Assessment of Mercury Contamination in Water and Soil Surrounding a Chlor-Alkali Plant: A Case Study

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(Received on 15th august 2014, accepted in revised form 23 December 2014)

Summary: As a consequence of increasing industrialization without environmental governance, Pakistan is seriously confronted by many complex and difficult environmental challenges related to water and soil pollution. Among these pollution types, pollution due to heavy metals is of serious concern due to their harmful effects on living organisms. In Pakistan, a mercury-cell chlor-alkali plant (MCCAP), installed at Kala Shah Kaku industrial zone, is causing serious environmental degradation in nearby areas due to the direct discharge of its wastewater in the fresh water of Nullah Daik. The production capacity of the MCCAP is, approximately, 33 thousand metric tons per year. Furthermore, due to monsoon flooding every year, agricultural fields around the Nullah Daik are also suspected to significant contamination. Therefore, assessment of contamination in the waters of Nullah Daik as well as nearby agriculture fields is an important task to study. This study was conducted to analyse the mercury level in both water and soil samples surrounding MCCAP using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Results confirm the presence of heterogeneous Hg contamination with concentrations ranging between 0.1 to 6.71 µg L-1 in the water samples. Furthermore, significant Hg concentration, ranging between 0.1 – 14.8 mg kg-1, was also observed in the soil samples collected along the banks of Nullah Daik. However, water and soil samples collected from the upstream, from point of convergence of the MCCAP's wastewater to the Nullah, do not show any Hg contamination. Hence, the study suggests the development of specific legislative instruments in Pakistan concerning with the surface and soil water pollution and application of treatment strategies in highly polluted areas in order to avoid potential health concern on communities dwelling banks of Nullah Daik and River Ravi.

Keywords: Mercury (Hg), Chlor-alkali plants, Nullah Daik , Soil, Contamination.

Introduction

Similar to other developing countries, Pakistan is continuously disposing large quantities of untreated domestic and industrial wastewater into natural streams and rivers. Due to the negligence and lack of implementation of environmental laws, the conditions are getting deteriorating day by day [1]. The mercury release has been reported to impart significant impacts on public health as it has been declared as a neurotoxin and a bioaccumulator [2, 3].

During the last decade, different studies have been carried out to illustrate the environmental concerns of chlor-alkali plants on biotic and abiotic factors [4-8]. In principle, the chlor-alkali plants uses Mercury (Hg) as a cathode for the electrolytic production of caustic soda (NaOH) and Chlorine (Cl_2) and, hence, have been considered as potential sources of Mercury (Hg) pollution [4, 5]. The mathematical expression of the abovementioned phenomenon can be written as

$$2Na^+ + Cl^- + 2Hg \rightarrow 2Na - Hg + Cl_2$$

(Reaction in the Electrolyzer)

$$2Na - Hg + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_{2(g)} + 2Hg$$

(Reaction in the Decomposer)

Nowadays, more than 100 mercury cell chlor-alkali plants (MCCAPs) are in operation in 44 countries having 6.5 million tonnes annual production capacity. Among them, one MCCAP is located in Pakistan at Kala Shah Kaku (Punjab) with nameplate production capacity of 33 thousands metric tonnes per year [9]. The wastewater generated from this MCCAP is drained directly into Nullah Daik, a monsoon rainy water channel originating from Kashmir [10]. Since Nullah Daik is ultimately ending into the river Ravi through Khanpur Canal, therefore, it is causing a serious risk of Hg contamination to the aquatic ecosystem [11]. Furthermore, water from the downstream of the

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Nullah is also being used for irrigation purposes that contaminate the soil in the surrounding areas. This contamination is further enhanced during monsoon season when the flooded water spreads over the wide areas of nearby soil ecosystems.

Earlier studies have shown that the cultivation on Hg contaminated agricultural soil ecosystems results into the uptake and bioaccumulation of Hg which is further biomagnified in the secondary and tertiary consumers in the food chain. In addition to this, the second route of Hg exposure to the tertiary consumers including humans and other carnivores is the consumption of Hg contaminated fish [12]. Therefore, high levels of Hg in living organisms results into serious health disorders [13]. The present study aims to assess the release of Hg from the MCCAP (Kala Shah Kaku, Punjab) to the Nullah Daik water and nearby agricultural soil.

Experimental

Nullah Daik which originates from Jammu & Kashmir is the Indo-Pak transboundary monsoon rainwater stream that enters into Pakistan and passes through Kala Shah Kaku (Punjab) industrial area, crossing G.T. road (N5) and Lahore-Peshawar main railway line of Pakistan. Fig. 1 shows both the location of MCCAP that discharges its wastewater directly into Nullah Daik and sampling stations. From 20 different sites, 10 samples of water and 10 samples of soils were obtained. The detail of sampling sites is given in Table-1. Samples were handled and preserved according to the American Public Health Association [14]. Wastewater samples were collected and preserved in borosilicate bottles and then rinsed with 10% nitric acid (HNO_3) for further analysis. The pH of water samples was set to 2.0 using concentrated HNO_3. Lastly, after acidification, the samples were stored at 4^oC in a refrigerator to prevent evaporation. GPS coordinates for all samples were also recorded using GARMIN eTrex 20. Samples collection was done from 0-25cm depth for the soil samples and, at each sampling site, approximately 4m^2 soil samples was obtained and mixed to get a homogenous sample.

Inductively coupled plasma optical emission spectrometry (ICP-OES - Perkin–Elmer Optima 5300 DV) was employed to determine the Hg concentration in both water and soil samples. Standards were prepared by appropriate dilution of mercury standard stock solution manufactured by Fisher Scientific (1000 ppm J/8047/08). Digestion of water samples was conducted using potassium permanganate and potassium peroxodisulfate, followed by the addition of hyroxylammonium chloride and tin (II) chloride. In case of the soil, samples were air dried and sieved through a 2-mm (10 mesh) sieve to obtain subsample of 20 gram each. Soil samples (10 gram) were further subjected to digestion in a flask under reflux at a temperature of 110°C using 1:1:1 solution of HCl, HNO_3 and HF. Upon cooling, the dilution was performed with H_3BO_3 saturated solution (anhydrous boric acid) in order to dissolve fluorides, and then filtered and volume made up to the 250 ml. Hg concentrations were then found using ICP–OES. Lastly, the accuracy of Hg analysis was assessed using advanced mercury analyzer by running samples in duplicates. Recovery varied between 95.6 and 101.7%. A good agreement was found between the obtained mean and the certified value. Furthermore, 15% of the randomly selected samples were analyzed thrice in order to evaluate the reproducibility.

For the statistical analysis, mercury concentration data in water and sample samples was analyzed by using Minitab software package. One-way analysis of variance (ANOVA) was used for the comparisons between treatments and Tukey's test was performed for ANOVA after testing homogeneity of variance.

Table-1: Mercury concentration in the (a) water samples (b) surrounding soil samples of the Nullah Daik, Kala Shah Kaku, Punjab.

Serial Number	Mercury concentration in the water samples		Mercury concentration in the soil samples	
	Sample Number	Mercury (µg/L)	Sample Number	Mercury (mg/kg)
1	W01	BDL	S01	BDL
2	W02	BDL	S02	0.11(0.01)^h
3	W03	0. 10(0.01)^g	S03	2.55(0.07)^f
4	W04	6.68(0.05)^a	S04	14.5(0.42)^a
5	W05	3.48(0.04)^b	S05	13.5(0.28)^b
6	W06	2.47(0.04)^c	S06	9.75(0.07)^c
7	W07	1.56(0.04)^d	S07	7.61(0.14)^d
8	W08	1.45(0.01)^d	S08	5.75(0.07)^e
9	W09	0.86(0.07)^e	S09	3.15(0.07)^f
10	W10	0.48(0.23)^f	S10	1.25(0.07)^g

BDL = Below Detection Limit

Each value is the mean of duplicate. The means in the same column followed by the same letter are not significantly different at a 5% level of significance. This explains that the letters having different alphabets are significantly different from the letters having same alphabets. The standard error of three replicates is presented in parentheses.

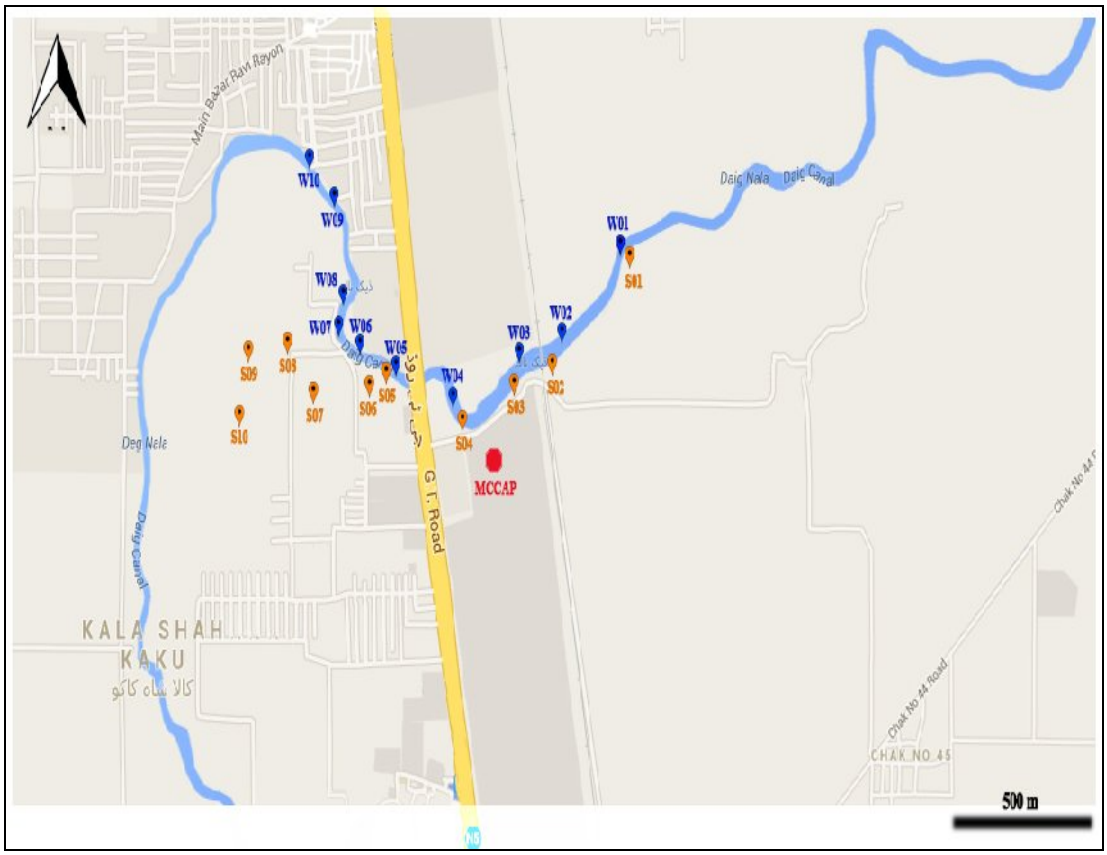

Fig. 1. Schematic representation of the study area indicating sampling stations, from S01-S10 for the soil and W0-W10 for the wastewater, in the vicinity of Nullah Daik.

Results and Discussion

The Hg concentration in the collected water and soil samples were determined in and around the Nullah Daik. Among the water samples, Hg concentrations ranged between 0.1-6.71 µg/L with a mean value of 2.42µg/L (Table-1). No Hg was detected for the samples obtained from upstream of MCCAP discharge, marked as W-01 and W-02, and, hence, their level is considered as below detection limit (BDL). Furthermore, samples collected downstream from the MCCAP and located as W07, W08, W09 and W10 showed reduced concentration of Hg. This reduced concentration might be attributed to the dilution of the wastewaters of other units located on both sides of the Nullah. Results of ANOVA test further confirm this dilution and has been shown as letter "d, e, and f" as they significantly differ from the initial letters concentrations shown as "a, b, and c" (Table-1).

In Pakistan, currently, there is no regulatory standard or legislative instrument exist that defines the acceptable mercury concentration in the surface water bodies. The only existing standard for mercury is the one dealing with the discharges of municipal or industrial wastewater into water bodies, i.e. 0.01mg/L [15]. However, internationally different maximum permissible limits for mercury in surface water have been set that vary from country to country [16]. The European Union Directive 2008/105/EC sets a maximum allowable concentration for mercury in inland surface water to be 0.07µg/L [17]. While, the US EPA's national recommended water quality criteria set 1.4µg/L as permissible limit for mercury in fresh water to protect aquatic life [18]. Generally speaking, the Hg concentration in all the water samples, downstream to the MCCAP was exceeding all of these enforceable limits due to different regulatory bodies. This Hg concentration is also subjected to increase during monsoon flood period due to addition of Hg into Nullah water from bank deposits, bed sediments and flood plain soil. Specifically, a change in hydrological conditions during seasonal variations significantly affects the concentration of Hg in surface water and changes the water chemistry [19].

The high Hg concentration in the water bodies is also subjected to various photochemical or bacterial processes that may reduce the dissolved Hg to gaseous form that could ultimately lost by volatilization into atmosphere. A similar observation has been reported by Ullrich *et al.* [7] in which atmospheric emission of Hg was recorded from water surface of a MCCAP affected lake in Kazakhstan.

In addition, the Hg presence in aquatic system could also be transformed to methylmercury (MeHg), which has been considered as highly neurotoxic and bioaccumulative mercury [20]. Since the Nullah Daik falls into the river Ravi, Hg may accumulate in the fish body tissues. Earlier studies conducted on the same area confirm the accumulation of high Hg concentration in fish samples, ranging between 83.03 – 92.35 mg/kg [21]. Moreover, during monsoon, inundation of the Nullah into the surrounding agricultural land increases the risk of Hg accumulation in soil up to phototoxic level and, thus, in agricultural crops grown in the vicinity. Ullrich *et al.* [7] and Gibičar *et al.*, [22] reported that the mercury do not readily accumulates in the vegetable grown in the Chlor-Alkali affected areas, however, the potential associated health risks with the consumption of local contaminated food can not be overlooked [23]. Similarly, another study reported a weak correlation with the local livestock due to consumption of contaminated surface water and grazing over contaminated feed [7]. Therefore, the contamination of surface water may affect the biotic components of the local ecosystem especially humans and animal population.

Similar to the water samples, the samples obtained from the nearby soils also reflect the higher level of Hg contamination. In Pakistan, similar to surface water, no permissible limit has been set to restrict the concentration of mercury in the soil. Normally, the mercury concentration in soil ranges from 0.05 to 0.08 μg/g that typically do not exceed 0.1 mg/kg in soil [24]. However in the study soil samples, the Hg concentrations ranged between 0.1 and 14.8 mg/kg with a mean value of 6.46 mg/kg. However, no Hg was detected in the samples collected from the upstream of the source. The ANOVA test confirms the similar trend of mercury contamination in soil as of water with highest concentration in station 4 and, then, decreasing along the length of the Nullah. Compared to the Hg concentration in water, higher level of Hg concentration was found in soil samples owing to the fact that Hg in water is predominantly adsorbed to the particulates [19]. Maserti and Ferrara [25] reported similar results indicating that 90% of total Hg from the discharge water of a MCCAP was found on particulates, and only 10% remained in dissolved form in the water. Another study by Wang and Driscoll [26] illustrate that 60% of total Hg was associated with particulate matter in Onondaga Lake, New York, USA. From these studies, it can be established that the water of the Nullah Daik inundates the surrounding fields during every rainy season, and consequently, lead to deposition of Hg containing particulates on the top soil due to the fact that both organic and inorganic Hg can be adsorbed easily in the soil. Nevertheless, the high Hg concentration determined in the soil may be a result of the application of mercury containing pesticides by farmers, however, the results of MCCAP in the downstream cannot be ignored. Resultantly, in certain circumstances, a portion of inorganic Hg sediments also undergoes methylation and hence transforms into MeHg causing a great ecological threat through its accumulation in food web as the major plantation in this area are agricultural crops. Therefore, the Hg presence in local soil may influence the environment due to the non-biodegradability, persistency, and low mobility in soil [4].

In general, the effects of Hg on living organisms are ubiquitous and have been reported in terms of neurologic and mutagenic disorders [27]. It is a well-established fact that Hg poisoning can lead to the damaging of various cell types such as astrocytes, renal cells, lymphoma cells, alveolar epithelial cells, human gingival fibroblast cells, and pancreatic islet β-cells [28]. This damage is attributed to the disruption in the cellular functions mainly mutations, mitosis impairment, and neuronal migration disruption [29]. Resultantly, the ultimate effects of Hg intoxication are mental retardation, seizures, cerebral palsy, metabolic disorders (i.e. diabetes), and in some cases death [30]. Among body organs, kidneys are the most susceptible to disease at organ level that may lead to failure in certain situations [31]. Besides this, cardiomyopathy, arrhythmias, and diabetes have also been associated with acute mercury toxicity. The patients of cardiomyopathic and diabetes have been found to have very high concentrations of mercury in their hairs [32].

Conclusion

The present study was conducted to determine the effects of wastewater discharge from a mercury cell chlor-alkali plant (MCCAP) located in the vicinity of Kala Shah Kaku industrial zone. This wastewater contaminates a fresh water stream (Nullah Daik) and surrounding soils. ICP-OES analyses of soil and water samples showed the Hg

contamination ranged between 0.1 – 14.8 mg/kg and 0.1-6.71 µg/L, respectively. Moreover, the Hg concentrations were only observed downstream water and soil samples to the MCCAP discharge. This situation may pose health risks to the human and animal population and, therefore, a special attention is required to avert the discharge of Hg emissions to chlor-alkali plant's vicinity. Moreover, the study suggests the development of specific legislative instruments in Pakistan concerning with the surface water and soil pollution.

References

1. M. Baqar, M. N., Chaudhry and A. Mahmood, In *Pollution of River Ravi*, Lap LAMBERT Academic Publishing, Saarbrücken (2014).
2. R. S. F. Bakir, L. Damlugi, M. Amin-Azki, M. Murtadha, A. Khaldi, A. Al-Rawi, S. Tikriti, H. I. Dhahir, T. W. Clarkson, C. Smith and R. A. Doherty, Methylmercury poisoning in Iraq, *Science*, **181**, 230 (1973).
3. J. Ui, *Industrial Pollution in Japan*, United Nations University Press, New York, (1992).
4. H. Biester, G. Muller and H. F. Scholer, Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants, *Sci. Total Environ.,* **284**, 191 (2002).
5. G. R. Southworth, S. E. Lindberg, H. Zhang and F. R. Anscombe, Fugitive mercury emissions from a chlor-alkali factory: Sources and fluxes to the atmosphere, *Atmos. Environ.*, **38**, 597 (2004).
6. S. M. Ullrich, M. A. Ilyushchenko, I. Kamberov and T. W. Tanton, . Mercury contamination in the vicinity of a derelict chlor-alkali plant. Part I: Sediment and water contamination of Lake balkyldak and the River Irtysh, *Sci. Total Environ.,* **381**, 1 (2007).
7. S. M. Ullrich, M. A. Ilyushchenko, T. W. Tanton and G. A. Uskov, 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, *Sci. Total Environ.*, **381**, 290 (2007).
8. S. M. Ullrich, M. A. Ilyushchenko, G. A. Uskov and T. W. Tanton, Mercury distribution and transport in a contaminated river system in Kazakhstan and associated impacts on aquatic biota, *Appl. Geochem.,* **22**, 2706 (2007).
9. United Nations Environment Programme (UNEP), *Global estimate of global mercury cell chlorine capacity*. UNEP Chemicals, Geneva, Switzerland (2010). URL:http://www.unep.org/hazardoussubstances/Portals/9/Mercury/Documents/chloralkali/Hg-cell%20chlor-alkali%20facility%20global%20inventory%20table_final.xls [Online: accessed July 2013].
10. L. Rabbani and M. Latif, In *Proceedings of 69th Annual Session of Pakistan Engineering Congress*, Lahore, Pakistan (2000).
11. M. Sarfraz, S. M. Mehdi, G. Hassan and S. T. Abbas, Metal contamination in Nullah Dek Water and accumulation in rice, *Pedosphere*, **17**, 130 (2007).
12. T. W. Clarkson, L. Magos and G. J. Myers, Human exposure to mercury: The three modern dilemmas, *J. Trace Elem. Exp. Med.*, **16**, 321 (2003).
13. S. T. Abbas, M. Sarfraz, S. M. Mehdi, G. Hassan and Obaid-ur-Rehman, Trace elements accumulation in soil and rice plants irrigated with the contaminated water, *Soil Till. Res.,* **94,** 503 (2007).
14. American Public Health Association (APHA), *Standard Methods for the Examination of Water and Wastewater,* 21st ed., American Public Health Association (APHA), Washington, D.C. (2005).
15. Ministry of Environment (MOE), *National Environmental quality standards for municipal and liquid industrial effluents*. Pakistan Environmental Protection Agency, Islamabad, Pakistan (2000).
16. United Nations Environment Programme (UNEP), In *Global mercury assessment. UNEP Chemicals*, Geneva, Switzerland (2010). URL: http://www.unep.org/gc/gc22/Document/UNEP-GC22-INF3.pdf
17. European Commission, Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council, Official Journal of the European Union (2008).
18. United States Environmental Protection Agency (USEPA), *National Recommended Water Quality Criteria*, U.S. Environmental Protection Agency, Washington, D.C. (2009). URL: http://www.epa.gov/ost/criteria/wqctable/
19. C. Hissler and J. L. Probst, Chlor-alkali industrial contamination and riverine transport of mercury: Distribution and partitioning of mercury between water, suspended matter, and bottom sediment of the Thur River, France, *Appl. Geochem.,***21**,1837 (2006).
20. J. M. Benoit, C. C. Gilmour, A. Heyes, R. P. Mason and C. L. Miller, Geochemical and

biological controls over methylmercury production and degradation in aquatic ecosystems. In: biogeochemistry of environmentally important trace elements, *ACS Sym. Ser.,* **835**, 262 (2003).

21. S. Nawaz, S. A. Nagra, Y. Saleem and A. Priyadarshi, Determination of heavy metals in fresh water fish species of the River Ravi, Pakistan compared to farmed fish varieties, *Environ. Monit. Assess.*, **167**, 461 (2010).
22. D. Gibičar, M. Horvat, M. Logar, V. Fajon, I. Falnoga, R. Ferrara and J. Pacyna, Human exposure to mercury in the vicinity of chlor-alkali plant. *Environ. Res.,* **109,** 355 (2009).
23. S. Woodruff and S. Dack, Analysis of risk from mercury contamination at the Khimprom plant in Kazakhstan, *Land Contam. Reclamat.,* **12,** 213 (2004).
24. World Bank Group, In *Pollution Prevention and Abatement Handbook, 1998: Toward Cleaner Production*, World Bank Publications, Washington, D. C. (1999).
25. B. E. Maserti and R. Ferrara, Mercury in plants, soil and atmosphere near a chloralkali complex, *Water Air Soil Poll.,* **56**, 15 (1991).
26. W. Wang and C. T. Driscoll, Patterns of total mercury concentrations in Onondaga Lake, New York. *Environ. Sci. Technol.*, **29**, 2261 (1995).
27. P. B. Tchounwou, W. K. Ayensu, N. Ninashvili and D. Sutton, Environmental exposure to mercury and its toxicopathologic implications for public health, *Environ. Toxicol.,* **18***, 149* (2003).
28. Y. W. Chen, C. Y. Yang, C. F. Huang, D. Z. Hung, Y. M. Leung and S. H. Liu, Heavy metals, islet function and diabetes development, *Landes Biosci*., ***1,*** *169* (2009).
29. P. R. Sager, M. Aschner and P. M. Roder, Persistent differential alteration in developing cerebellar cortex of male and female mice after methylmercury exposure, *Dev. Brain Res.*, **12**, 1 (1984).
30. World Health Organization, In *Methylmercury*. *Environmental Health Criteria 101*. Geneva, World Health Organization (1990).
31. R. Tominack, J. Weber, C. Blume, M. Madhok, T. Murphy, M. Thompson, Elemental mercury as an attractive nuisance: multiple exposures from a pilfered school supply with severe consequences, *Pediatr. Emerg. Care*, **18**, 97 (2002).
32. W. F. Fitzgerald and T. W. Clarkson, Mercury and monomethylmercury: present and future concerns, *Environ. Health Perspect.,* **96***,* 159 (1991).