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Mercury contaminated sediment sites—An evaluation of remedial options

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ABSTRACT

Mercury (Hg) is a naturally-occurring element that is ubiquitous in the aquatic environment. Though efforts have been made in recent years to decrease Hg emissions, historically-emitted Hg can be retained in the sediments of aquatic bodies where they may be slowly converted to methylmercury (MeHg). Consequently, Hg in historically-contaminated sediments can result in high levels of significant exposure for aquatic species, wildlife and human populations consuming fish. Even if source control of contaminated wastewater is achievable, it may take a very long time, perhaps decades, for Hg-contaminated aquatic systems to reach relatively safe Hg levels in both water and surface sediment naturally. It may take even longer if Hg is present at higher concentration levels in deep sediment. Hg contaminated sediment results from previous releases or ongoing contributions from sources that are difficult to identify. Due to human activities or physical, chemical, or biological processes (e.g. hydrodynamic flows, bioturbation, molecular diffusion, and chemical transformation), the buried Hg can be remobilized into the overlying water. Hg speciation in the water column and sediments critically affect the reactivity (i.e. conversion of inorganic Hg(II) to MeHg), transport, and its exposure to living organisms. Also, geochemical conditions affect the activity of methylating bacteria and its availability for methylation. This review paper discusses remedial considerations (e.g. key chemical factors in fate and transport of Hg, source characterization and control, environmental management procedures, remediation options, modeling tools) and includes practical case studies for cleaning up Hg-contaminated sediment sites.

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1. Introduction

Mercury accumulates in sediment globally from many physical, chemical, biological, geological and anthropogenic environmental processes (U.S.EPA, 1997, 2006; Benoit et al., 1999b; Braga et al., 2000; Hylander et al., 2000; Ullrich et al., 2001; Huibregtse, 2006; Sunderland et al., 2006; Swain et al., 2007; UNEP, 2011). Direct (point source) Hg contamination is usually the result from abandoned Hg mines, gold-mining activities (Ebinghaus et al., 1998; Meech et al., 1998; Veiga and Meech, 1999; Telmer and Veiga, 2009; Cordy et al., 2011; Drace et al., 2012; Krisnayanti et al., 2012), ore refining, and products and processes such as recycled mercury processing or the chlor-alkali industry (Randall et al., 2006; Ullrich et al., 2007; Reis et al., 2009; Gluszcz et al., 2012; Ilyushchenko et al., 2012). With artisanal and small scale gold mining, Telmer and Veiga (2009) estimates that approximately 1000 metric tons/yr of Hg was released from at least 70 countries. Approximately, 350 metric tons/yr of this amount is directly emitted to the atmosphere while the remainder, 650 metric tons/yr, is released into the hydrosphere (i.e. rivers, lakes, soils, tailings). Indirect (non-point source) Hg contamination is largely attributed to atmospheric deposition (wet and dry) originating from coal-fired power plants. Global mercury emissions from coal-fired power plants were estimated at approximately 850 metric tons/yr (Pirrone et al., 2010). Other indirect sources to the aquatic environment can be attributed to runoff to water bodies or leaching from groundwater flows in the upper soil layers.

At large contaminated sediment sites, engineers and scientists face many challenges primarily due to the large volumes of sediment that are typically involved. Usually, the remediation timeframes and spatial scales are in many ways unprecedented. The complexities and high costs associated with characterization and cleanup are magnified by evolving regulatory requirements and the difficulties inherent in tracking the contaminants in aquatic environments. Remedial strategies often require unexpected adjustments in response to new knowledge about site conditions or advances in technology (such as improved dredge or cap design or in situ sorption materials and treatments). Regulators and engineers adapt continuously to evolving conditions and environmental responses. Depending on site specific conditions,

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effective management of Hg contaminated sites includes more adaptive site investigation, remedy selection, and remedy implementation. In a remedial investigation and screening of potential alternatives, practitioners may consider various approaches including: (a) dredging and excavation with sediment dewatering and handling, (b) sediment treatment of dredged materials by physical, chemical and biological processes, (c) in-situ/ex-situ subaqueous capping in combination with dredging), (d) in-situ/ex-situ capping treatments that contain contaminants by chemical and biological processes, (e) containment in contained disposal facilities (CDFs), contained aquatic disposal (CAD), and landfills, (f) monitored natural recovery (MNR), (g) phytoremediation and (h) combination of above mentioned options. Hg contaminated sites sometimes implement a suite of remedial approaches to clean-up the site. For example, at the Lavaca Bay Point Comfort site (TX, USA), Alcoa spent approximately $110 million to implement several remedial options (i.e. dredging, capping, MNR, disposal in a CDF, long-term monitoring) in and around the bay (U.S.EPA, 2012).

There are several U.S. agencies (i.e. U.S. Army Corps of Engineers (USACE), National Oceanic and Atmospheric Administration (NOAA), U.S. Geological Survey (USGS), and the Department of the Navy) that manage contaminated sediment programs including Hg contaminated sediments sites. U.S. EPA's Great Lakes National Program Office estimates that 76 million cubic yards of contaminated sediments in the Great Lakes require remediation at an approximate cost of $1.6 to $4.4 billion (U.S.EPA, 2006). The Department of the Navy has estimated that there are more than 200 contaminated sediment sites which they manage with a projected remediation cost to cleanup of $1.3 billion dollars (Blake et al., 2007). Although the U.S. EPA has historically emphasized that no presumptive remedy exists for sediments, most removal actions have included dredging (e.g. 56 of the 63 sediment sites in 2006) (Huibregtse, 2006; U.S.EPA, 2006). However, remedial actions recently have included reactive thin-layer capping, phytoremediation, and other remedial alternatives to reduce the resuspension and mobility of contaminants, carbon footprint, and other factors. Moreover, selection of remedial options is dependent on site-specific conditions that constitute acceptable levels of effectiveness and performance.

In Hg contaminated site cleanup, most remedial technologies focus on highly contaminated areas and are not suitable for remediating vast, diffuse, Hg contaminants at low concentrations. Speciation of Hg is an important consideration that concerns the identification and quantification of specific chemical forms of Hg and is a critical determinant of its mobility, reactivity, and potential bioavailability in the impacted sediment-water systems. Since each remedial action can result in a change in the physical, chemical and biological conditions of the sediment, it is expected that the speciation and transport properties of Hg might change as the result of implementing a remedial action. However, the effectiveness of many remediation practices and long-term reliability has not been adequately assessed (Degetto et al., 1997).

Fish advisories on contaminated water bodies are plentiful in the U.S. because of the inorganic Hg(II) that is converted to MeHg and thus, moves up the food chain. In the U.S. fish advisories are due to five (5) bioaccumulative chemical contaminants: mercury, polychlorinated biphenyls (PCBs), chlordane, dioxins, and dichlorodiphenyltrichloroethane (DDT). In 2010, the EPA reported more than 4598 fish advisories with 81% due to Hg (U.S.EPA, 2011). The accumulation of Hg in the food chain depends primarily on the concentration of MeHg, rather than total Hg, in water. It has been reported in the literature that only a minor fraction of Hg in natural water is in the form of MeHg; however, MeHg concentrations generally in surface water are extremely low, near the detection limit of the currently available techniques (<50 femto-molar)(Kraepiel et al., 2003). To protect aquatic life, a scientific benchmark or reference point called the sediment quality guidelines (SQG) was developed (U.S.EPA, 1989; Long and Morgan, 1990; Coates and Delfino, 1993; MacDonald, 1994; Chapman, 1995; Long et al., 1995, 1998a, 1998b; Carr et al., 1996; Smith et al., 1996; Long and MacDonald, 1998; MacDonald et al., 2000; Anderson et al., 2001; Batley et al., 2002; Canadian Council of Ministers of the Environment (CCME), 2003; O'Connor, 2004; McCready et al., 2006a, 2006b, 2006c; Environment Canada, 2007). SQGs attempt to foresee and assess the potential for observing adverse biological effects in aquatic systems for chemical contaminants (i.e. metals and metalloids, organic compounds, polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides, and others).

NOAA annually collects and analyzes sediment samples from sites located in coastal marine and estuarine environments throughout the U.S. They evaluated a wide variety of marine sediment toxicity studies that were conducted in laboratories and in the field for the effects of sediment concentrations on benthic organisms. They established effects range-low (ERL) and effects range-medium (ERM) concentrations for each constituent evaluated. ERL and ERM values are those concentrations above which adverse biological effects were seen in 10% and 50%, respectively. ERL and ERM values together define the concentration ranges that were (1) rarely and (2) frequently associated with adverse effects. Long et al. (1995) reported ERL and ERM for total Hg as 0.15 mg per kilogram (mg/kg) and 0.71 mg/kg dry weight basis, respectively. ERL is not a threshold below which sediment toxicity is impossible and above which it is likely. Rather, an ERL is simply a low point on a continuum of bulk chemical concentrations in sediment that roughly relate to sediment toxicity (Beckvar et al., 1996; O'Connor, 2004). Another criterion limit is the apparent effects threshold (AET) values derived from a correlation of the weight of evidence from multiple matched chemical and biological effect data sets (laboratory toxicity testing on field sediment samples). The AET value for a particular contaminant is defined as the sediment concentration above which an adverse biological effect is always statistically observed (U.S.EPA, 1989). For example, the ERL for Hg is 0.15 mg/kg of sediments, ERM is 0.71 mg/kg, and the AET is 2.1 mg/kg (Baumgarten and Panel, 2001) in Alcoa's Lavaca Bay Point Comfort site, Texas USA. For PAHs, the ERL and ERM in sediments are 4.02 mg/kg and 44.79 mg/kg, respectively.

Similar criteria were adopted by Canada to protect aquatic life. The Canadian Council of Ministers of the Environment (CCME) derived two reference values for some 30 substances in freshwater and marine sediments: a threshold effect level (TEL) and a probable effect level (PEL). These two values were adopted for the assessment of sediment quality in Quebec and were developed using a nationally-approved protocol (Canadian Council of Ministers of the Environment (CCME), 2003). The Hg TEL and PEL values for freshwater sediment are 0.17 mg/kg and 0.49 mg/kg, respectively; and the same for marine sediments are 0.13 mg/kg and 0.70 mg/kg, respectively (Smith et al., 1996; Canadian Council of Ministers of the Environment (CCME), 2003; Environment Canada, 2007).

Massachusetts Department of Environmental Protection (MDEP) assessed the screening criteria by adopting consensus-based threshold effect concentrations (TECs) for the 28 chemicals, including Hg, to determine risk to benthic organisms in freshwater sediment (MacDonald et al., 2000; Massachusetts Department of Environmental Protection (MDEP), 2002). The TECs are intended to identify contaminant concentrations below which harmful effects on sediment-dwelling organisms are not expected. These concentrations may not necessarily be protective of higher level organisms exposed to bioaccumulating chemicals. These consensus-based TEC values were chosen because they incorporate a large data set,