EMISSIONS OF PCBS AND MERCURY FROM STABILIZED HARBOR SEDIMENTS

Final Project Summary

A Report to the

New Jersey Marine Sciences Consortium and New Jersey Department of Transportation
Office of Maritime Resources

Principal Investigators:
John R. Reinfelder, Gera Stenchikov, Lisa A. Totten
Department of Environmental Sciences, Rutgers University
14 College Farm Road, New Brunswick, NJ 08901

Robert Miskewitz, Richard I. Hires, George P. Korfiatis
Stevens Institute of Technology
Hoboken, NJ 07030

June 30, 2006

Emissions of PCBs and Mercury from Stabilized Harbor Sediments

Final Project Summary

Introduction

The Port of New York and New Jersey is the largest container and petroleum port on the East Coast of the United States. Natural depth of New York Harbor is only 6 meters, necessitating construction of over 400 km of engineered waterways that require nearly continuous improvement and maintenance. Between 3 and 5 million cubic meters of sediment are dredged annually, with actual volumes depending on construction and maintenance schedules. Historically, dredged material management relied almost exclusively on in-water disposal, despite the fact that much of the material dredged is fine grained and tends to contain varying levels of anthropogenic chemicals and trace metals. In the early 1990s, increasing environmental awareness resulted in a regional shift away from disposal toward upland beneficial use (McDonough et al., 1999).

The primary beneficial use strategy has been to use stabilized dredged material (SDM) as a capping and/or filling material for landfills, industrial sites, and abandoned mines (Douglas *et al.*, 2003). Stabilized dredged material, or SDM, is fine grained dredged material that has been mixed with a pozzolanic additive such as Type II Portland Cement, coal fly ash or incinerator ash to achieve a product with soil-like engineering properties. The strategy has multiple positive environmental benefits including reduction of runoff and leachate from contaminated sites, reduction of use of greenfields for industrial development, and providing affordable reliable locations to place dredged material. Since 1997, over 7 million cubic meters of contaminated dredged material have been successfully utilized upland in the States of New Jersey, New York and Pennsylvania (USACE 2006).

The success of the upland beneficial use strategy necessitates a firm understanding of the environmental risks and benefits. Since the beginning of the program, the State of New Jersey has had a policy that limits the placement of contaminated sediments to those sites that are already contaminated with similar substances in similar or higher amounts. The SDM is used specifically to implement a remedial action on the site consistent with a reduction or elimination of loss of contaminants into surrounding water bodies, groundwater or into the food chain. Rigorous monitoring of these sites confirms that not only are the remedial actions successful at ensuring that contaminants in SDM are not mobilized, but also those contaminants that were present on the site initially are no longer posing an ongoing threat (Douglas et al. 2005). Polychlorinated biphenyls (PCBs) and mercury (Hg) are two contaminants of particular concern with regard to the land application of SDM since they may volatilize to the atmosphere. Once in the atmosphere, these contaminants can deposit in proximate or remote ecosystems and become enriched in aquatic and terrestrial animals including humans where they may have toxic effects (Stern et al., 1996; Burger and Gochfeld, 1997; Watras et al., 1998; Gnamus et al., 2000; Berglund et al., 2001; Borga et al., 2004). Thus the atmospheric cycles of PCBs and Hg are critical to understanding and managing their environmental impact. An evaluation of the potential for SDM or the SDM manufacturing process to release PCBs and Hg into the atmosphere was initiated in 2001. This study included an evaluation of the air quality surrounding processing equipment and a placement site in northern New Jersey, as well as controlled laboratory evaluations of contaminant flux. The results of these studies are presented in this report.

Project Scope and Rationale

The goals of this project were to assess the volatilization of polychlorinated biphenyls (PCBs) and mercury (Hg) from land-applied, stabilized dredge material (SDM), the effects of cement stabilization on the release of these contaminants, and potential impacts of land-applied SDM to the ambient air quality of placement sites and adjacent areas. Thus the first phase of this project (see Korfiatis et al., 2003) included in situ measurements of PCB and Hg concentrations and land-air fluxes at a site in Bayonne, New Jersey where SDM from the NY/NJ Harbor was placed. The results of that project demonstrated that PCBs and Hg were emitted from SDM, but pointed to gaps in our understanding of the sediment side controls of PCB and Hg volatilization, the aerosol partitioning of PCBs emitted from SDM, and the relative importance of SDM PCB emissions to the local atmosphere compared with other sources in the New York/New Jersey metropolitan area. The second phase of this project therefore included laboratory flux chamber measurements of PCB volatilization from cement-stabilized Newtown Creek sediment (see Miskewitz et al., 2005), and evaluations of the gas phase-aerosol partitioning of PCBs at the Bayonne site, the development of a local atmospheric transport model of PCBs in the harbor atmosphere, and flux chamber studies of Hg volatilization from cement-stabilized Berry's Creek sediment (see Reinfelder et al., 2006). The major findings of these studies and their implications for the land-application of SDM, where appropriate, are summarized below.

Assessment of PCB emissions from land-applied SDM

PCB concentrations and volatilization fluxes at the Bayonne SDM placement site

At the Bayonne SDM site, gaseous air concentrations of ΣPCBs measured directly above SDM (3 – 14 ng m^{-3}) as it cured were relatively high compared to regional background values (1 – 3 ng m^{-3}), but they were two orders of magnitude below the NIOSH recommended exposure limit of 1μg m^{-3} and five orders of magnitude lower than the OSHA permissible exposure limits of 0.5 to 1.0 mg m^{-3} (Korfiatis et al., 2003). Average ΣPCB concentrations at the SDM application site were approximately two times higher than those at an urban reference site 3.5 km west of the SDM site, but approximately 20% of the time, PCB concentrations at the urban reference site were greater than those at the SDM application site (Korfiatis et al., 2003). Upwind /downwind concentration gradients of PCBs were rare (5 of 29 cases) at the SDM landfill site. This suggests that SDM is not the only or dominant source of PCBs to the air above the landfill and that other offsite sources may be important.

Estimated vertical fluxes of PCBs from SDM at the Bayonne site ranged from 72 to 15,000 ng m^{-2} h^{-1} and averaged 2050 ng m^{-2} h^{-1}. Modeling results show that the transport of PCB emissions of this magnitude from the SDM placement site could produce concentration spikes of only 1/4th to 1/10th of those observed at the urban reference site indicating that PCB emissions from the SDM placement site have a small effect on the overall levels of PCBs measured within 3.5 km of its perimeter. Due to the high background concentrations of PCBs in both the gas and particle phases in the NYC metropolitan area, emissions of either gas- or particle-phase PCBs from the Bayonne SDM site are not large enough to alter the gas/particle partitioning of PCBs in this region. These emissions could, however, be important if SDM were placed in a more remote location where the background PCB signal is lower.

Effect of cement stabilization on the volatilization of PCBs from SDM

In the Bayonne field study, PCB fluxes from recently placed SDM were initially high, but decreased quickly as the SDM dried (Korfiatis et al., 2003). This was also observed in the laboratory flux chamber study where the rate at which the PCB flux decreased was found to be highly dependent on the degree of cement stabilization (Miskewitz et al., 2005). The average time constant for the decrease of PCB fluxes from unstabilized sediments was 61 h, while that for sediment stabilized with 8% portland cement was 15 h. Thus the addition of cement acts to decrease PCB fluxes from dredged sediment. The stabilization process will dry the sediment and thus reduce the amount of PCB volatilized (see *Effects of site and atmospheric conditions* section below).

What fraction of the sediment PCBs is lost to the atmosphere?

The fraction of ΣPCBs in New York/New Jersey Harbor dredged material that escapes to the atmosphere during land-application can be estimated from the average sediment PCB concentration and the average time dependent area PCB volatilization rate for SDM at the Bayonne site. The average PCB concentration in New York/New Jersey Harbor sediments exceeds 400 ng g^{-1} dry wt (Ho et al., 2000). Using a dry sediment mass density of 500 kg m^{-3} and a sediment PCB concentration of 400 ng g^{-1} dry wt yields a total sediment PCB concentration of 0.2 g m^{-3}. PCB area loads to the atmosphere from unstabilized and 8% cement-stabilized sediments were estimated by integrating the maximum initial PCB flux observed at the Bayonne SDM site (15,000 ng m^{-2} h^{-1}; Korfiatis et al., 2003) over periods of 215 and 54 h, respectively, (i.e. five half-lives of the logarithmic decreases observed in the laboratory flux chamber experiments, final flux = 3% of initial flux, see by Miskewitz et al., 2005). The resulting PCB loads to the atmosphere are 900 and 200 μg m^{-2}, for unstabilized and 8% cement-stabilized sediments, respectively. With an average SDM depth of 2 m, this is equivalent to losses of 450 and 100 μg m^{-3}. Thus without stabilization, an average of about 0.2% of the ΣPCBs in land applied sediments would be lost to the atmosphere, but only 0.05% of the ΣPCBs in land applied sediments stabilized with 8% cement would be lost to the atmosphere.

Effects of site and atmospheric conditions on the volatilization of PCBs from SDM

Estimated PCB flux rates exhibited a large dependence on the atmospheric and site conditions. Since the atmosphere tends to be stable at night, nighttime PCB fluxes were low. Very low PCB fluxes also occurred during daytime intervals when it was cloudy and cool, such as on the morning. The moisture content of the dredged material may also have an effect on PCB volatilization. Dry sediments have a greater affinity for volatile contaminants than wet sediments because of the competition for adsorption or absorption space with water (Valsaraj et al., 1997). As the sediment particles in upper layers of the sediment dry they not only hold the contaminant absorbed to them tighter, they will also absorb free contaminants that would otherwise diffuse to the surface, thus further increasing the sediment-side resistance to contaminant flux to the atmosphere. In the Bayonne field study, the sensible heat flux from dry SDM exceeded the latent heat flux indicating restricted transport of water vapor out of the SDM and estimated PCB fluxes above dry SDM were zero or directed into the ground (Korfiatis et al., 2003). In the laboratory flux chamber experiments, temperature was also found to exert a large influence on the magnitude of PCB fluxes from SDM (Miskewitz et al., 2005). Thus sediment that is stabilized and applied to the land during warmer summer months will release more PCBs to the atmosphere.

Assessment of Hg emissions from land-applied SDM

Hg concentrations and volatilization fluxes at the Bayonne SDM placement site

Total gaseous mercury (TGM) concentrations at the Bayonne SDM site ranged from 2 to 7 ng m^{-3}, compared with 1.7 to 3.3 ng m^{-3} at an urban reference site 3.5 km west of the SDM site. Daily average concentrations of TGM at the Bayonne SDM site during active placement were <5 ng m^{-3}, and much lower than the human chronic effects limit for total gaseous mercury (200 ng m^{-3}) established by the Agency for Toxic Substances and Disease Registry. Thus there is no direct human impact of Hg emissions from the placement of SDM as carried out at the Bayonne site.

The emissions of Hg to the atmosphere are primarily of environmental concern because of the long residence time of Hg in the atmosphere (Mason et al., 1994) and the deposition of Hg in proximate or remote water bodies where it may be transformed and bioaccumulated (Lindqvist et al., 1991). Maximum seasonal and annual Hg emissions from the SDM placement site were estimated using the solar radiation-Hg flux relationship of Goodrow et al., 2005 and diurnal sunlight patterns for winter and summer months and assuming continuous 20% coverage of the SDM site. These estimates show that the average Hg volatilization flux from the SDM placement site in Bayonne, NJ was 130 g y^{-1} or 0.36 g d^{-1} (Goodrow et al., 2006), much lower than major industrial sources of Hg to the atmosphere in New Jersey (140 to 450 kg y^{-1}) and approximately 0.03% of New Jersey's atmospheric deposition flux. Given the transient nature of SDM placement sites which are eventually capped, effectively reducing Hg emissions to those from background soils, Hg emissions from the placement of SDM as carried out at the Bayonne site is expected to present only a minor emissions source of Hg to the atmosphere.

Effects of cement stabilization on Hg volatilization from SDM

Cement stabilization did not reduce Hg fluxes over the course of two days at the SDM site (Korfiatis et al., 2003). This was also observed in the laboratory experiments where the volatilization fluxes of Hg from cement stabilized sediments were twice as high as those from unstabilized sediments (Reinfelder et al., 2005). We conclude that cement stabilization does not reduce Hg volatilization from land-applied SDM over the course of a few days.

What fraction of the sediment Hg is lost to the atmosphere?

The fraction of total mercury in dredged material that escapes to the atmosphere during land-application can be estimated from the average sediment Hg concentration and the average area Hg volatilization rate for SDM at the Bayonne site. Using a dry sediment mass density of 500 kg m^{-3} and a sediment Hg concentration of 2 μg g^{-1} dry wt yields a total sediment mercury concentration of 1 g m^{-3}. Over the two year active lifetime of the Bayonne SDM site, the average area volatilization rate of Hg was 500 μg m^{2}. With an average SDM depth of 2 m, this is equivalent to a loss rate of 250 μg m^{-3}. Thus ¼ of one one-thousandth or 0.025% of the total Hg content of dredged sediment was lost to the atmosphere.

Hg volatilization fluxes expected from SDM with higher Hg concentrations

For soils, Hg volatilization fluxes generally increase with Hg soil concentration according to a log-linear relationship (Gustin et al., 2000; Nacht et al., 2004). This is also likely the case for sediments and indeed the estimated fluxes of Hg from cement-stabilized Berry's Creek sediment which contained 20 to 40 μg Hg g^{-1} dry wt (Reinfelder et al., 2005) are four to ten times higher than those observed at the Bayonne SDM placement site which contained 1 to 3 μg

Hg g^{-1} dry wt. Assuming that the land application of SDM with a Hg concentration of 40 μg g^{-1} at a site similar to that in Bayonne will result in a ten-fold higher Hg volatilization flux, the average Hg volatilization flux would be about 1.3 kg y^{-1} or 3.6 g d^{-1}. Thus the land application of SDM with a Hg concentration of up to 40 μg g^{-1} is unlikely to present a major source of Hg to the atmosphere. The impact on the environment of the land application of SDM with a Hg concentration significantly greater than 40 μg g^{-1} requires further evaluation.

Effects of light on Hg volatilization from SDM

The volatilization of mercury from estuarine sediments does not decrease with time as was observed for PCBs (Miskewitz et al., 2005), but is primarily controlled by light. The dominant role of light in controlling Hg volatilization from sediments in the laboratory flux chamber is consistent with in situ sediment-air Hg flux observations at the SDM placement site in Bayonne, NJ which were significantly correlated ($r^2 = 0.81$) with solar radiation (Goodrow et al., 2005). Decreasing the time of exposure of SDM to light during cement stabilization and placement would reduce Hg emissions to the atmosphere from this source.

Summary Conclusions

The field and laboratory results from this project allow us to evaluate the land application of cement-stabilized dredge materials from the perspective of its possible impact on the emissions of contaminants to the atmosphere. Perhaps one of the most important findings is that although emissions of PCBs and Hg to the atmosphere will occur during the land application of SDM, these represent very small fractions (<0.05%) of the total contaminant loads contained in the sediments. For the contaminant concentrations in the sediments used at the Bayonne site, these emissions therefore represent minor contributions to the local or region atmosphere. Interestingly, cement stabilization appears to have opposite effects on the volatilization of PCBs (retards) and Hg (enhances), but emissions of both are transient decreasing rapidly in only a few days in the case of PCBs and stopping altogether when covered. Based on these findings, we conclude that the land application of SDM represents a very minor impact on atmospheric levels and cycling of PCBs and Hg.

References

Berglund, O., Larsson, P., Ewald, G., and Okla, L. 2001. The effect of lake trophy on lipid content and PCB concentrations in planktonic food webs. *Ecology* 82:1078-1088.

Borga, K., Fisk, A.T., Hoekstra, P.F., and D.C.G. Muir. 2004. Biological and chemical factors of importance in the bioaccumulation and trophic transfer of persistent organochlorine contaminants in arctic marine food webs. *Environ. Toxicol. Chem.* 23: 2367–2385.

Burger, J. and Gochfeld, M. 1997. Risk, mercury levels, and birds - relating adverse laboratory effects to field biomonitoring. Environ. Res. 75: 160-172.

Douglas, W.S., Baier, L.J., Gimello, R.J., and Lodge, J. (2003). A comprehensive strategy for managing contaminated dredged material in the Port of NY and NJ. *J. Dredging Eng.* 5(3):1-12.

Douglas, W.S., Maher A, Jafari F. 2005. An analysis of the environmental effects of the use of stabilized dredged material from the New York/New Jersey harbor in the construction of roadway embankments. *Integrated Environ. Assess. Mgmt*. 1(4):1-10.

Gnamus, A., Byrne, A.R., and Horvat, M. 2000. Mercury in the soil-plant-deer-predator food chain of a temperate forest in Slovenia *Environ. Sci. Technol.* 34: 3337-3345.

Goodrow, S.M., R. Miskewitz, R.I. Hires, S.J. Eisenreich, W.S. Douglas, and J.R. Reinfelder. 2005. Mercury emissions from cement-stabilized dredged material. *Environ. Sci. Technol.* 39: 8185-8190.

Goodrow S.M., R. Miskewitz, R.I. Hires, S.J. Eisenreich, W.S. Douglas, and J.R. Reinfelder. 2006. *Correction to* Mercury emissions from cement-stabilized dredged material. *Environ. Sci. Technol.* 40: 409.

Gustin, M.S., Lindberg, S.E., Austin, K., Coolbaugh, M., Vette, A., and Zhang, H. 2000. Assessing the contribution of natural sources to regional atmospheric mercury budgets. *Sci. Total Environ.* 259: 61-71.

Ho, K., R. Burgess, M. Pelletier, J. Serbst, S. Ryba, M. Cantwell, A. Kuhn, and P. Raczelowski. 2000. An Overview of Toxicant Identification in Sediments and Dredged Materials. Conference on Dredge Material Management: Options and Environmental Considerations, Massachusetts Institute of Technology, Cambridge Massachusetts, USA.

Korfiatis, G.P., R.I. Hires, J.R. Reinfelder, L.A. Totten, and S.J. Eisenreich. 2003. Monitoring of PCB and Hg Air Emissions in Sites Receiving Stabilized Harbor Sediment. Report to the New Jersey Marine Sciences Consortium and New Jersey Department of Transportation Office of Maritime Resources.

Lindqvist, O., Johansson, K., Astrup, M., Anderson, A., Bringmark, L., Hovsenius, G., Hakanson, L., Iverfeldt, A., Meili, M., Timm, B. 1991. Mercury in the Swedish environment: recent research on causes consequences and corrective methods. *Water Air Soil Pollut.* 55:23-32.

Mason, R.P., Fitzgerald W.F., and Morel, F.M.M. 1994. The biogiochemical cycling of elemental mercury: anthropogenic influences. *Geochim. Cosmochim. Acta* 58: 3191-3198.

McDonough, F.M., Boehm, G.A., Douglas, W.S. (1999). Dredged material management in New Jersey: A multifaceted approach for meeting statewide dredging needs in the 21st century. *Proc., 31st Annual Dredging Seminar*. Western Dredging Association.

Miskewitz, R., R. Hires, and G. Korfiatis. 2005. Measurement of PCB Fluxes to the Atmosphere from Stabilized Dredged Material. Report to the New Jersey Marine Sciences Consortium and New Jersey Department of Transportation Office of Maritime Resources.

Nacht, D.M., Gustin, M.S., Engle, M.A., Zehner, R.E., and Giglini, A.D. 2004. Atmospheric mercury emissions and speciation at the sulphur bank mercury mine superfund site, northern California. *Environ. Sci. Technol.* 38: 1977-1983.

Reinfelder, J.R., G. Stenchikov, and L.A. Totten. 2005. Emissions and Atmospheric Transport of PCBs and Hg from Stabilized Harbor Sediments. Report to the New Jersey Marine Sciences Consortium and New Jersey Department of Transportation Office of Maritime Resources.

Stern, A.H., Korn, L.R. and Ruppel, B.E. 1996. Estimation of fish consumption and methylmercury intake in the New Jersey population. *J Exp. Analysis Environ. Epidem.* 6: 503-525.

U.S. Army Corps of Engineers. (2006). Dredged material management plan for the port of New York and New Jersey: 2005 Update. USACE – NY District, New York, NY.

Valsaraj, K.T., Choy, B., Ravikrishna, R., Reible, D.D., Thibodeaux, L.J., Price, C.B., Brannon, J.M., Myers, T.E. 1997. Air emissions from exposed contaminated sediments and dredged materials 1. Experimental data in laboratory microcosms and mathematical modeling. *J Haz. Mat.* 54:65-87.

Watras, C.J., Back, R.C., Halvorsen, S., Hudson, R.J.M., Morrison, K.A., and Wente, S.P. 1998. Bioaccumulation of mercury in pelagic freshwater food webs. *Sci. Total Environ.* 219: 183-208.