

ASSESSMENT OF MERCURY POLLUTION IN SOILS ALONG JALA AND SPREČA RIVER BANKS IN BOSNIA AND HERZEGOVINA

Amira Cipurković, Ilvana Trumić
Department of Chemistry, Faculty of
Science, University of Tuzla,
Bosnia and Herzegovina

Jozo Tunjić
Administration of Lukavac City,
Lukavac
Bosnia and Herzegovina

Vahida Selimbašić, Abdel Djozić
Department of Environmental
Protection, Faculty of Technology,
University of Tuzla,
Bosnia and Herzegovina

Zana Đulović Jusić
Outpatient Hospital, Department for
Health, Care and School Children
Tuzla,
Bosnia and Herzegovina

ABSTRACT

The objective of this work was to determine the degree of mercury contamination in soils collected from the banks of Jala and Spreča Rivers and the extent to which the soils quality has deteriorated. As possible source of this hazardous heavy metal, it was also investigated the pollution of soils in the area of Ltd. Polihem plant, in which Hg was applied as cathode in process of chlorine-alkali electrolysis during a period of 1977-1992. Mercury content of 3,864 g/kg in soil near electrolysis plant was measured. The extent of soils quality deterioration was observed in all the sampling points from river banks below Ltd. Polihem, which demonstrates that the contamination may be attributed mainly to wastewater dispersion of mercury from factory. The levels of mercury decreased with an increase in distance of sampling points from Ltd Polihem. In this study, metal in the soil was determined using ICP-OES method. The study revealed that Hg levels were higher than the EU Directives proposed limit. The mercury contamination in the soils was also evaluated by applying enrichment factor (EF), contamination factor (CF), geo-accumulation factor (I_{geo}) and pollution-load index (PLI). Based on EF, the soils from river banks have moderate to extremely high enrichment factor. According to CF, mercury is responsible for significant contamination to very high. According to I_{geo} , soils are moderately to extremely polluted by Hg. Based on PLI, all sampling sites suggest overall pollution of site quality. Depending on Hg content, these soils cannot be recommended for agricultural activities because the accumulated metal in the soil may risk the agricultural plants. It is most likely that the foodstuff in this study environment might be at the highest risk of induced mercury contamination, which may have hazardous effect on human health.

Keywords: soil, mercury, chlorine-alkali electrolysis, contamination, pollution

1. INTRODUCTION

Soil is a thin part of the system on the Earth's surface which is in the interaction between nature and a man, and in fact is a very complex ecosystem that balances the natural and anthropogenic influences. [1] Environmental pollution by heavy metals is the current central problem of modern ecology in many countries of the world as well as in our. Accumulation of heavy metals in the soil becomes a danger to human health because these substances come into the food over plants and animals. Industrialization areas of Tuzla Canton have influenced the increase in emissions of heavy metals in this area, with a great contribution of TPP Tuzla, chemical and other industries. [2.3] Soil

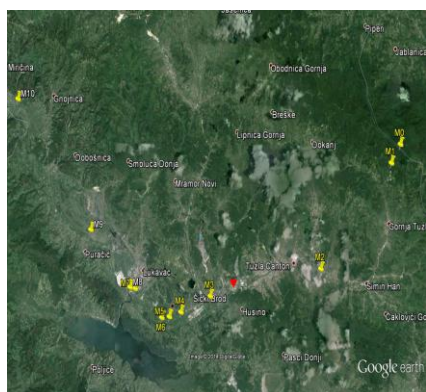
contamination caused by introducing heavy metals in the soil can lead to some changes in the chemical and biological properties of the soil, which results in reducing surface suitable for food production. [4] Mercury is non-essential element and exhibit toxic effects at very low concentrations. The long running process of NaCl electrolysis in Ltd Polihem with the use of mercury cathode contributed to the Hg splintering into the environment, either by evaporation or discharge into the river Jala as a recipient of waste water. [5] Risk of anthropogenic mercury emissions is large, so it is necessary to carry out its monitoring.

The aim of this study was to determine the presence and distribution of mercury in the soil of the former factory for chlor-alkali electrolysis Ltd. Polihem Tuzla, as well as in the part of the agricultural land on the banks of the river Jala and Spreča, especially downstream from TPP Tuzla and Polihem.

2. EXPERIMENTAL

Surface soil samples were taken in the industrial zone "join-stock company Polihem Tuzla" in the area of the four factories at depths up to 30 cm and were analyzed on Hg content. Soil samples were also collected from the banks of the river Jala and Spreča on the same depth. Sampling was carried out at ten selected sites (Figure 1). All samples were taken close to the riverbed, at a distance up to 50 m in April 2013. Methodology of soil sampling was carried out according to the instructions on the procedure, practices and conditions for control of soil fertility. [6] Soil samples were analyzed in the Laboratory of Technology and Faculty of Mining Geology and Civil Engineering in Tuzla.

The average sample was obtained by homogenisation of five samples from every measurement points, stored in PVC bags and labeled. Soil samples were dried at room temperature and sieved to a sieve system hole diameter 0.2 mm. Thereafter, samples were prepared according to ISO Standards. [7] Total Hg concentrations were measured in soil extracts by ICP-OES method (Optima 2100 DV, Perkin-Elmer).



- M0: Source of Jala river, upstream from salt mine Tetima
- M1: Tetima, near 1200 m downstream from Jala source, near salt main Tetima;
- M2: city settlement at intake of Solina in Jala;
- M3: settlement Šićki brod between TPS Tuzla and highway M 17;
- M4; M5; M6: Bistarac fields;
- M7: Bokavići field near intake of Jala in Spreča;
- M8: river Spreča bank;
- M9: in settlement Puračić;
- M10: in settlement Miričina.

Figure 1. Measurement Points

Assesment of mercury pollution in soils along river banks was done using four parameters:

- The **enrichment factor (EF)** of metals is a useful indicator reflecting the status and degree of environmental contamination. [8, 9] The EF calculations compare each value with a given background level, using iron as the element of normalization due to low occurrence variability. Five contamination categories are recognised on the basis of the enrichment factor. [10]
- The level of contamination of soil by metal is expressed in terms of a **contamination factor (CF)** calculated. Five CF values are recognized for describing the contamination level. [11]
- The **Pollution Load Index (PLI)**, provides simple but comparative means for assessing a site quality, where a value of $PLI < 1$ denote perfection; $PLI = 1$ present that only baseline levels of pollutants are present and $PLI > 1$ would indicate deterioration of site quality. [12]
- The degree of metal pollution is assessed in terms of seven contamination classes based on the increasing numerical value of the **geoaccumulation index (I_{geo})**. [13]

3. RESULTS AND DISCUSSION

Results of soil analyse (in mg Hg/kg dry substance) in Ltd. Polihem area are as follows: Electrolysis, sample 1 (3864), sample 2 (113); Solana (116); Kaporit (111); Na-chlorate (84). The highest concentration of mercury was found in the immediate front of the Electrolysis plant. This is not unexpected, concerning that during the labor Electrolysis plant there were 50 tons of mercury, which was there most likely due to a various land scattering from the drive. The measured Hg concentrations within the industrial plants Ltd. Polihem greatly exceed allowable concentration of agricultural land [6], and the limit value of 1.0 ppm for Hg concentration in the soil according to the European standard. [14]

Mercury concentration in soils at measurement points along Jala and Spreča rivers are shown at Fig. 2. Mercury was not detected in any of the samples from M0 (Jala source) to M4 reflecting the lack of contamination with mercury. This was attributed to the facts that there were no lithogen or anthropogenic source of mercury. Enrichment factors (EF) of mercury in the soils in sampled zones are shown at Fig. 3. CF values of mercury along measurement points are shown at Fig. 4. Results of the calculation of Geo-accumulation Index (Igeo) in soils are shown at Fig. 5.

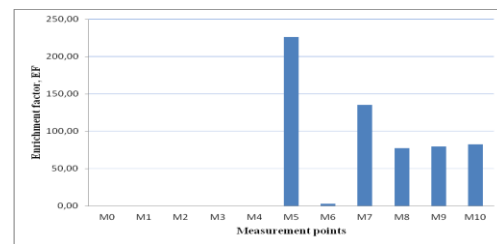
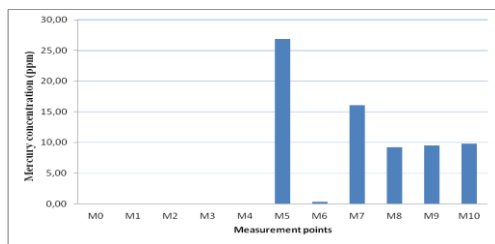


Fig. 2. Mercury concentration at measurement points Fig 3. Enrichment factor (EF) values

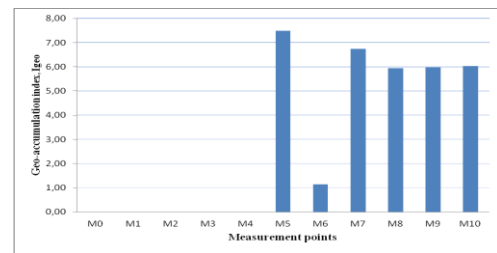
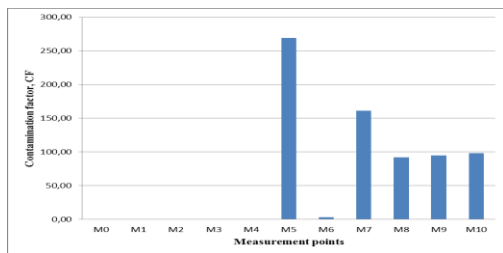


Fig. 4. Contamination factor (CF) values Fig 5. Geo-accumulation Index (Igeo) values

Mercury concentration, EF, CF and Igeo values at other measurement points decreased in the following order: M5 >> M7 >> M10 > M9 > M8 >> M6

The results show that in all of these measuring points, except the M6, the maximum allowed value was exceeded of 1 ppm Hg prescribed for silty loam soil as well as agricultural land for organic food production. [6, 14] All measuring sites where Hg is found are located downstream from Electrolysis plant which leads to the conclusion that this plant is the source of Hg contamination of the test area, and the presence of mercury in the soil due to the discharge of the same into the river Jala during high water levels and Hg soil contamination is caused by overflowing rivers and flooding of some parts of the test areas. The concentration of Hg in the soil at the test sites depends on the frequency and timing of flooding of the test sites, as well as the length of retention of water at a particular location.

Since this study is the first of this kind for these soils, there is no local information in literature available for comparison to calculate EF value. Background levels of Hg in soils are not easy to estimate due to widespread Hg pollution. Data reported for various soils on a worldwide basis show that mean concentrations of Hg in surface soils do not exceed 400 ppb. [1] Therefore, here we used background data given for silty and loamy soils calculated as mean concentration on the world scale (0,1 ppm) to examine the extent of contamination by Hg, because soil composition at examined area nearly corresponds to this soil texture. [1, 15] Of the various sampling sites, M6 was found to be least polluted with Hg (moderate enrichment), while EF at M5 and M7-M10 show extremely high

enrichment. Normally, as the EF values increase, the contributions of the anthropogenic origins also increase. Contamination factors (CF) values show very high contamination by mercury (CF>6) at all locations, except at M6 (considerable soil contamination). The PLI value for mercury in examined soils is 70,46. The PLI is aimed at providing a measure of the degree of overall contamination at a sampling site. High PLI value suggests input from anthropogenic sources. Furthermore, locations M5-M10 are along Jala and Spreča rivers which shows progressive deterioration and need to be monitored. The values of Igeo in soils indicate that soil was moderately (M6) or strongly (M8, M9) to extremely polluted by mercury (M7, M10). These data show that the sources of Hg in this area are coming from the industrial sources. The impact of Hg released into rivers and on plants and soils has been extensively investigated in recent years. There is also much evidence that increasing soil Hg generally causes an increase in the Hg content of plants (which accumulate much Hg). [1, 3]

4. CONCLUSION

Increased levels of Hg are observed in soils around chemical plants, especially in front of plant for chloralkali electrolysis in Ltd. Polihem Tuzla. Soil samples from Jala source to M4 were not contaminated by mercury. Mercury content in soils below chloralkali electrolysis was much more than 1 ppm, except M6. On the basis of estimated factors (EF, CF, PLI, Igeo) it was confirmed that the most polluted place with Hg was M5, while the least polluted place was M6. All the other places below M7 were also strongly to extremely polluted with mercury. The enriched Hg concentration and contamination factor values of soils at the area near intake of Jala river into the Spreča, and below, at the banks of river Spreča, were due to a strong anthropogenic influence. Source of contamination of soil with Hg are related mainly to chloralkali electrolysis from Ltd. Polihem Tuzla, where the often uncontrolled discharge into the river Jala, and due to frequent flooding, made the part of the test soil extremely polluted. Part of the test soil on the banks of these rivers is extensively used for agricultural production, although it exceeded the maximum permitted value prescribed for agricultural land to organic food production. In order to preserve the health of the entire ecosystem, it is necessary to suspend agricultural production and take measures to remediate soil or access to his conversion.

5. ACKNOWLEDGEMENT

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