The Determination of Mercury (Hg) in the Soils Collected in the Bay of Vlora

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Abstract

Vlora is a city in the South-West of Albania, it stretches along the bay with the same name. In the northern part of Vlora (5*km*), with an area of about 1km^2, there is the territory of the former industrial complex of Soda PVC. This complex used mercury (Hg) and its derivatives during the industrial processes (1976-1992). The remnants of this complex which lay close to the sea, rich in high concentration of mercury, are deposited around its buildings thus polluting the environment.

In 2007-2008, after being considered by the UNEP report as a "*Hot Spot*" area, a remedation project was implemented. It consisted of encapsulation, excavation of contaminated soils and waste disposal in land.

The first monitoring was conducted after the rehabilitation, in December 2015. Soil samples were analyzed at different depths. The Hg concentration in samples was determined by means of CVAAS method. After the remediation the presentation of the results on the concentration of Hg in soil samples of the area, showed that the concentration of mercury in soil samples was lower than the concentration before remeditation, but still high compared to the rates allowed by UNEP. This study highlighted the aims of the environmental problem, and his dangerousness to the Bay.

KEYWORDS: Soda-PVC, the concentration of Hg, monitoring, CVAAS

Introduction

Mercury is a metal of a heavy transition, its colour is white to silver, characterized by the symbol of Hg and its atomic number 80; it is one of three elements that in environment temperature is liquid.

In nature it is rarely found as a single metal; is often found in the form of amalgam, for example, in korderit, in livingtonit and especially cinabro (HgS), which is extracted after being heated in air flow and subsequent condensation of the gas produced. [2]

Hg may be present in the environment in the chemical form of elemental, inorganic and organic mercury.

Elemental mercury in a gaseous state, is the most dangerous of all other kinds , because of the fact that, once absorbed by the lungs, it immediately passes in the blood and in the brain. [1]

Mercury is one of the most toxic pollutants and the most convoluted to the human health; its components are unstable in the environment and are released from a variety of sources both natural and anthropic.

Natural emission sources are represented by volcanoes, fires, degradation of mineral substances from the land surface erosion, evaporation of soil and water.

The release of Hg from natural resources remains virtually invariant (unchanged) over the centuries; on the contrary, great importance have anthropic emission sources, which besides the industrial revolution, have made a significant contribution to the emission of Hg in the environment.
The anthropic emission can be found in various processes such as in: the processes of the production of energy through the burning of oil and coal, in plastics industry, where it is used as a catalyst in the synthesis of poliuetan of chloride vinyl, in paint and paper industry, where it is used as anti-mold, in chloro-sodiu plants, where it is used as a cathode in the electrolysis of sodium chloride, in manufacturing electrical equipments (gas mercury lamps, batteries, mercury key), in the production of lime and cement, mineral industry, the processes of amalgamation for the extraction of gold and silver in a small-scale and the production of thermometers and barometers. [5]

A classic example of a typical anthropic source occurred in modern times in Albania, in the former Soda PVC plant in Vlora. This plant operated during 1976-1992 producing chlorine-alkali products, vinyl chloride monomer and polyvinyl chloride, using mercury as a cathode for the electrolysis of NaCl and $HgCl_2$ as catalyst for monomer synthesis of C_2H_3Cl.
The pollution caused in this territory by the mercury, came as a result of several factors:
1. Old Chinese Technology (Failure to correct technology)
2. Failure of the proper waste disposal in the former plant. The waste was discharged into an area with sandy geological composition, located about 200m from the sea.
3. The closure of the plant was not done according to known technological protocol procedures, emplemented for the closure of these types of plants, so in the end the plant was abandoned.
4. The unawareness of people about the evident dangers, made the area be populated (especially after 1997) from people in the abandoned buildings of the former plant.
Due to the high level of pollution, this area was declared a "Hot Spot" by UNEP [6].
For this, in 2007-2008, rehabilitation of the area was conducted [3].
The purpose of this article is to assess which is the level of mercury pollution in soils of the area after rehabilitation.

Materials and Methods

Sampling procedures

Soil samples were taken in the area where the former plant was built. They were taken in 10 different points of the area to a depth of 50cm. Geographic coordinates of these points are measured by GPS system. Once taken, the samples were passed in strainer of 2mm then stored in plastic bags to be ready for analysis.

Analytical procedures of Soil Samples

As it is generally known, , mercury is present in very low concentrations in environmental samples, so, very sensitive methods are needed for its analysis.

The method we used for the determination of mercury in samples of these soils was cold vapor atomic absorption spectrometry technique (CVAAS); due to its sensitivity and high selectivity.

Measurements were performed in the laboratory of the Chemistry Department close to Faculty of Natural Sciences, in Tirana, with "Varian SPECTRAA 10 Plus" device type, equipped with CVAAS system. The sensitivity of the determination of Hg with this system amounts to 0.2ppb. The analytical procedure for soil sampling is performed according to the Reference Method provided by UNEP / IAEA for the Study of pollution [7].

Samples in the amount of 0.3-0.5g were treated beforehand with acid mixture HNO_3 + HCl reports (9:1). This mixture was treated at a temperature of 70º-80º for 3 hours in half airtight canisters PTFE. Once cooled this mixture 1 ml of 5% K_2Cr_2O7 solution was added, it was poured in 50ml of distilled water and left to decantate. In conclusion a certain volume of this solution was taken to be determined in the cold vapor atomic absorption system (CV-AAS).

All reagents used for the determination of mercury are MERCK reagent that contain low mercury.

The determination of Mercury

Mercury was determined in cold vapor with atomic absorption system (CV-AAS). The prepared system for the evaporation and atomisation of Hg is shown schematically in Figure 1. [4]. Optimal operating conditions of cold vapor system are: 20ml sample and air flow rate of about 2.0 L/min.

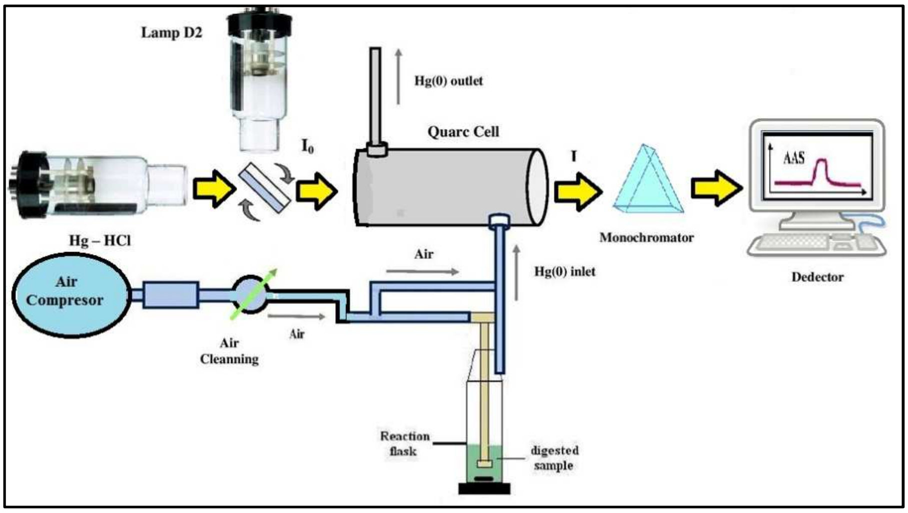

Fig 1. *Schematic diagram of CVAAS system for the evaporation and atomisation of mercury*

The operation of the cold vapor system

Chemically treated samples ready for the analysis of mercury are passed in reaction vessel where is added 15% $SnCl_2$ solution , in HCl environment (10 mL). The air that is accumulated in the container leads the mercury (Hg^0) to the quartz cell, placed in the optical path of the apparatus. After the recording of the signal of the samples, the direction of air in the system is changed for the rinse of the system and it is prepared and measured with the method of supplements after expiration of mercury vapor sample. The white solution is prepared with distilled water and is treated like the samples.

Used reagents

All reagents used are reagents of a degree of analytical purity and meet the requirements for the determination of mercury. To reduce Hg^{2+} to Hg^0 the concentration of 10% solution was used in a HCl environment of tin chloride (II). The solution was cleaned for about 10 minutes in a flow of air blown in about 2.0 L/min.

Ensuring the quality of data

Along with the samples of sediment samples were analyzed and two certified samples (CRM), SDM/2-TM and IAEA 405 bought by IAEA Monaco. It should be noted that our results correspond to those declared.

Results and discutions

Table 1. shows the results of the concentrations of Hg (mg/kg, DW), which are obtained from laboratory tests.
In the first line are are represented the determined points (Si) where samples were taken. In the second and third line are represented the results of concentrations of Hg (in mg/kg, DW) obtained in these points before and after rehabilitation (coordinates of points (Si) where samples are taken, both before and after rehabilitation which are almost the same).

No. Sample		S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Sampling depth -0.5m	Befor remeditation	1.6	26.4	15.1	0.75	15.7	0.17	0.8	6.9	1.8	0.52
	Actual study	0.298	0.011	0.021	0.209	1.689	0.006	0.024	0.007	0.231	1.181

Table 1. *The concentration of Hg (mg / kg DW) in soils before and after the rehabilitation in the former Soda PVC plant in Vlora*

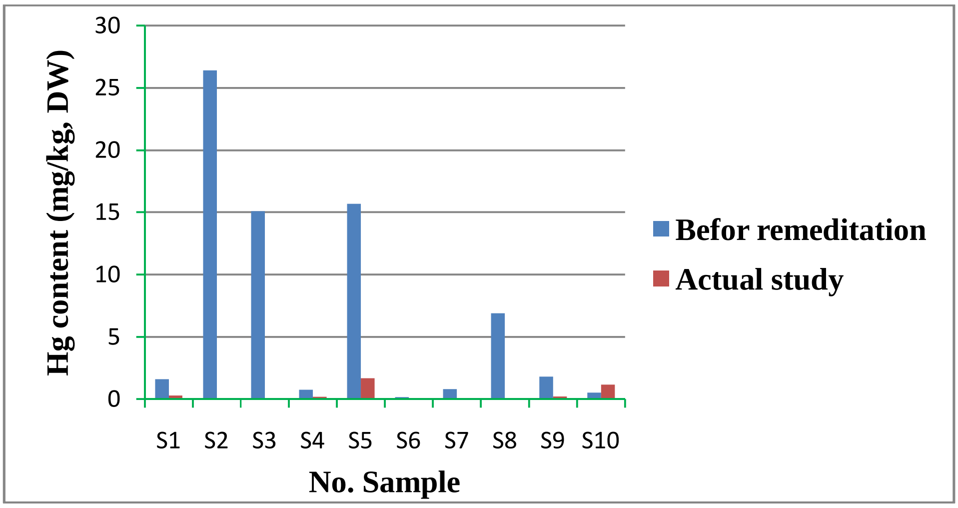

Chart 1. *The concentration of Hg (mg / kg DW) in soils before and after the rehabilitation in the former Soda PVC plant in Vlora*

As clearly seen from Table 1 and Chart 1, the concentration of mercury found in the area before rehabilitation ranged from the minimum value of 0.52 mg/kg (DW) to the maximum value of 26.4 mg/kg (DW); with an average of about 6.974 mg / kg. Whereas, the concentration of mercury after rehabilitation, in the same points (Si), range from the minimum value of 0.006mg/kg (DW) to the maximum value of 1.689 mg/kg (DW); with an average of about 0.367mg/kg.

The outcome of the statistical description of the analysis of mercury concentration, determined in soil samples of the present study are shown in Table 2.

Statistical Parameters	Mean	Median	Standard Deviation	Sample Variance	CV%	Kurtosis	Skeëness	Minimum	Maximum	Count
Values	0.368	0.117	0.585	0.343	1.59	2.294	1.813	0.006	1.689	10.000

Table 2. *The results of statisticaly treated data*

After monitoring the data obtained, a high variation of the concentration of mercury in the soil samples is observed. The coefficient of variation (CV%) is too high (159%>75%). The Skewness coefficient is higher than 0, and kurtosis coefficient is lower than 3, indicating that the frequency distribution of Hg in the area, after monitoring, deviates greatly.

The current concentration of Hg in soil samples is lower than the level of concentration before rehabilitation. Comparing the range of concentrations before and after rehabilitation, this can be presented in Table 3.

	Hg (Mean)	Rang of Hg concentration
Before remediation	6.974	0.52 – 26.4
Actual study	0.367	0.006 – 1.689

Table 3. *The concentration of Hg (mg / kg DW) in different periods*

The concentration of mercury in the present study was lower than in the period before rehabilitation, but is even high near the area of Electrolysis building (C =1.689 mg/kg DW).
Some of the samples in the study belong to a higher level than 0.3 mg / kg. ("Preliminary critical limit to prevent ecological effects" determined by UNEP Chemicals).

Conclusion

Mercury is one of the most toxic known metals, which may appear in nature in different forms: organic and inorganic.
Elemental mercury in the gaseous phase is the most dangerous of all types.
Mercury and its components are released from a variety of resources both natural and anthropic.
A typical example of an anthropic source in our country is the area of the former industrial complex of soda PVC.
This area represents the highest pollution mercury region. This pollution is due to technological waste disposed in an uncontrolled manner.
The remeditation of the area was performed during the period 2007-2008.
Soils contaminated with mercury (> 10mg/kg DW) were replaced with clean soils (not contaminated with mercury) and the whole area will be planted with grass and trees.
Measurements of the area, at a depth of 50cm include these soils, precisely.
Although the area has been rehabilitated, from the results of measurements carried out, turns out an average value of Hg concentration of 0.367mg/kg.
About 20% of the analyzed samples result in a concentration higher than 0.3 mg / kg, indicating that the concentration of mercury in the former soda plant PVC is still high compared to the rates allowed by UNEP.

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