Chlor-alkali plant: “Kaustik” plant in Volgograd, Mercury Hot Spot in Russia

IPEN Mercury-Free Campaign Report

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Introduction

In 2009, the Governing Council of the United Nations Environment Programme (UNEP GC) decided to develop a global legally binding instrument on mercury to reduce risks to human health and the environment (UNEP GC25/5). The UNEP GC noted that mercury is a substance of global concern due to its long-range transport, persistence, ability to bioaccumulate, and toxicity. Its conclusions were based in part on the 2002 UNEP Global Mercury Assessment which noted that mercury is present in fish all over the globe at levels that adversely affect humans and wildlife. (UNEP 2002) Mercury is present in different forms but the organic form of mercury, methylmercury, is especially toxic to humans and wildlife because it is readily absorbed by the body and accumulates in blood and tissue. In humans, hair is widely accepted as a matrix for reliable estimations of the body burden of methylmercury, which likely comes from eating fish (Grandjean, Weihe et al. 1998); (Harada, Nakachi et al. 1999); (Knobeloch, Gliori et al. 2007); (Myers, Davidson et al. 2000).

This report focuses on a chlor-alkali plant JSC (joint stock company) “Kaustik” in Volgograd, Russia. The JSC "Kaustik” facility is a well-known permanent source of mercury pollution located in the South of Volgograd city (48 ° 42 'north latitude and 44 ° 29' east longitude).
The chlor-alkali industry produces chlorine gas and alkali (sodium hydroxide) by a process that applies electrolysis to saltwater. Some chlor-alkali plants use a mercury-cell process in which mercury is used as the electrolysis cathode. This occurs at the “Kaustik” facility in Volgograd. A single mercury-cell plant may contain hundreds of tons of elemental mercury for use in production and may have even more mercury in its warehouses to replenish lost mercury.

Fish and hair samples were collected close to “Kaustik” in the districts Krasnoarmeysky and Svetloyarsky, and village Raygorod on South of Volgograd city to confirm whether the long lasting production of chlorine by using mercury in amalgam electrolysis resulted in food source contamination of fish and also had potentially influenced levels of mercury in local population of people. In addition, since local mercury releases become global problems due to long range transport we considered how the draft treaty text will address chlor-alkali plants and contaminated sites such as “Kaustik” facility and its surrounding.

Materials and methods

Local NGO Volgograd Eco-Press conducted fish and hair sampling. Ten samples of each of the three fish species (perch, carp and catfish) were caught in collaboration with local fisherman using protocols developed by the Biodiversity Research Institute (BRI 2011). The Research Centre of Volgograd, public organization “Centre of Environmental Control” measured mercury levels (total mercury content = THg) in fish samples in laboratory in Volgograd, Russia. Volgograd Eco-Press characterized the site and provided information about its history and presumptive mercury sources.

Results and discussion

Chlor-alkali plant “Kaustik” is close to the Volga River in Krasnoarmeysky district and north of the Lake Sarpa. Mercury-based production of chlorine was launched in 1968 in “Kaustik”, while in 1984 diaphragm electrolysers were also put into operation. Now, both production lines are operational.

According to the inventory results conducted by the regional Service for Supervision of Natural Resource Usage_and Environmental Prosecutor’s office in 2008, overall, the facility releases 0.689 ton of mercury.

There is also a significant amount of waste produced by "Kaustik" Co. including wastes containing mercury (Kaustic Co. 2007). In 2009, there were barrels and drums completely filled with mercury-containing waste and sludge and stored on the bare ground without any protective covers or soil lining.[a] As a result, in warm seasons, mercury vapour releases from the dump cause mercury pollution of the ambient air.

The amount of mercury in the waste-water disposal system is about 395.8 kg per year. A so-called “dirty Section” № 2 of „Kaustik“ storage pond is of greatest concern due to neutralization and disposal of liquid waste from both "Kaustik" and JSC "Plastcard" that have been processed at the pond[b] located in Svetloyarsky district of Volgograd area, 4-5 km south-east of "Kaustik."

For this study, three fish species were sampled from three different localities: perch (Krasnoarmeysky), carp (Kaustik sewage pond) and catfish (Svetloyarsky). Table 1 shows the levels of mercury (Hg) in each type of fish.

Table 1 shows that average mercury levels in catfish and perch samples were more than twice the US EPA reference dose, and average levels in carp also exceeded the reference dose. In fact, all of the perch and catfish samples exceeded the reference dose and 90% of the carp samples were above this level. Two samples of carp and three samples of both catfish and perch exceeded also EU maximum level for mercury in foodstuffs (fish), which is at the same value as MPC (Maximum Permissible Concentration) for fish in Russia (Moiseenko, Kudryavtseva et al. 2005). Five samples also exceeded the limit value for mercury in fish set up in Russia at 0.6 ppm w.w. There is not much data available on mercury levels in fish for Russia in comparison with most of other countries, especially taking into account size of its territory. This makes the data in Table 1 especially significant.

[a] There are 107 barrels containing about 70.0 tons of waste.
[b] The site capacity is 12,363 tons per year of dehydrated waste.

Table 1: Mercury content of fish sampled in lake Sarpa (locality Krasnoarmeysky; fish: perch), Volga river (locality Svetloyarsky; fish: catfish), and "Kaustik" sewage pond (fish: carp) in the vicinity of Volgograd, Russia.

	Sample Size	Hg Average (ppm, ww)	St Dev	Min Hg (ppm)	Max Hg (ppm)	Reference dose[c] (ppm)	Fraction of samples over Ref. Dose	Limit(s)[d] (ppm)
All fish samples	30	0.443	0.157	0.187	0.843	0.22	97%	0.5
Perch	10	0.468	0.157	0.269	0.786	0.22	100%	0.5
Carp	10	0.362	0.138	0.187	0.613	0.22	90%	0.5
Catfish	10	0.498	0.156	0.264	0.843	0.22	100%	0.5

Abbreviations: Hg, mercury; ppm, parts per million or mg/kg; ww, wet weight; min, minimum; max, maximum

Moiseenko, Kudryavtseva et al. (2005) observed much lower mercury levels in bream in the Volga River (<0.001 – 0.127 ppm d. w.) than the levels of mercury found in fish by this study.[e] A previous study carried out by Prevoznikov and Bogdanova (1999) found Hg concentrations from 0.02 ppm to 0.90 ppm in the muscles and liver of breams, caught in August–September of 1990–1992 in different parts of reservoirs in the Volga River. The highest level was observed in Kuibyshev Reservoir. *"This difference can be explained by the decrease in the level of water contamination, observed during the last decade, as well as by the location of sampling points described herein outside heavily contaminated water areas of the investigated reservoirs,"* (Moiseenko, Kudryavtseva et al. (2005). The results of this study show that the Volga River is highly contaminated in surrounding area of the "Kaustik" plant according THg levels measured in fish.

Table 2 shows the levels of mercury (Hg) in hair samples from two sites in the neighborhood of JSC "Kaustik" and summary of all samples taken in the vicinity of Volgograd, Russia for this report.

The average level of THg in the hair of all 28 volunteers from Krasnarmeysky District and Raygorod was nearly two-times higher than the US EPA reference dose. Approximately two-thirds of the people exceeded the reference dose. The maximum level of THg in hair was

[c] Figure derived from the reference dose used as U.S. EPA consumption guidelines for fish (0.2 $mg.kg^{-1}$ methylmercury) based on the presumption that methylmercury counts for 90% of THg levels, limit value used by Canada is similar . Japan and/or UK use 0.3 reference dose. Source: US EPA (2001). Water Quality Criterion for the Protection of Human Health: Methylmercury. Final. EPA-823-R-01-001, Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency Washington, DC: 303.

[d] Limit for mercury in fish issued by EU: European Commission (2001). Commission Regulation (EC) No 466/2001 of 8 March 2001 setting maximum levels for certain contaminants in foodstuffs (Text with EEA relevance). European Commission. Official Journal of the European Communities. EC 466/2001: L 77/71-13. Several other countries use the same limit value UNEP (2002). Global Mercury Assessment. Geneva, Switzerland, UNEP: 258.

[e] Moiseenko, Kudryavtseva et al. (2005) measured levels of mercury in ppm of dry weight, which are mostly 4-times higher than levels expressed for wet weight (w.w.) as it is in this study. Their study contains also data in w.w., but only for Middle Volga: 0.005 – 0.021 ppm in muscles of bream respective 0.004 – 0.059 ppm in liver of bream.

almost 5,5-times higher than the reference dose. There was clear difference of THg concentrations in hair between two groups. The higher level of mercury in hair of persons living in Raygorod compared to those from Krasnoarmeysky can be explained by the older age of participants and slight difference in diet. The average age of the Raygorod participants was 46 while the average age of the Krasnoarmeysky group was 29,5 years old. Volunteers in the group from Raygorod also eat more often fish comparing to those living in Krasnoarmeysky.

Table 2: Mercury content in hair samples from Krasnoarmeysky and Raygorod, both in neighborhood of JSC "Kaustik" in the vicinity of Volgograd, Russia.

	Sample Size	**Hg Mean (ppm)**	**St Dev**	**Min Hg (ppm)**	**Max Hg (ppm)**	**Reference dose (ppm)**[f]	**Fraction of samples over Ref. Dose**
All hair samples	28	1.928	1.509	0.003	5.470	1.00	67%
Krasnoarmeysky	14	1.524	1.256	0.100	4.240	1.00	64%
Raygorod	14	2.332	1.674	0.003	5.470	1.00	71%

Abbreviations: Hg, mercury; ppm, parts per million or mg/kg; st dev, std deviation; min, minimum; max, maximum

Since the beginning of the 1990s a group of medical doctors from Volgograd Medical Academy have been working in the Krasnoarmeysky district of Volgograd with the goal to analyse the health status of inhabitants living in the area (Volgograd Medicine Academy 2001). Young women in the Krasnoarmeysky district usually have weighed biological anamnesis including toxicoses of pregnancy, and higher risk of abortion. In general, 49% of the women living in the Krasnoarmeysky district have a normal course of pregnancy in comparison to 70% of the women in control areas. It was shown that in the Krasnoarmeysky district the level of infectious and parasitic diseases was higher than in the country as a whole, which also reflects immunity status.

According to results of quantitative analysis of ambient air samples, collected by the Centre of Laboratory Analysis and Technical Metrology on the collector pond at the distance of 10 km SW from "Kaustik", mercury levels were found to exceed the relevant maximum allowed concentration by 1.2 times (With MAC of 0,0003 mg/m^3 mercury level was 0,00032 mg/m^3) [g],. The analysis results confirm that wastewater flows channelled to the collector pond and shows Hg levels in water of 0.14 mg/m^3. This causes mercury emissions from the pond.

Besides JCS "Kaustic" there are four specialized facilities near the hotspot dealing with collection and treatment of mercury containing waste, mainly mercury light bulbs. Solid waste landfills are also a potential source of mercury releases. Revich and Gaponenko (2005) also notice that *„accidental discharge of mercury containing wastewater in Volgograd caused mercury content in bottom sediments along hundreds of kilometers of Volga flow up to its delta, where the sturgeons were also contaminated. This contamination consequences are not known even today.“* The source of the discharge is not specified.

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[f] U.S. EPA's RfD is associated with a blood mercury concentration of 4-5 µg/L and a hair mercury concentration of approximately 1µg/g." US EPA (1997). Mercury study report to Congress, Volume IV, An assessment of exposure to mercury in the United States. EPA-452/R-97-006**:** 293.

[g] Hygienic regulations 2.1.6.1338-03. Maximum Allowable Concentrations of polluting substances in the ambient air of residential zone http://stroyoffis.ru/gn_gigienicesk/gn_2_1_6_1338_03/gn_2_1_6_1338_03.php

Chlor-alkali plants using mercury and contaminated sites and the mercury treaty

The “Kaustik” and its surrounding on the South of Volgograd provoke questions about how the mercury treaty might mandate actions to eliminate mercury pollution of the environment and fish from sites where chlorine was long time produced by using amalgam electrolysis.

The current treaty text proposes elimination of mercury in chlor-alkali production in either 2020 or 2025. However, no agreement exists on whether countries have to identify and characterize mercury use at chlor-alkali facilities or whether to allow new mercury-using chlor-alkali facilities under certain circumstances in the future.

The mercury contamination left by chlor-alkali production is another problem. The current treaty text (UNEP (DTIE) 2012) does not require the cleanup of contaminated sites and leaves the matter to voluntary action.[h] This seems unlikely at the Volgograd hotspot site considering the long-term serious contamination of some parts of the Volga River and its sediments at such places as the pond sewage pond at the “Kaustik” plant. As stated by UNEP in the Global Mercury Assessment “Highly contaminated industrial sites and abandoned mining operations continue to release mercury.” The report is even more specific in another part stating, „ Contaminated sediments at the bottom of surface waters can serve as an important mercury reservoir, with sediment-bound mercury recycling back into the aquatic ecosystem for decades or longer.“ (UNEP 2002).

Wastes left by chlor-alkali plants are another concern. The current treaty text provides no guidance on a health-protective value that defines waste as hazardous (UNEP (DTIE) 2012). [i] In the case of hotspot in Volgograd, this would be helpful to insure protection of human health and environment from toxic mercury wastes. To prevent similar problems in the future, it would be helpful for the treaty to require the minimization and prevention of generating mercury-containing waste, but the current text does not do this (UNEP (DTIE) 2012). [j]

More recent studies by (Pirrone, Cinnirella et al. 2010); (Mukherjee, Bhattacharya et al. 2009) also calculate total mercury releases to air from the chlor-alkali sector 3-times higher than the original UNEP Chemicals (2008) air emissions inventory, while global releases to water caused by chlor-alkali plants were not estimated at all. These findings as well as case documented in this study underline need to set up as early date for phasing out mercury use in chlorine production as possible.

This study also shows the need to make data about mercury releases and overall levels in the environment publicly available. Requiring a register of publicly available information which identifies these facilities and estimates their annual amount of Hg used would be helpful.

To prevent continuous mercury pollution of the Volga River ecosystems and fish serving as food for the local communities in the vicinity of Volgograd as well as downstream in the Caspian Sea, it is necessary to eliminate use of mercury in chlorine production in “Kaustik”, and prevent further releases from the contaminated area and wastes. This site represents a

[h] **UNEP**(DTIE)/Hg/INC.5/3; Article 14 para 1 “Each Party shall endeavour to develop appropriate strategies for identifying and assessing sites contaminated by mercury or mercury compounds.”

[i] **UNEP**(DTIE)/Hg/INC.5/3; Article 14 para 1 “Each Party shall endeavour to develop appropriate strategies for identifying and assessing sites contaminated by mercury or mercury compounds.”

[j] **UNEP**(DTIE)/Hg/INC.5/3; Not present in Article 13 on Wastes

typical situation for many sites across Eastern and Central Europe as well as Central Asia. Until this problem is addressed, mercury will continue to contaminate both the local area and contribute to global mercury pollution.

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