THE IMPACT OF MERCURY POLLUTION ON ECOSYSTEMS SOIL, WATER / SEDIMENT FROM OLT RIVER BASIN

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Abstract

Mercury is a metal that exists naturally in the Earth's Crust. It can be released by rock weathering and transported by stream waters and may go through a series of chemical transformation according to the bio-physical-chemical conditions. Thus, in reaction with inorganic ligands or organic matter, different forms of mercury can bioaccumulate in the high organisms through the sediments and the food chain. A fraction of this trace element can be trapped into the soils by close relationship with organic matter, iron and aluminium oxides or sorbed onto the mineral particles. Some natural processes (water, soil and vegetation degassing, volcanic emissions) allow it to degas and to flow

back into the atmosphere, creating an atmospheric dispersion and a diffuse deposition on the terrestrial ecosystems.

Mercury has become one of the most important environmental pollutants. Due to industrial, domestic and medical activities, the amount of total mercury in the environment and mainly in the atmosphere has been increasing since the 20th century. Approximately 5000 tons of mercury is introduced in the Earth's atmosphere every year

The main objective of this study is to quantify the real impact of the mercury emissions downstream the chemical plants and to determine the mercury pollution in such an area

This study is not only there to demonstrate the significance of the ecosystems soil, water/sediment pathway in the mercury pollution downstream the human activities, but also to show the major role of the mercury in the persistent contamination of the Olt catchment.

Keywords: water surface, sediment, possible heavy metals, mercury

1. Introduction

Olt River is one of the most important rivers in Romania, springs from the Massif Hasmasu Great Eastern Carpathians, Romanian central area at an altitude of 1400 m and flows into the Danube at an altitude of 18 m, covering a length of 615 km from north to south. Waters collect hydrographic network of 9872 km (12.5% of the total length of the network in the country) with a density of 0.41 km/km2 national average is higher (0.33 km/km^2). Water catchment area is 24,050 km^2, the average slope is 2 ‰ Olt.

River Basin is an area of great economic and social value by supporting agriculture, industry, fishing and drinking water. All these activities are potential sources of water pollution and river sediments. Thus, supervision Olt river water quality are of special importance because it highlights, the concentrations of pollutants in the aquatic environment.

Mercury is a non-essential element with no biochemical or nutritional function to bioorganisms and is ubiquitous in the environment in its presence. Its compounds are present as trace contaminants in various biological and environmental samples such as air, water, soil, animal tissues, plant matrices and coal fly ash as a result of both natural and anthropogenic activities [3]. Being an element, mercury is persistent. It cannot be broken down in the environment, only its form can change. All forms of mercury are extremely toxic. Mercury in its methylated form as a trace contaminant in the environment is especially of great concern because of its toxicity and its special ability to bioaccumulate to levels as high as 100,000 in marine organisms [4]. Despite a number of stringent regulations anthropological sources still emit quantities that result in dangerously high levels of this contaminant in the environment [5]. Thus constant monitoring of the environment is essential.

This study aims to determine the current level of mercury in water, sediments and soils of the River Basin and to compare these values with the legislation.

2. Materials and methods

2.1. Reagents and apparatus

For atomic absorption spectroscopy (AAS) measurements 10% $SnCl_2$ solution and concentrated nitric acid, from Merck, have been used. The measurements have been done on AAS Unicam atomic spectrometer.

The samples (water, sediments and soils) were taken and prepared in standard condition. The samples have been analysed by atomic absorption spectroscopy according to the standard procedures (SR EN 1483: 2003 and SR EN 1238:2003).

2.2. Collection and processing of samples

All the samples were collected in jun 2009, may and September 2010, and also in may and august 2011. As shown in Fig. 1, the Olt River basin comes from mountains Hasmasu High (Harghita county) and flows into the Danube in Turnu Magurele county. The localities where samples were taken found in Figure 1. The sampling points were chosen to cover the whole circumference of the Olt hydrographic basin. From each sampling location, one water sample and one sediment sample were collected.

Water samples were collected about 2 m from the shore to avoid various suspended objects and debris. Water samples were collected from 30 cm below the surface to avoid dead leaves and other floating debris. Sediment samples were collected from the same locations as the water samples.

The soil samples were collected upstream and downstream from industrial sites in the River basin, on two levels deep. After collection the samples were transported to the laboratory and then stored at low temperatures further processing. Sediment and soils samples were separated from gravel (>2 mm) and were air dried at ambient temperature in a clean room. After drying to a constant weight, the samples were sieved and particles better than 100 mesh were collected and stored in polythene bottles.

3. Experimental

The samples (water, sediments and soils) were taken and prepared in standard condition. The samples have been analysed by atomic absorption spectroscopy according to the standard procedures (SR EN 1483: 2003 and SR EN 1238:2003).

The study results (Findings) on mercury pollution of Olt River Basin ecosystems, conducted by INCD-ECOIND Branch Ramnicu Valcea, in the period 2009 - 2011, showed mercury pollution of water, sediments and soils in the periods investigated, comparing results with reference values allowed by law in force [6]. It was also found that both mercury pollution of the sediment and surface water are affected by weather conditions (floods, drought).

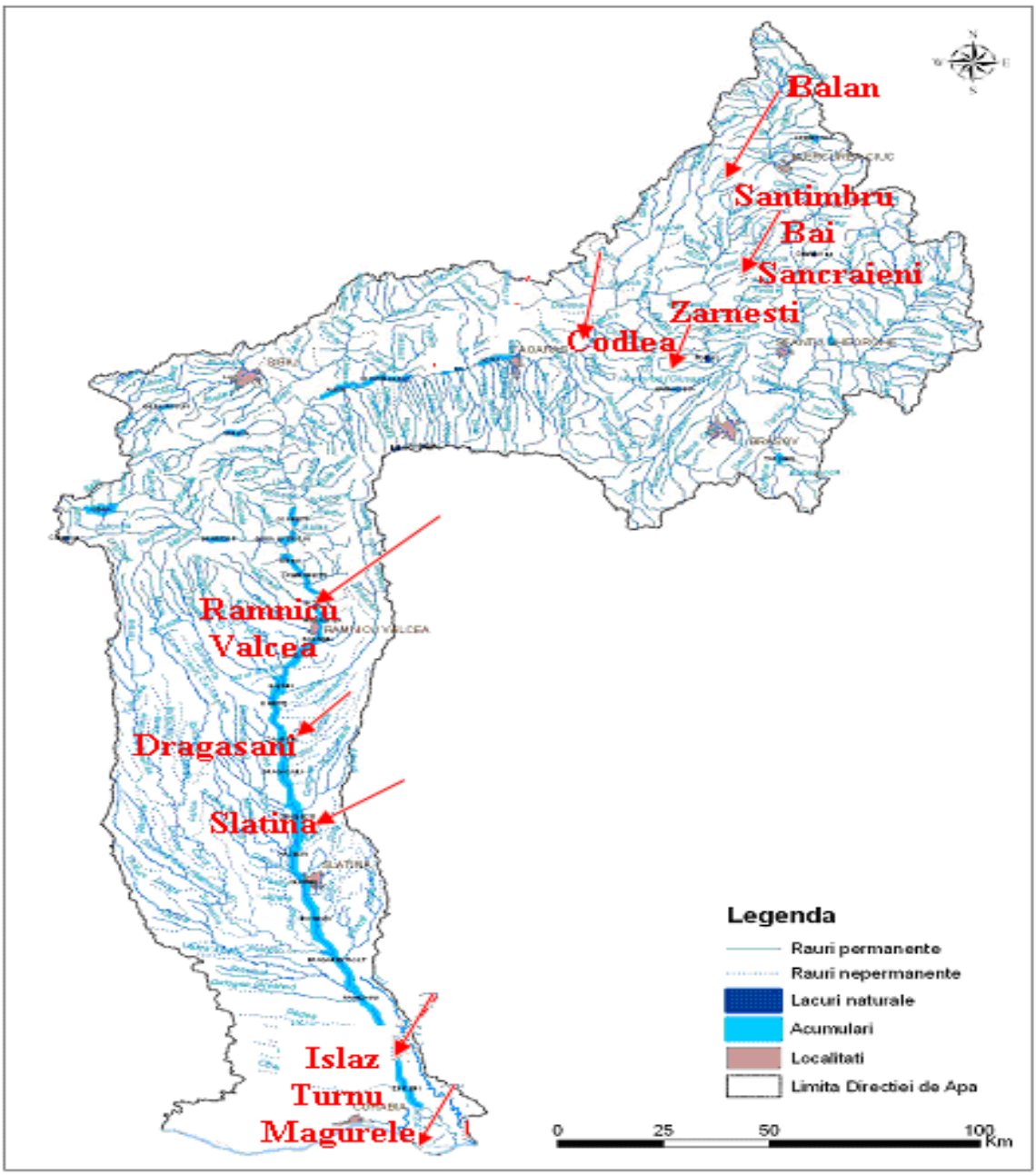

Figure 1. The Olt River basin and the localities from where samples were taken

The primary endpoint was to obtain an overview of mercury pollution of the two ecosystems (water / sediment) based on the results of laboratory analysis of mercury and its assessment of trends.

The activities were held to obtain an accurate assessment of the state average mercury pollution of aquatic ecosystems monitored are:

- determination of mercury in water samples taken from 35 points momentary sampling of Olt River Basin;
- determination of mercury in sediments and comparing the results with normative benchmarks for classification of surface water (Ministry of Environment and Water Order no. 161/2006);

- assess quality framing in classes in order to establish water quality in terms of mercury pollution from the state water assessment procedure in accordance with the limit values specified by the regulation;
- comparative analysis of the evolution of state of mercury pollution of Olt River Basin ecosystems tracked in the 3 consecutive years of investigation.

4. Results and discussion

The present mercury concentrations of the waters, sediment and soil of Olt River Basin have been determined and compared with the normative benchmarks for classification of surface water (Ministry of Environment and Water Order no. 161/2006).

In Tables 1, 2 and 3 are mercury limits imposed on water quality conditions and sediment according to the Order 161/2006 and in Table 4 are reference values for traces of chemical elements in soil, according to Order no. 756/1997.

Table 1. Mercury limit for water quality indicator according to the order 161/2006

Nr. crt.	Indicator de calitate	U.M.	Clasa de calitate				
			I	II	III	IV	V
1	**Mercur**	mg/l	0,0001	0,0003	0,0005	0,001	>0,001

Table 2. Allowable limit of mercury to sediment under Order 161/2006

Nr. crt.	Indicator de calitate	U.M.	Valoare limita (Standard de calitate)
1	**Mercur**	mg/kg s.u.	0,3

Table 3. Values for traces of mercury in soil, according to Order no. 756/1997

Urme de element	Valori normale	Praguri de alerta/ Tipuri de folosinta		Praguri de interventie/ Tipuri de folosinta	
		Sensibile	Mai putin sensibile	Sensibile	Mai putin sensibile
Metale					
Mercur (mg/kg s.u.)	0,1	1	4	2	10

Table 4. Maximum allowable mercury concentration for drinking water

Impurificator	C.M.A. (mg/l)	Legea
0	*1*	*2*
Mercur, mg/l	0,001	Legii 458/2002 (Privind calitatea apei potabile si Legea 311/2004 pentru modificarea si completarea legii 458/2002 privind calitatea apei potabile - Praguri de interventie

0	*1*	*2*
	0,0007	Legea 458/2002 Privind calitatea apei potabile si Legea 311/2004 pentru modificarea si completarea legii 458/2002 privind calitatea apei potabile Praguri de alertă - 70 % din pragul de interventie

The mercury values have been determined in the Olt River Basin from water, sediment and soil and given in Figures 2, 3 and 4, respectively.

In Figure 2 are the concentrations of mercury for water samples taken from the Olt River Basin during 2009-2011. As seen in this figure, the concentration of mercury exceeds the limit imposed under Order 161/2006 in the localities Fagaras, Izlaz, Turnu Magurele, Slatina and Ramnicu Valcea. It also notes that in 2009 and 2010 concentrations of mercury found in water samples are higher than 2011, year in which the concentration of mercury for nearly all water samples collected below are permitted in the legislation.

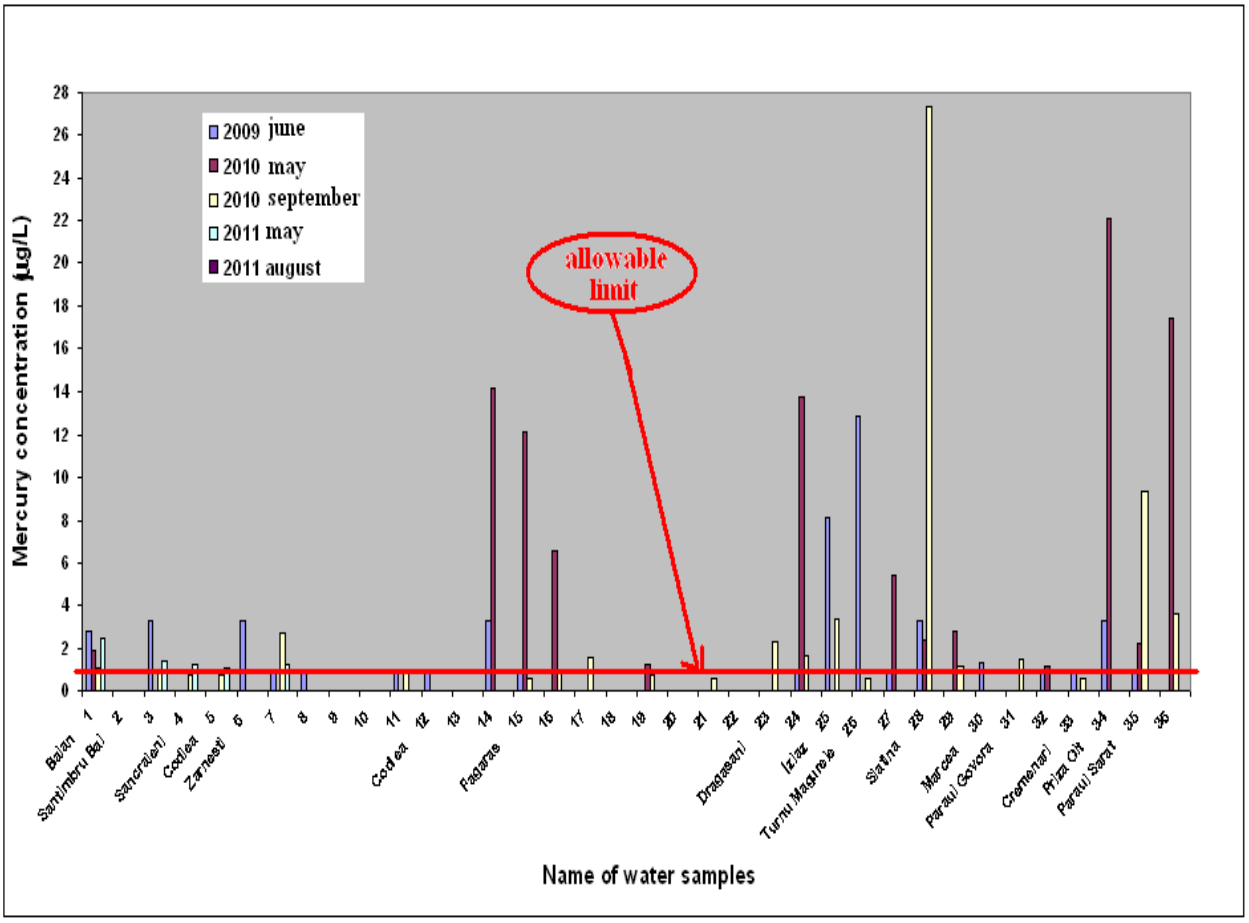

Figure 2. Variation of mercury concentration for water samples collected from the Olt River Basin

Sediment samples (Figure 3) taken from the River Basin of the same points as the water samples, exceed the limit allowed under Order 161/2006 nearly all localities where samples were taken during the period investigated. But much higher mercury concentrations than the limit allowed under law in viguoare, sediment samples were found in localities Zarnesti, Fagaras and Ramnicu Valcea.

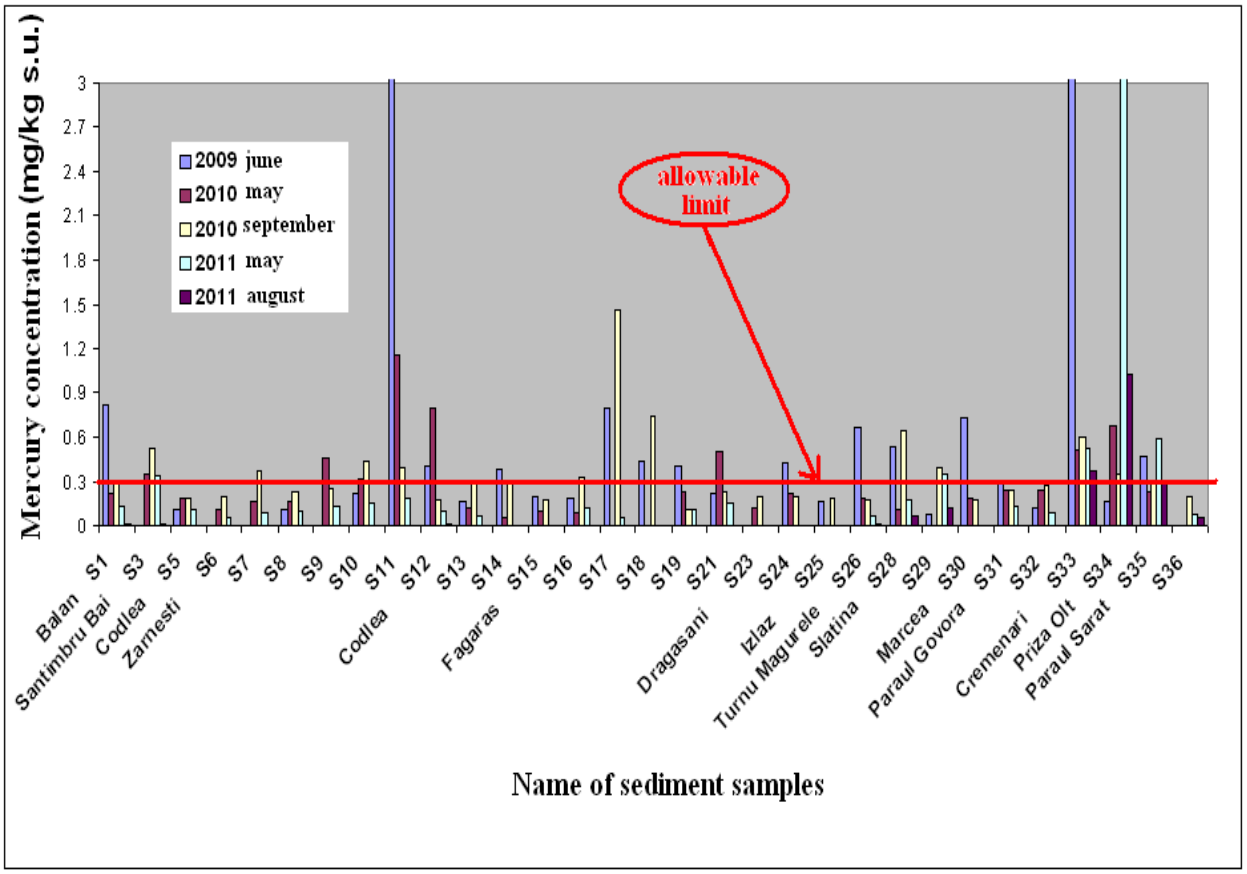

Figure 3. Variation of mercury concentration of sediment samples collected from the Olt River Basin

Regarding the mercury concentration in soil samples collected during the investigation period, it falls under Order 756/1997 in the "Intervention thresholds / less sensitive types of use" for samples of Santimbru Bai village. Village where many years ago there was a mercury mine. Which explains soil pollution with mercury in the area. The concentration of mercury in soil samples investigated in other areas generally fall in the "Alert threshold / types of use areas".

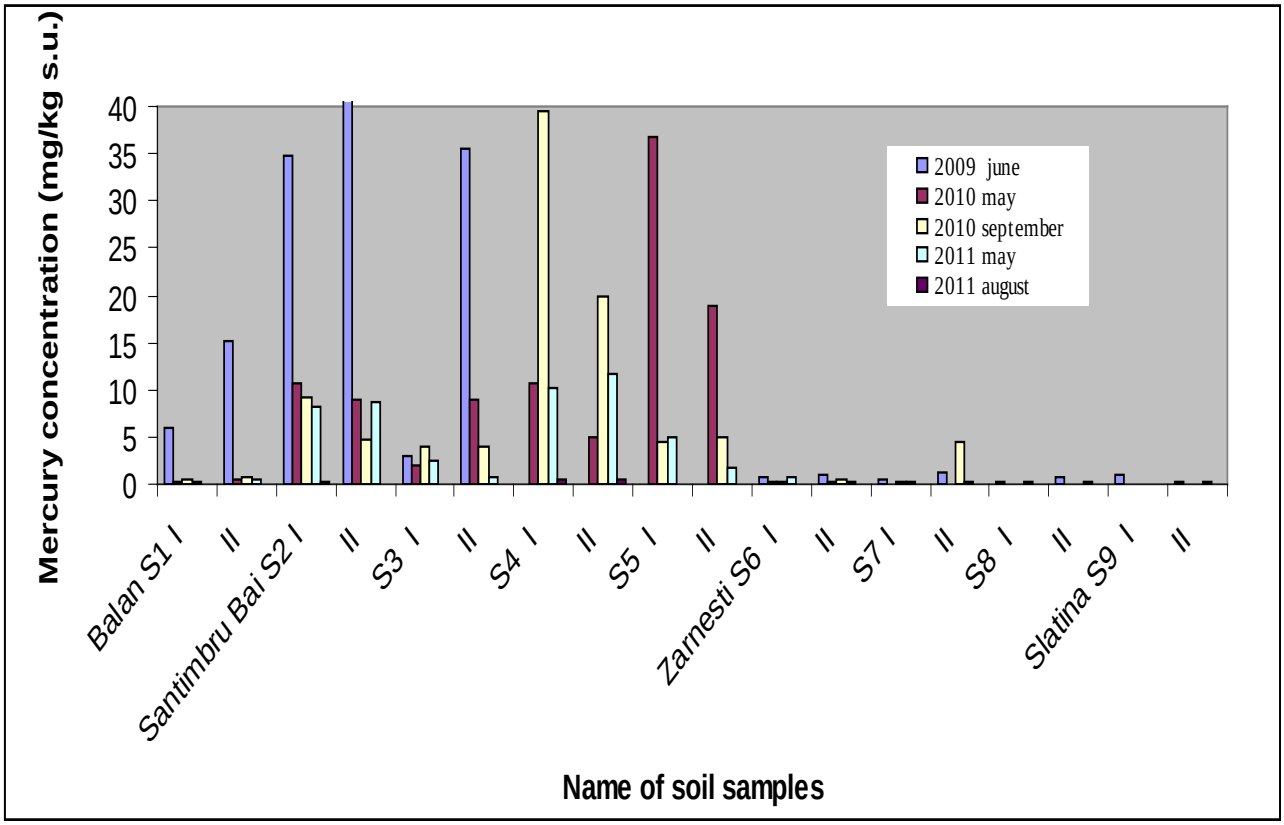

Figure 4. Variation of mercury concentration for soil samples collected

4. Conclusions

The levels of mercury found in water samples collected from River basin are generally low and is due to high average flow of the river Olt. Although concentrations of mercury water samples are small we can see that in sediment samples collected mercury concentration was above the permissible under the law in viguare which confirms accumulation of mercury in sediments.

It is possible that the elemental Hg emitted only had limited residence time in the vicinity of the sources, with limited deposition and re-emission to the atmosphere from the water bodies. However, the contaminated soils and the sediment are continuously eroded and serve as a continuous source of mercury discharge to the olt river basin waters which is confirmed by the fact that even years after the closure of the mercury mine elevated levels of mercury are found in soil.

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