

Assessment of total mercury content in water of the Balkyldak Lake-reservoir, Pavlodar, Kazakhstan

A V Korobeinyk^{1,2*}, V R Yapyiev¹, S Azat¹ and V J Inglezakis¹

1 Environmental Science & Technology Group (ESTg), Chemical Engineering Department, School of Engineering, Nazarbayev University, Astana, Kazakhstan
2 O. O. Chuiko Institute of Surface Chemistry of NAS of Ukraine, Kyiv, Ukraine
E-mail: alina.v.korobeinyk@gmail.com

Abstract. This study aimed at determining the levels of total mercury in water samples collected in the vicinity of the Lake-reservoir Balkyldak in Pavlodar, Kazakhstan. Legacy of the chloralkali process in Pavlodar which involved the mercury cell method while producing a chlorine-free sodium hydroxide leads to serious environmental problems. At the time of the unit continuous operation in between 1971-1993 approximately 1000 metric tons of metallic mercury has been released into the wastewater holding pond at the chemical plant. For many years, mercury collected in the wastewater pond was a subject of the Kazakhstan sharply continental climate fluctuation and overflow to the Balkyldak Lake-reservoir, creating a significant mercury contamination issue for the whole region. Mercury emitted from industrial eluents in environment carries predominantly anthropogenic pollutants. Due to its natural cycle through atmosphere, water and soil in different forms prompts the widespread global mercury pollution. In present investigation, samples collected in a close proximity of the Balkyldak Lake were analyzed in respect to the geological location of collection.

1. Introduction

The USSR heritage in terms of industrial activity, environmental pollution with waste of chloralkali plant inputs into the Pavlodar region has disturbed the equilibrium of its ecosystem. The chloralkali plant was on operation for 18 years and estimated mercury losses are in order of 1000 metric tons of Hg [1]. According to authors [2] more than 700 metric tons of metallic Hg is speed through the soil below the plant and significant amount of mercury entered the Lake-reservoir Balkyldak [3]. Mercury as a global and highly mobile pollutant affects ecosystem[4] and human health[5]. The first study dedicated to health effects awareness of Hg was published in the early 1950s based on the Minatama (Japan) case study where Hg contaminated fish were consumed as a main food source [6]. Mercury exposure [7] even at low concentrations (>2 mg/Kg body weight per day) is responsible for many fatal diseases. Considering the amount of mercury released in to the environment and the fact that the last field research was conducted ten years ago the primary objective of this study was to monitor the Hg concentration in aqueous samples collected in close proximity from ex-chloralkali plant.

2. Materials and methods

2.1. Apparatus

The apparatus used was a Lumex RA-915+ atomic absorption (AA) spectrometer coupled with a PYRO-915 pyrolysis attachment (Lumex Instruments) [8]. The setup consists of a first atomizer section, where at a temperature near 750 °C, the mercury compounds in samples are decomposed into



volatile Hg species in molecular or elemental forms. A sample is placed into a quartz boat, which is inserted into the evaporator, where temperature is varied from ambient to 850 °C. The atomized mercury and is transferred through the catalytic converter to analytical AA detector.

2.2. Sampling area and sample collection

The lake-reservoir Balkyldak is located North of Pavlodar city (20 km North), so-called Northern industrial area of Pavlodar, in Pavlodar's region of Kazakhstan. A "Khumprom" chemical plant is a major and largest source of mercury pollution in North-Kazakhstan region, which operated before 1989 for 14 year employed mercury as a cathode in production of chlorine and caustic soda. The Balkuldak lake-reservoir was created to settle the mercury bearing sediments. Figure 1 shows the study area and sampling points.

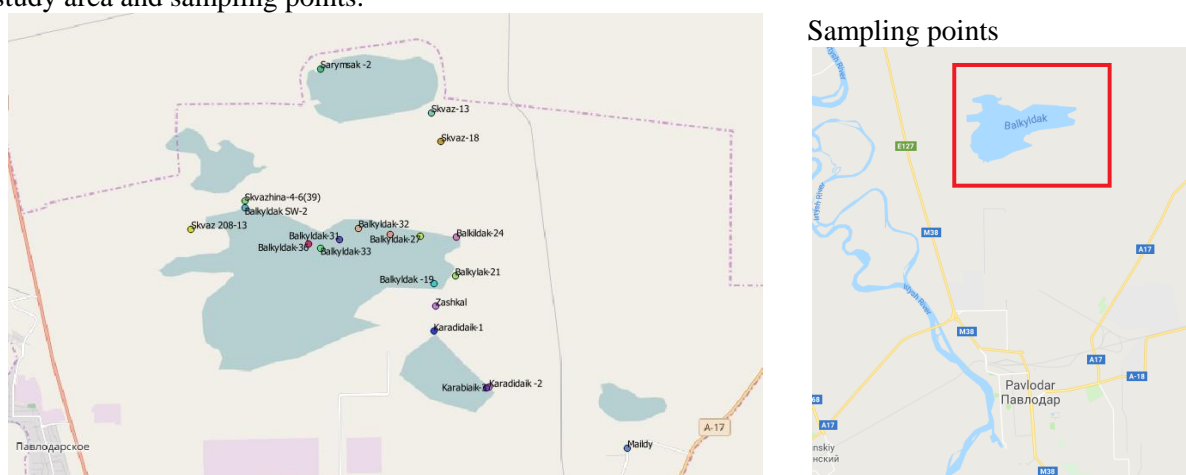


Figure 1. Sample location map of the study area (street view map, 2017)

Twenty five (17 Balkyldak lake-reservoir, 5 revision well and 3 wetland) samples were collected from legacy chloralkali plant tailings dams and their surrounding areas in summer (August) period in 2017. Water samples were collected by dipping thoroughly acid washed glass scintillation bottle 5 cm below the water surface. The precautions as prescribed by the USEPA Method 7471B and 245.1 for sampling procedures were carefully employed throughout the sampling processes [9]. The collected samples were transported to the laboratory and refrigerated until analysis commenced.

2.3. Data analysis

All the samples were prepared in triplicate and from the triplicate measurements the average and standard deviations were calculated. Statistical analysis to test for variations and relationships of concentrations were calculated using Microsoft office excel 2010.

3. Results and discussion

Basing of the commenced analysis, the average Hg concentration in water samples of Pavlodar region is evaluated as ≈ 30 ppb, which is almost fifteen times higher than MCLG [10]. The maximum contaminant level goal (MCLG) is a non-enforceable level that is based solely on possible health risks and exposure. In the National Primary Drinking Water Regulations formulated by US Environmental Protection Agency (EPA), MCLG for mercury in drinking water is set at 2 ppb [10]. The total mercury content in the studied samples exhibits high variability and changes in a range of 10 to 100 ppb (Figure 2). Figure 2 represent left to right: total mercury content in all aqueous samples collected from 5 revision wells; in all 17 lake-reservoir Balkyldak samples; and wetlands 3 samples. All samples were measured in triplicates and the averages are presented. The average (10 ppb) of total Hg concentration in all 17 analyzed samples collected from Balkyldak is lower as compared to that in all 5 wells water samples having average 65 ppb. It should be noted that the elevated mercury content in revision wells samples is governed by samples having the highest Hg concentration and geographically situated right next to ex-chloralkali plant which confirms continuous leakage of mercury from the building [2].

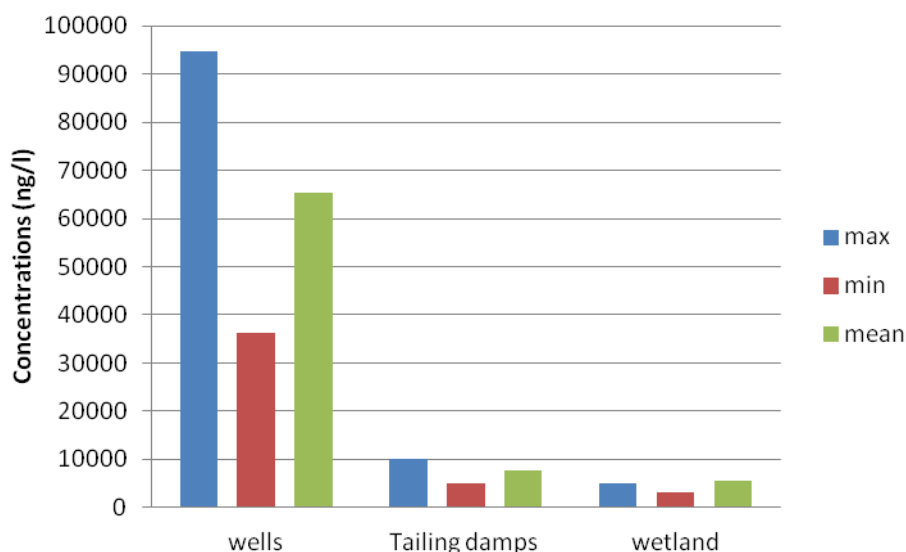


Figure 2. Concentrations of THg in aqueous samples from revision wells, tailings dams, and wetlands (1000 ng/l= 1 ppb).

As can be seen in Figure 2, THg of lake-reservoir Balkyldak samples were lower than those collected from nearby wells. This can be explained by static condition of mercury in the lake and a movement of the underground water in the revision wells. This may be attributed to increased deposition of runoff eroded Hg on sediments in the lake. The study conducted so far have confirmed the presence of Hg in legacy chloralkali plant and these may pose health threat to the communities living within the vicinity of the ex-chloralkali plant.

4. Conclusion

This study has shown the presence of Hg in the lake-reservoir Balkyldak, revision wells and water samples collected from wetlands of the ex-chloralkali plant surrounding area where metallic Hg was used as cathode in producing of a sodium hydroxide. The highest concentration was observed in the revision wells in close proximity from the ex-plant building compared to the other environmental samples. On the basis of collected data, it can be inferred that the legacy chloralkali plant is primary source of Hg contamination in the study area. The majority of concentrations of THg determined were found to be above the recommended limits, and, therefore, it is of concern to surrounding communities. Several adsorbents can be used in the extraction of this pollutant from the solution such as sulfurized activated carbon, mineral zeolites, Hg-specific resins, polymer membranes and etc. Nevertheless, utilization of those filter materials in a field where concentration of Hg is high is limited due to high cost, bio/mechanical filter clogging or low filter capacity.

5. References

- [1] Lushin E N, Krakhaleva T E and Krakhalev A F, *Results of the determination of the level of mercury contamination at the site of chlorine and caustic soda production of the Pavlodar Chemical Plant*. 1990, Pavlodar Hydrogeological Expedition and Scientific-Research Centre "Tekhnolog": Pavlodar. p. 194.
- [2] Ullrich S M, et al., *Mercury contamination in the vicinity of a derelict chlor-alkali plant. Part I: Sediment and water contamination of Lake Balkyldak and the River Irtysh*. Science of The Total Environment, 2007. **381**(1): p. 1-16.
- [3] Ullrich S M, et al., *Mercury contamination in the vicinity of a derelict chlor-alkali plant: Part II: Contamination of the aquatic and terrestrial food chain and potential risks to the local population*. Science of The Total Environment, 2007. **381**(1): p. 290-306.

- [4] Unep, *Global Mercury Assessment 2013: Sources, Emissions, Releases, and Environmental Transport*. UNEP, 2013: p. 42.
- [5] Ballester F, et al., *Prenatal exposure to mercury and longitudinally assessed fetal growth: Relation and effect modifiers*. Environmental Research, 2018. **160**: p. 97-106.
- [6] Kurland L T, Faro S N and Siedler H, *Minamata disease. The outbreak of a neurologic disorder in Minamata, Japan, and its relationship to the ingestion of seafood contaminated by mercuric compounds*. World neurology, 1960. **1**: p. 370-395.
- [7] Cadet J L and Bolla K I, *CHAPTER 111 - ENVIRONMENTAL TOXINS AND DISORDERS OF THE NERVOUS SYSTEM A2 - Schapira, Anthony H.V*, in *Neurology and Clinical Neuroscience*, A. Editors, et al., Editors. 2007, Mosby: Philadelphia. p. 1477-1488.
- [8] Kolker A, et al., *Mercury and trace element contents of Donbas coals and associated mine water in the vicinity of Donetsk, Ukraine*. International Journal of Coal Geology, 2009. **79**(3): p. 83-91.
- [9] Agency, U.S.E.P., *Method 7471B: mercury in solid or semisolid waste (manual cold-vapor technique)*. 2007. p. 1-11.
- [10] Wakuda D, Kim K S, and Suganuma K, *Room temperature sintering of Ag nanoparticles by drying solvent*. Scripta Materialia, 2008. **59**(6): p. 649-652.

Acknowledgements

The financial assistance of Nazarbayev University (project ORAU “HyperActiv”), Kazakhstan, European Commission, Horizon 2020 MSCA-RISE-2016 project ‘NanoMed’, and the Royal Academy of Engineering (UK), projects IAPP/1516/46 and IAPP/1516/3 research grants towards this research is hereby acknowledged.