CHEMICAL STABILIZATION OF MERCURY COMPOUNDS IN CONTAMINATED SOIL

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Abstract

This manuscript presents the results of a U.S. Department of Energy sponsored project that was carried out by Florida State University and the Institute for Ecology of Industrial Areas, Katowice. The problem of mercury soil contamination is very complex as the feature of this contaminant and its behavior in the environment changes from site to site. The key issue is bioavailability, which depends on speciation of mercury. Mercury speciation is critical in determining the mobility of mercury in the environment and its availability to living organisms. Mobility and toxicity of mercury compounds can be presented in a simplified way in the following order, representing the decreasing environmental adverse effects of its various fractions: water-soluble, exchangeable, fulvic/humic acids, organic and sulfide, residual. Stabilization processes are used to convert the contaminants into a less soluble, mobile or toxic form in which the physical nature of the soil is not necessarily altered.

This manuscript presents the results of the studies on mercury chemical stabilization in soil. The experiments were carried out in field plots located in the vicinity of cell house within the area of a chemical plant in Southern Poland. Granular sulfur was used for chemical stabilization - 0.5% by weight of soil. After 64 weeks from the addition of sulfur no significant differences in soil pH were observed. Water-soluble, exchangeable and fulvic/humic acid mercury fractions in topsoil were converted to a more stable, insoluble and less toxic mercury sulfide.

Introduction

Mercury is a widespread environmental contaminant, which is mobile and difficult to handle due to physical and chemical properties. Numerous industrial activities, e.g. chlor-alkali production and gold mining result in mercury contamination of terrestrial and aquatic ecosystems [1,2,3,4].

Published data on mercury concentration in contaminated soils is limited, although mercury contamination in soil is a problem found at many industrial sites both active and inactive [3,5,6]. Soil concentrations of a few to several thousands mg of mercury per kg of soil were found in the vicinity of industrial facilities where mercury and its compounds are or were used [5,7,8,9]. Mercury and its compounds in soil can undergo a number of processes, including volatilization, dissolution and contamination of groundwater and chemical, physical and biological processes (e.g. methylation). In this context, mercury presents an ongoing source of contamination to air, soil and groundwater [10].

Mercury speciation is a key factor in determining the mobility of mercury in the soil as well as its availability and toxicity to living organisms. Mobility and toxicity of mercury compounds in soil can be presented in a simplified way in the following order of adverse environmental impacts of individual mercury fractions: water-soluble, exchangeable, fulvic/humic acids, organic/sulfide, and residual [5,7,11,12,13,14].

Several treatment technologies exist for mercury contaminated soil and their applicability varies depending on the form and concentrations of mercury present in soil. Excavation and disposal, acid leaching, soil washing, stabilization, amalgamation and thermal desorption are current options for removing mercury from soil [15,16,17,18,19]. The existing remediation technologies applied for mercury-contaminated soil are generally *ex situ* methods and have a number of significant drawbacks. The major disadvantages are high capital costs and effectiveness only at rather high mercury concentrations. Most reported deployments were for waste-water and sewage sludge rather than soil remediation. These reported deployments were complex, multiphase operations and required preparation and pretreatment of the target media.

In the absence of practical processes and effective removal technologies, *in situ* stabilization has been considered as it would eliminate a number of the disadvantages of existing technologies.

Stabilization of mercury was focused on reducing bioavailability of mercury compounds in soil. The following substances are used for chemical mercury stabilization in waste, sludge and soil: sulfur, sulfur polymer, zeolites, modified sulfur cement, soluble phosphates and calcium sulfate [15,20-26].

This paper presents efforts to develop and evaluate such a method using a combination of chemical additives and plants. Granular sulfur was used for chemical stabilization and meadow grass for phytostabilization. Research on mercury stabilization in soil was performed within the area of a chemical plant located in southern Poland.

Experiment

Twelve experimental plots, each 9 m^2 (3 m × 3 m) were delineated within the selected sub-site located in the vicinity of the inactive cell house. Site preparation activities included vegetation clearing and soil conditioning using a rototiller and mulcher to homogenize mercury levels across plots. The experimental site was divided randomly into three blocks. Experimental plots within each block were selected in the same manner. The plots were as follows: reference plots without granular sulfur and meadow grass (*Poa pratentis*), plots treated with granular sulfur, plots treated with granular sulfur and meadow grass, and plots treated with meadow grass. Samples of soil (depth 0 – 25 cm) from each plot were taken: after soil preparation but before the experiment start-up (June 2001), six weeks after granular sulfur addition – before grass planting (July 2001), at the end of growing season (October 2001), before the beginning of the growing season (March 2002), in the middle of growing season (June 2002) and at the end of growing season (September 2002).

The following analyses were conducted on soil samples collected from each plot during sampling campaign in 2001 and 2002: soil pH in KCl, water-soluble mercury fraction and exchangeable mercury fraction. Concentration of total fulvic/humic acids and sulfide mercury fraction in soil samples were determined at the beginning of the experiment and 64 weeks after granular sulfur addition.

Samples of meadow grass were taken at the end of the growing season (September 2002). Samples of meadow grass (roots and shoots) were analyzed for total mercury concentration.

Teflon vacuum cup lysimeters were installed at the depth of 25 cm to monitor the pH changes and mercury concentration in soil solution at reference plots and plots treated with granular sulfur and meadow grass. Soil sampling were collected every two weeks (excluding winter season 2001/2002). Soil solution was analyzed for pH, determination and concentration of total Hg, Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and DOC (Dissolved Organic Carbon).

All statistical analysis including ANOVA and LSD test were conducted using STATISTICA software. A probability of 0.5 or less was considered to be statistically significant.

Results and Discussion

No statistically significant differences (LSD, $p < 0.05$) were found in soil pH among the reference plots and plots treated with granular sulfur and plants during the experiment.

Concentration of mean water-soluble mercury fraction in soil vs. period and treated plots are presented in Figure 1. Statistically significant differences (LSD, $p < 0.05$) were found in the concentration of water-soluble mercury fraction in soil among the reference plots and plots treated with granular sulfur and plants. No statistically significant differences (LSD, $p < 0.05$) were found in the concentration of water-soluble mercury fraction in soil at individual plots before and after winter season.
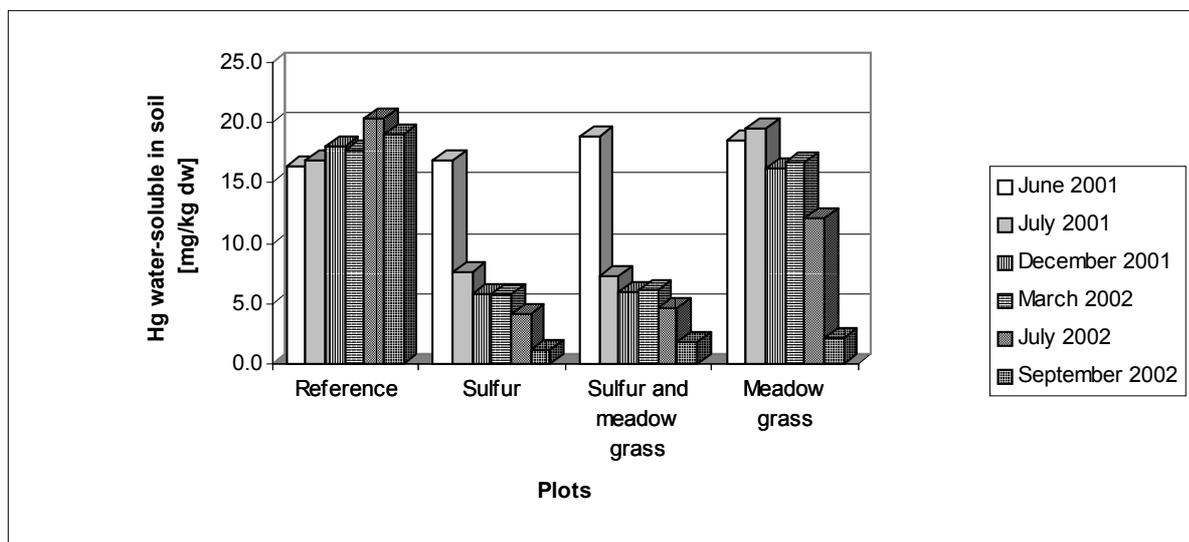

Figure 1. Concentration of mean mercury water-soluble fraction vs. period and treated plots.

Differences in the concentration of water-soluble mercury fraction at reference plot topsoil were observed during the experiment (Figure 1). For reference plots correlation coefficient – r^2 and regression equation for soil and soil solution pH were calculated. The statistically significant regression equation and correlation coefficient were calculated in the following way: soil pH = 1.5140 + 0.7681 $\times$ soil solution pH, r^2 = 0.47. Correlation coefficient – r^2 and regression equations for concentration water-soluble mercury fraction in topsoil vs. Cl^-, NO_3^-, SO_4^{2-} and DOC in soil solution were also calculated. The statistically significant regression equations and correlation coefficient were calculated as follows: water-soluble Hg in topsoil = 21.750 − 0.1814 $\times$ Cl^- in soil solution, r^2 = − 0.36, water-soluble Hg in topsoil = 20.532 − 0.2157 $\times$ DOC in soil solution, r^2 = − 0.40.

Concentration of mean exchangeable mercury fraction in soil vs. period and treated plots are given in Figure 2. Statistically significant differences (LSD, $p < 0.05$) were found in the concentration of exchangeable mercury fractions in soil among the reference plots and plots treated with granular sulfur during the experiment. No statistically significant differences (LSD, $p < 0.05$) were found in exchangeable mercury fraction in soil among the reference plots and plots treated with plant during the experiment. No statistically significant differences (LSD, $p < 0.05$) were found in the concentration of exchangeable mercury fraction in soil for individual plots before and after winter season.
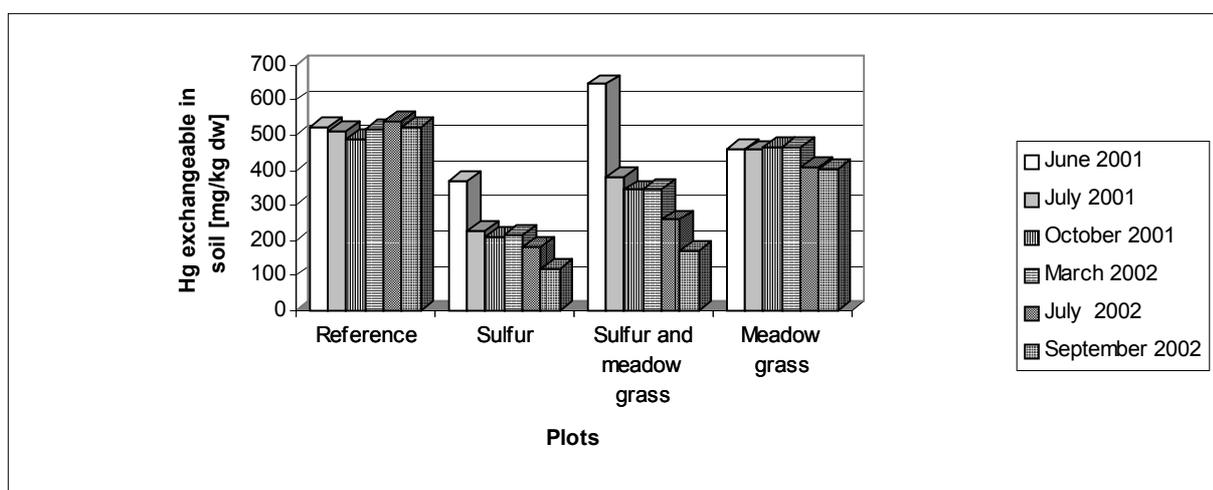

Figure 2. Concentration of mean mercury exchangeable fraction in soil vs. period and treated plots

Reduction of water-soluble and exchangeable mercury compounds concentration in topsoil was calculated as the proportion of these compounds in treated plots (sulfur and plants) to reference plots. Compared to data from reference plot, concentration of water-soluble mercury fraction has decreased by nearly 90%. In the case of exchangeable mercury fraction a nearly 70% reduction occurred after sulfur addition.

Statistically significant differences (LSD, $p < 0.05$) were found in the concentration of fulvic/humic acid mercury fraction in soil among the reference plots and plots treated with granular sulfur (Table 1). Compared to data from reference plots, concentration of fulvic/humic acid mercury fraction on plots treated with granular sulfur has decreased by nearly 49%.

Statistically significant differences (LSD, $p < 0.05$) were found in the concentration of mercury sulfide fraction in soil among the reference plots and plots treated with granular sulfur during the experiment (Table 1). Compared to data from reference plots, concentration of mercury sulfide on plots treated with granular sulfur has increased by nearly 27 %. The total concentration of the reduced water-soluble, exchangeable and fulvic/humic acid mercury fractions in soil 64 weeks after sulfur addition corresponds to the increase of mercury sulfide concentration in the period.

Table 1. Mean values of mercury fraction concentration in soil [mg/kg dw]

Plots	Hg fulvic/humic acid fraction		Hg sulfide fraction	
	June 2001	September 2002	June 2001	September 2002
Reference	192.4 ± 62.5	186.1 ± 37.7	1536.0 ± 303.5	1502.60 ± 301.8
Chemical stabilization	189.1 ± 22.9	93.9.1 ± 9.05	1485.0 ± 297.5	1748.0 ± 309.5
Chemical and phytostabilization	167.2 ± 26.0	85.9 ± 11.1	1686.9 ± 214.2	2067.0 ± 218.8
Phytostabilization	170.0 ± 28.9	174.0 ± 25.3	1880.0 ± 314.2	1856.0 ± 316.4

In the first growing season no phytostabilization was observed, probably due to slow growth and development of newly introduced plant species resulting from flooding. During the second growing season plant cover of 85 – 100% was observed on the plots treated with granular sulfur and meadow grass.

Table 2 presents total mercury concentration in shoots and roots of meadow grass. A decrease of total mercury concentration in meadow grass (shoots and roots) was observed on plots treated with granular sulfur and meadow grass. Reduction of mercury concentration in meadow grass was calculated as the proportion of this concentration in plots treated with granular sulfur and plants to plots treated only with plants. In comparison to data from plots treated with plant mercury concentrations in shoots and roots have decreased by nearly 37%. Approximately a fourfold increase of mercury concentration was observed in roots compared to shoots of meadow grass (Table 2).

Table 2. Mercury concentration in meadow grass

Plots	Plant part	Hg concentration [mg/kg dw]
Chemical and phytostabilization	Shoots	309.9 ± 88.8
	Roots	1179.0 ± 83.1
Phytostabilization	Shoots	540.9 ± 74.2
	Roots	1822.0 ± 49.9

Weighted averages for soil solution pH in 2001 and 2002 are given in Table 3.

Table 3. Weighted averages for soil solution pH

Plots	Weighted pH averages	
	2001	2002
Reference	7.32	7.31
Chemical stabilization	7.42	7.37
Phytostabilization	7.29	7.71

No statistically significant differences (LSD, $p < 0.05$) in soil solution pH were observed among the reference plots and plots treated with sulfur during the experiment. Increase of soil solution pH was observed on plots with meadow grass during the experiment.

Significant differences in mean volume of soil solution were observed between the reference plots and plots treated with plants during growing season. Plant cover (meadow grass) reduces the amount of water moving through the soil by approximately 50%.

Mean mercury concentration in soil solution from reference plots was 492.2 μg/L. In the case of soil solution from plots treated with granular sulfur or plants, mercury concentration varied from 4.03 to 9.24 μg/L.

Conclusions

◊ No significant differences in soil pH were observed between reference plots and plots treated with granular sulfur.
◊ Concentration of water-soluble mercury fraction in topsoil has decreased by nearly 90%.
◊ Concentration of exchangeable mercury fraction in topsoil has decreased by nearly 70%.
◊ Concentration of fulvic/humic acid mercury fraction in topsoil has decreased by nearly 49%.
◊ Water-soluble, exchangeable and fulvic/humic acid mercury fractions in topsoil 64 weeks after sulfur addition were converted to more stable, insoluble and less toxic mercury sulfide.
◊ Mercury contaminated soil does not restrict plant cover.
◊ Granular sulfur addition to contaminated soil does not restrict plant cover.
◊ Mercury concentration in soil solution from treated plots is 50 times lower in comparison to reference plots.
◊ No significant differences in soil solution pH were observed between reference plots and plots treated with granular sulfur.

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