "Methodology of Pedological Studies Development (MPSD)", Research Institute for Soil and Agrochemistry, Bucharest (in Romanian) 1987.
[20]. Order no. 756 of 3 November 1997 approving the regulation on environmental pollution assessment, published in Of.M. no. 303 bis/6 nov. 1997.
[21]. Y. Hu, X. Liu, J. Bai, K. Shih, E.Y. Zeng, H. Cheng, *Environmental Science and Pollution Research*, **2013**, *20*, 6150.
[22]. C.L. Yang, R.P. Guo, Q.L. Yue, K. Zhou, Z.F. Wu, *Environmental Earth Sciences*, **2013**, *70*, 1903.
[23]. J. Cheng, Z. Shi, Y. Zhu, *Journal of Environmental Science*, **2007**, 19, 50.
[24] A., Enb, M.A., Abou Donia, N.S., Abd-Rabou, A.A.K., Abou-Arab and M.H., El-Senaity, *Global Veterinaria*, **2009,** *3*, 268.
[25] E.E, Ogabiela, U.U, Udiba, O.B, Adesina, C.,Hammuel, F. A, Ade-Ajayi, G.G, Yebpella, U.J., Mmereole and M., Abdullahi, *Journal of Basic and Applied Scientific Research,* **2011**, *7*, 533.
[26] N. Bilandžić, M. Dokić, M. Sedak, B. Solonum, I. Varenina, Z., Knežević and M., Benić, *Food Chemistry,* **2011**, *127,* 63.
[27] E., Rahini, *Food Chemistry*, **2013**, *136,* 389.
[28]. Y.J. Cui, Y.G. Zhu, R. Zhai, Y. Huang, Y. Qiu, J. Liang, *Environment International*, **2005**, *31*, 784.
[29]. A. Kabata-Pendias, "Trace elements in soils and plants" CRC Press, Third Edition, USA, **2001,** 331.
[30]. A. Kabata-Pendias, B.A. Mukherjee, "Trace Elements from Soil to Human", Springer, Berlin, **2007**, 193-268.
[31]. M. Miclean, E. Levei, O. Cadar, M. Șenilă, I.S. Groza, *Carpathian Journal of Earth and Environmental Sciences*, **2013**, 8 (4) 93.
[32]. M. Şenilă, E.A. Levei, R.L. Şenilă, M.G. Oprea, M.C., Roman, *Journal of Environmental Science and Health*, **2012**, *47*, 614-621.
[33]. United States Environmental Protection Agency (USEPA), Integrated Risk Information System (IRIS), 2015, http://cfpub.epa.gov/ncea/iris/compare.cfm
[34]. SR 7184-1: 1984 Soils. Sampling for pedologycal and agrochemical investigations.
[35]. ISO 11464:2006 Soil quality -- Pretreatment of samples for physico-chemical analysis.
[36]. SR ISO 11466:1999 Soil quality. Extraction of trace elements soluble in aqua regia.

[37]. SR ISO 14870:2002 Soil quality. Extraction of trace elements in a buffered solution diethylenetriamine pentaacetic acid (DTPA).
[38]. SR 7184-13:2001 Soils. Determination of pH in water and saline suspensions (mass/volume) and in saturated paste.
[39]. STAS 7184/21-82 Soils. Humus content determination.
[40]. SR ISO 11261:2000 Soil quality. Determination of total nitrogen. Kjeldahl modified method.