# PENOBSCOT RIVER MERCURY STUDY

## Chapter 20

# Investigation of Two Materials for Potential Application in Reducing Filter-passing Mercury in the Penobscot River

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# 1 SUMMARY

Mercury (Hg) is commonly understood to have a high affinity for particulate matter as reflected in its relatively high partition coefficients (Kds) in natural waters. For example, suspended solids (TSS) in Penobscot River water have log Kds[1] for inorganic Hg that range up to 6.4. As a possible remedy for elevated Hg concentrations in biota in the Penobscot River and estuary, the possibility of introducing new materials to this system either in surface water or applied over mud flats and marshes is being considered. The goal of such an action would be to achieve at least a reduction in surface sediment concentration (by simple dilution) but also to reduce filter-passing Hg (e.g., 0.45 micron), the most bioavailable fraction, concentrations in surface water and sediment porewater. Accordingly, materials are being sought that are available in large quantities and at low cost while offering similar or higher affinity for mercury than indigenous TSS and bed sediments. For this study two clays obtained from local quarries in Maine and a zeolite from Nevada were selected for evaluation. The clays were selected mainly because of local abundance and availability and the possibility that they might be at least as effective as river sediments in binding Hg. The zeolite was selected because it is often used in water treatment because of it sorptive properties, including for inorganic and methyl Hg (Campbell et al. 2006), and because it is available in large quantities at relatively low cost ($160/ton plus transportation). No zeolite mines were identified in New England. Zeolite was also investigated because it was not already being tested at Mendall Marsh as a marsh sediment amendment (see Chapter 19) and could be a candidate for marsh application.

The two clay samples were obtained from pits (Dysart and Folsom) near Bangor.

The Dysart clay was mainly an illite (77%), with lesser amounts of chlorite (12%), kaolinite (11%), and smectite (2%). The Folsom clay was also mainly an illite (83%) with lesser amounts of chlorite (9.1%) and kaolinite (7.9%). No mixed layer clays were detected in either sample. The zeolite sample was provided and tested in two size grades, 4-8 mesh (coarse) and 8-14 mesh (fine). The zeolite vendor reported the predominant zeolite mineral in the sample to be clinoptilolite.

Evaluation of the clays entailed determination of Kds for inorganic mercury using both Penobscot River water and brackish water (10.7 parts per thousand [ppth]) from Penobscot Bay, three clay concentrations (10, 100 and 1000 mg/L) and two Hg concentrations (22 and 75 ng/L). The reaction time was 18 hrs with a subset also run at 4 hrs to assess the kinetics of adsorption. For the zeolite samples, actual Mendall Marsh porewater was used to determine partitioning for both inorganic and methyl Hg. Zeolite was added to porewater at concentrations of 500, 2000 and 4000 mg/L and equilibrated for 18 hrs. After recovering the treated porewater by filtration (0.45 µm), the used zeolite was contacted (~4 hrs) with filtered river water to evaluate desorption. In a separate experiment, three porewater samples from different locations on Mendall Marsh were also collected and maintained in zero headspace syringes (50 mL)

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[1] Kd is defined as the ratio of solid concentration (ng/g) to aqueous conconcentration (ng/L), has units of mL/g and is typically expressed a log values.

containing 100 mg of zeolite (fine). The latter experiment was run to evaluate whether precipitation of elemental sulfur in the initial adsorption study had affected results.

The clays removed an average of 75% (66% to 84%) of added Hg in brackish water while removals in freshwater averaged 24% (0% to 51%) (Table 20-1). Depending on TSS and Hg concentration, partition coefficients varied widely. At the lowest TSS concentration tested (10 mg/L) and at the lower mercury concentration (22 ng/L) $\log K_D$s were 5.3 and 4.5 for brackish and fresh water, respectively, for both clays. $\mathrm{Log}K_D$s decreased with increasing TSS and added Hg concentration while percent removals increased in both fresh and brackish treatments. The same order of magnitude difference in $K_D$s between fresh and brackish treatments persisted at higher TSS and mercury concentrations but the $K_D$s decreased with increasing TSS and Hg concentration. The results for clays do not suggest that the materials from local clay pits would be any better at binding Hg than indigenous TSS being carried by the river.

Results for the zeolite samples (Table 20-2A and 20-2B) showed some removal (up to 52%) of inorganic Hg from native Mendall Marsh porewater but no significant removal of methyl Hg, and some minor desorption of inorganic Hg when used zeolite was exposed to river water. Porewater used in these experiments was 40% to 88% methyl Hg. The results for zeolite do not support further evaluation of this material for marsh application.

## 2 REFERENCES

Campbell, L.S., A. Chimedtsogzol, and A. Dyer. 2006. Species sensitivity of zeolite minerals for uptake of mercury solutes. Mineralogical Magazine. 70(4):361-371.

**Table 20-1: Summary of clay adsorption results.**

| Clay (mg/L) | Hg (ng/L) | Post Hg (ng/L) | %Rem | Sorbent Hg (ng) | Sorbent Hg (ug/g) | Kd (mL/g) | LogKd (mL/g) |
|---|---|---|---|---|---|---|---|
| **Dysart-Fresh** | | | | | | | |
| 10 | 22.6 | 17.1 | 24.3 | 5.5 | 0.55 | 32164 | 4.51 |
| 100 | 22.6 | 15.7 | 30.5 | 6.9 | 0.07 | 4395 | 3.64 |
| 1000 | 22.6 | 11 | 51.3 | 11.6 | 0.01 | 1055 | 3.02 |
| 10 | 71.5 | 68.2 | 4.6 | 3.3 | 0.33 | 4839 | 3.68 |
| 100 | 71.5 | 65.4 | 8.5 | 6.1 | 0.06 | 933 | 2.97 |
| 1000 | 71.5 | 34.9 | 51.2 | 36.6 | 0.04 | 1049 | 3.02 |
| **Folsom-Fresh** | | | | | | | |
| 10 | 22.6 | 17 | 24.8 | 5.6 | 0.56 | 32941 | 4.52 |
| 100 | 22.6 | 17.7 | 21.7 | 4.9 | 0.05 | 2768 | 3.44 |
| 1000 | 22.6 | 12.9 | 42.9 | 9.7 | 0.01 | 752 | 2.88 |
| 10 | 71.5 | 73.8 | -3.2 | -2.3 | -0.23 | - | - |
| 100 | 71.5 | 71 | 0.7 | 0.5 | 0.01 | 70 | 1.85 |
| 1000 | 71.5 | 49 | 31.5 | 22.5 | 0.02 | 459 | 2.66 |
| **Dysart - Brackish** | | | | | | | |
| 10 | 22.2 | 7.28 | 67.2 | 14.9 | 1.49 | 204945 | 5.31 |
| 100 | 22.2 | 5.86 | 73.6 | 16.3 | 0.16 | 27884 | 4.45 |
| 1000 | 22.2 | 5.05 | 77.3 | 17.2 | 0.02 | 3396 | 3.53 |
| 10 | 74 | 18.8 | 74.6 | 55.2 | 5.52 | 293617 | 5.47 |
| 100 | 74 | 16.1 | 78.2 | 57.9 | 0.58 | 35963 | 4.56 |
| 1000 | 74 | 11.7 | 84.2 | 62.3 | 0.06 | 5325 | 3.73 |
| **Folsom-Brackish** | | | | | | | |
| 10 | 22.2 | 7.53 | 66.1 | 14.7 | 1.47 | 194821 | 5.29 |
| 100 | 22.2 | 6.4 | 71.2 | 15.8 | 0.16 | 24688 | 4.39 |
| 1000 | 22.2 | 5.73 | 74.2 | 16.5 | 0.02 | 2874 | 3.46 |
| 10 | 74 | 17.6 | 76.2 | 56.4 | 5.64 | 320455 | 5.51 |
| 100 | 74 | 17.2 | 76.8 | 56.8 | 0.57 | 33023 | 4.52 |
| 1000 | 74 | 13 | 82.4 | 61.0 | 0.06 | 4692 | 3.67 |

**Table 20-2A: Summary of zeolite adsorption results.**

**Flask Isotherm Study**

**Run in 1000 mL teflon bottles with 0, 0.5, 2 and 4 g/L**

| Zeolite (g) | Pore water Total Hg (ng/L) | Total Hg (ng/L) | Desorbtion total Hg (ng/L) | Inorganic Hg (ng/L) | Inorganic Hg %Remaining | Hg Mass (ng) | Solid (ng/g) | $LogK_D$ |
|---|---|---|---|---|---|---|---|---|
| **Total Hg - Coarse** | | | | | | | | |
| 0 | 18.7 | | 1.37/2.07 | 7.5 | | | | |
| 0.5 | 18.7 | 14.8 | 3.37 | 3.6 | 52 | 3.9 | 7.8 | 3.34 |
| 2 | 18.7 | 16.2 | 3.07 | 5.4 | 28 | 2.1 | 1.05 | 2.29 |
| 4 | 18.7 | 15.7 | 2.95 | 4.6 | 39 | 2.9 | 0.725 | 2.20 |
| **Total Hg - Fine** | | | | | | | | |
| 0.5 | 18.7 | 14.5 | 2.54 | 4.1 | 45 | 3.4 | 6.8 | 3.22 |
| 2 | 18.7 | 14 | 2.75 | 3.6 | 52 | 3.9 | 1.95 | 2.73 |
| 4 | 18.7 | 15.3 | 2.88 | 6.5 | 13 | 0.96 | 0.24 | 1.56 |
| River $H_2O$ (ng/L) for Desorb | | | 2.20 | | | | | |
| **Methyl Hg - Coarse** | | | | | | | | |
| 0 | 11.2 | - | 0.612/0.426 | | - | | | |
| 0.5 | 11.2 | 11.2 | 0.936 | | 0.0 | 0 | 0 | - |
| 2 | 11.2 | 10.8 | 1.17 | | 3.6 | 0.40 | 0.2 | 1.27 |
| 4 | 11.2 | 11.1 | 0.904 | | 0.9 | 0.10 | 0.025 | 0.35 |
| **Methyl Hg -Fine** | | | | | | | | |
| 0.5 | 11.2 | 10.4 | 0.800 | | 7.1 | 0.80 | 1.6 | 2.19 |
| 2 | 11.2 | 10.4 | 0.880 | | 7.1 | 0.40 | 0.2 | 1.28 |
| 4 | 11.2 | 8.76 | 0.858 | | 21.8 | 0.10 | 0.025 | 0.46 |
| River $H_2O$ (ng/L) for Desorb | | | 0.132 | | | | | |

**Table 20-2B: Summary of zeolite adsorption results.**

**Anoxic study**

**Run in 50 mL syringes with 0.1 grams of zeolite**

**Total Hg**

| | Control (ng/L) | Treated (ng/L) | Inorg Hg (ng/L) | Inorg Hg %Rem | Hg Mass (ng) | Solid (ng/g) | LogKd |
|---|---|---|---|---|---|---|---|
| PW1 | 7.8 | 9 | | - | - | - | - |
| PW2 | 14.3 | 9.83 | 2.08 | 24.5 | 0.104 | 1.04 | 2.70 |
| PW3 | 18.2 | 18.3 | | - | - | - | - |
| **Methyl Hg** | | | | | | | |
| PW1 | 3.89 | 3.19 | | 18.0 | 0.035 | 0.35 | 2.04 |
| PW2 | 5.8 | 3.41 | | 41.2 | 0.120 | 1.20 | 2.54 |
| PW3 | 16.1 | 12.5 | | 22.4 | 0.18 | 1.8 | 2.16 |