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The assessment and remediation of mercury contaminated sites: a review of current approaches.

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Abstract

Remediation of mercury (Hg) contaminated sites has long relied on traditional approaches, such as removal and containment/capping. Here we review contemporary practices in the assessment and remediation of industrial-scale Hg contaminated sites and discuss recent advances. Significant improvements have been made in site assessment, including the use of XRF to rapidly identify the spatial extent of contamination, Hg stable isotope fractionation to identify sources and transformation processes, and solid-phase characterization (XAFS) to evaluate Hg forms. The understanding of Hg bioavailability for methylation has been improved by methods such as sequential chemical extractions and porewater measurements, including the use of diffuse gradient in thin-film (DGT) samplers. These approaches have shown varying success in identifying bioavailable Hg fractions and further study and field applications are needed. The downstream accumulation of methylmercury (MeHg) in biota is a concern at many contaminated sites. Identifying the variables limiting/controlling MeHg production—such as bioavailable inorganic Hg, organic carbon, and/or terminal electron acceptors (e.g. sulfate, iron) is critical. Mercury can be released from contaminated sites to the air and water, both of which are influenced by meteorological and hydrological conditions. Mercury mobilized from contaminated sites is predominantly bound to particles, highly correlated with total sediment solids (TSS) and, elevated during stormflow. Remediation techniques to address Hg contamination can include the removal or containment of Hg contaminated materials, the application of amendments to reduce mobility and bioavailability, landscape/waterbody manipulations to reduce MeHg production, and food web manipulations through stocking or extirpation to reduce MeHg accumulated in desired species.

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These approaches often rely on knowledge of the Hg forms/speciation at the site, and utilize physical, chemical, thermal and biological methods to achieve remediation goals. Overall, the complexity of Hg cycling allows for many different opportunities to reduce/mitigate impacts, which creates flexibility in determining suitable and logistically feasible remedies.

1. Introduction

Human use of mercury (Hg) has resulted in local hot spots of contamination, as well as global dispersal through the atmosphere. Examples of common industrial-scale Hg contaminated sites include abandoned Hg mines, gold and silver mines where Hg was used for amalgamation and/or co-occurs in the orebody, Hg recycling facilities, and chemical production facilities for bleach, plastics, electronics and lighting. In areas primarily impacted by global-pool atmospheric deposition, typical background soil Hg concentrations are 0.01 to 0.3 $mgkg^{-1}$(Agnan et al., 2016; Obrist et al., 2016); whereas Hg contaminated sites often have soil concentrations 2- to 4-orders of magnitude higher. The objective of this paper is to provide a review of contemporary practices and recent advances in the assessment and remediation of industrial-scale contaminated sites, as well as to synthesize information on Hg cycling (e.g. fluxes to water and air) at contaminated sites.

Contaminated site boundaries and clean-up goals are often based on whether concentrations are above or below applicable regulatory/criteria levels, which vary within and between nations and depend on the end-points of concern. Examples of criteria concentrations are provided in the Supporting Information (SI). For soil, sediment, water, and air, the criteria concentrations are typically well above proximate background concentrations in landscapes not displaying natural enrichment from the local geology. In addition, many waterbodies have Hg levels in fish above criteria concentrations (e.g. 0.3 $\mu g\ g^{-1}$ in the US) due to global-pool Hg deposition (Depew et al., 2013; Eagles-Smith et al., 2016). The potential for elevated concentrations that are not directly associated with releases from a specific industrial activity adds complexity to contaminated site management.

Cumulatively, Hg contaminated sites are estimated to have released ˜1000 Gg of Hg to terrestrial and aquatic systems (Streets et al., 2017). Ongoing releases to water have been estimated between 67 to 165 Mg/year, and releases to air from surface volatilization are within this same range around 70–95 Mg/year (Kocman et al., 2013). The majority (97%) of current releases originate from historical Hg and gold mining activities, with the remaining amount originating from metal production facilities, chlor-alkali sites, and other industrial sources (Kocman et al., 2017). Addressing releases of Hg from contaminated sites is one of the key requirements of the Minamata Convention on Mercury, which is a global treaty that has currently been ratified by 115 parties.

At sites predominantly impacted by atmospherically deposited Hg, the main toxicological concern for humans and wildlife is exposure to methylmercury (MeHg). MeHg is an organic form of Hg that is more toxic than inorganic Hg, and efficiently bioaccumulates in organisms, and is biomagnified in food webs. Exposure to MeHg in fish is often the main concern associated with Hg contaminated sites. However, at some sites inorganic mercury (Hg_i) concentrations in abiotic matrixes (soil, air, water) may be elevated to the point of direct exposure concern. Therefore, exposure pathways at Hg contaminated sites include bioaccumulated MeHg, but may also include inhalation and incidental ingestion of Hg_i.

2. Mercury contaminated site assessment

Contaminated site assessments typically occur prior to clean-up to identify: 1) the geographic distribution and speciation of the elevated Hg; 2) the major pathways of release from the site; 3) zones of methylation and the associated controlling variables; and 4) human and ecological Hg exposure and risk.

2.1. Determining spatial variability and the geographic extent of Hg contamination

Identifying source areas within a contaminated site and determining the geographic extent of contamination are a key step in the assessment process. The extent of contamination may extend for hundreds of kilometers surrounding and downstream of an industrial facility or mine site(Eckley et al., 2015a; Kocman et al., 2017; Merritt and Amirbahman, 2007). From a regulatory perspective, the boundaries of a site are determined by comparisons to site-specific criteria concentrations which can vary between governmental jurisdictions and can also vary depending on exposure concerns (e.g. ingestion of Hg_i versus areas where Hg may become methylated).

Concentrations of Hg at contaminated sites can be highly heterogenous. Depending on the site assessment objective, sampling approaches can be designed to identify and understand the variability and/or to create a representative average concentration from an area. Incremental sampling methods (ISM) are one option to obtain a site-wide average concentration with a limited number of samples. ISM provides an average concentration by collecting numerous samples from a defined area (e.g. 30–100 samples) that are systematically composited prior to analysis(ITRC, 2012). While average concentrations may be useful for some management purposes, they cannot define the boundary of site sources (e.g., piles of mining waste), and there are instances where understanding the site heterogeneity is preferred. For example, correlations with natural organic matter (NOM), grain size, and other metals have been used to help identify site boundaries and sources of contamination. Fine-grained soils/sediments often are associated with higher Hg concentrations; however, the relationship with NOM can be more complex and variable. On one hand Hg sorption to sulfur-based functional groups on NOM can result in a positive relationship, while lower NOM due to site contamination and/or Hg bound to minerals can result in a negative relationship (Eckley et al., 2015a; Merritt and Amirbahman, 2007).

2.1.1. Mercury analysis using XRF—Portable X-Ray Fluorescence Spectrometers (XRF) provide a field-portable method to measure total-Hg (THg) and other metal(loid) concentrations at contaminated sites(Bernaus et al., 2006; Guedron et al., 2009; McComb et al., 2014; Miller, 2013). XRF analysis is a non-destructive method that utilizes a radiation source to measure fluorescence wavelengths. XRFs provide concentrations in the field within seconds to minutes that allows for the collection of numerous measurements in a short period of time. The high density of data results in reduced uncertainty associated with spatial heterogeneity and increased representativeness. It also permits adaptive investigation and remedial strategies, because decisions can be made based on near-real-time field data.

XRF measurements are most useful at highly contaminated sites because reliable measurements can typically not be made below 20mgkg^{-1}. The analyzers tend towards false positives/overpredictions at lower concentrations, so they can be used to provide a conservative estimate during site investigations. Sampling procedures that can optimize XRF analysis are provided in the SI.

Studies from abandoned Hg mines have shown strong correlations between XRF and laboratory-based analysis (r^2-value's >0.80; see example in Fig.S1 in the SI) and insignificant differences between precision estimates of duplicate/triplicate measurements (Brent et al., 2017). Differences in analytical results when comparing XRF and laboratory data may originate from sample heterogeneity (that can be addressed with XRF measurement replication and averaging). In addition, differences may occur because the XRF quantifies the total element content whereas some fix-laboratory techniques using chemical extractions may result in the underprediction of Hg in mineralized forms due to incomplete digestion during laboratory analysis(Bloom, 2003).

The presence of elemental Hg (Hg^0) in soils/sediments can introduce extreme heterogeneity in Hg concentrations and can result in disagreements between XRF and laboratory analysis (Miller et al., 2013). Additional research is needed to determine if this can be addressed by sample preparation and analysis procedures. Types of sites where there may be significant fractions of Hg^0include chlor-alkali facilities, Hg ore processing areas, and gold/silver mines that utilized Hg amalgamation (Hunerlach, 2003; Huremovic, 2017).

2.2. Determining the source of mercury contamination using stable isotope fractionation

Regulatory criteria concentrations for direct exposure to THg in terrestrial landscapes are often relatively high (e.g. ≥23 mgkg^{-1}) and the source of the Hg pollution is typically assumed to be directly related to the industrial/anthropogenic activity that occurred at the site. However, downstream or downwind of contaminated sites the source of Hg pollution in soil/sediment, water, and biota can be more difficult to discern, especially when there are multiple potential sources. As such, techniques to track different sources of Hg pollution in the environment is an area of much interest for scientific and regulatory communities.

The application of Hg stable isotope analysis to contaminated systems has provided additional information regarding Hg sources and cycling that cannot be determined using concentration measurements (Blum et al., 2014; Yin et al., 2014). Mercury contains seven natural stable isotopes (listed in order of abundance: ^{202}Hg, ^{200}Hg, ^{199}Hg, ^{201}Hg, ^{198}Hg, ^{204}Hg, ^{196}Hg). With the exception of Hg^{196} that has very low abundance (0.15%) and Hg^{198} that is often used as the denominator for calculating the isotopic composition (delta value), the other five isotopes can be used to identify different sources and processes. Mercury isotopes undergo the process of mass dependent fractionation (MDF), which partitions isotopes based on mass during kinetic and equilibrium reactions (Bergquist and Blum, 2009), and is commonly represented as δ^{202}Hg because it has the highest abundance(Blum and Bergquist, 2007). Mercury is also subject to mass independent fractionation (MIF) that is created by the magnetic isotope and nuclear volume effects (Bergquist and Blum, 2007; Zheng and Hintelmann, 2010a; Zheng and Hintelmann, 2010b). MIF is commonly observed in the odd-isotopes ($^{199-}$Hg and ^{201}Hg) due to photochemical reactions (Bergquist and Blum, 2007; Zheng and Hintelmann, 2010a), but has also been observed in atmospheric pools of even-isotopes (^{200}Hg and ^{204}Hg), though the exact mechanism is unknown (Chen et al., 2012; Fu et al., 2014; Fu et al., 2016; Gratz et al., 2010; Sherman et al., 2015; Sun et al., 2016; Yu et al., 2016). The versatility of Hg isotopes and the wide range of reactions that can be examined make these promising tracers to identify different sources of Hg in the environment.

Studies have successfully used Hg isotopes to track industrial Hg sources in aquatic ecosystems (Donovan et al., 2013; Feng et al., 2010; Foucher et al., 2013; Foucher et al., 2009; Gehrke et al., 2011a; Wiederhold et al., 2013; Yin et al., 2013b). Mercury can be imprinted with distinct isotopic signatures from different processes, such as the utilization of Hg catalysts, which are preserved in the concentrated Hg waste products or discharges. The source signal imprinted on this industrially-derived Hg usually greatly outweighs additional environmental processing (e.g. reduction or methylation) that only influence a small percentage of the total Hg present, allowing the source Hg to be tracked within a system. Initial assessment of a contaminated site requires identification of isotopic end members, which often include samples to represent the reference isotopic composition of a region, absent of direct industrial Hg discharges, and samples from the original source of contamination (e.g. mining site or chlor-alkali plant). If the isotopic signature and concentration of the Hg source is distinct enough from the environmental background then mass balance approaches can be utilized to estimate the contribution of different Hg sources, such as deposition versus point source (Foucher et al., 2009; Liu et al., 2011; Yin et al., 2018) (Fig. 1a). Changes in isotopic composition have also been used in sediment cores to identify temporal changes in industrial effluents (Ma et al., 2013; Sonke et al., 2010; Yin et al., 2016a). As studies continue to utilize these tracers, a foundation of isotopic values for different industries and matrices will become available for comparison, aiding in the interpretation of new sites.

While Hg isotopes can be leveraged to track Hg in the environment (Wiederhold, 2015), caveats exist with the application of isotope tracersin the presence ofmultipleHg discharges within a single system (Bartov et al., 2012; Liu et al., 2011). Despite this challenge, Hg isotopic compositions can be distinguished between industry types in sediments, for instance coal ash spills versus metallic Hg usage (Fig. 1b). While differences between some Hg signatures are apparent, others become more difficult to tease apart using just the δ^{202}Hg signature (Fig. 1), for instance the difference between coal ash and background signatures of depositional Hg in reference sites. New techniques leveraging different isotopic tracers (Lepak et al., 2015; Sherman et al., 2015) and matrices (Demers et al., 2018; Washburn et al., 2017; Woerndle et al., 2018) are evolvingto tackle more complex source profiles. Application of multiple Hg isotopes, including Δ^{200}Hg, in sediments have proven useful in estimating the loading of atmospheric, watershed, and industrial Hg sources (Lepak et al., 2015; Yin et al., 2018). Additionally, pairing of other isotope systems such as Pb and Sr to Hg isotope studies have yielded helpful information for source attribution (Mil-Homens et al., 2013; Sherman et al., 2015). Measurements of suspended particulate matter, pore and surface water have recently shown the nuance associated with the evolution of Hg isotopic signatures in aquatic systems. Isotopic shifts between particulate and aqueous phases (Washburn et al., 2017) of Hg as well as spatial variation (Washburn et al., 2018) within these studies clearly show the impact of transport and partitioning on the isotopic compostion of Hg from point sources, which is not seen in sediment measurements. Additionally, aqueous phase reactions, such as mircobial and photochemicaldegradation, can transform the isotopic signatures of point source Hg (Demers et al., 2018; Donovan et al., 2016), and are vital to consider when applying isotope tracers in lower concentration matrices further removed from the original source.

Bioaccumulation of Hg within contaminated systems has also been explored with the Hg isotope technique. These investigations have shown systematic isotopic offset between fish tissue Hg and the total Hg present in sediments within contaminated systems (Gehrke et al., 2011b; Kwon et al., 2014) complicating source appropriation in higher trophic levels. While fractionation during biological uptake and internal cycling of Hg cannot be discounted (Kwon et al., 2013; Wang et al., 2013), changes to the source Hg could play a major role as well (Demers et al., 2018; Donovan et al., 2016; Washburn et al., 2017). An additional factor to consider is that all isotopic measurements being made currently in the literature relate to the total Hg isotopic composition whereas in the food web MeHg is the predominant form (Bloom, 1992; Lescord et al., 2018). The measurement of MeHg isotopic compositions in sediment (Janssen et al., 2015; Qin et al., 2018) and biological tissue (Bouchet et al., 2018; Masbou et al., 2013)have displayed differences between the total isotopic measurement (i.e. measurement of the total Hg present) and species-specific measurements of MeHg. Furthermore, sequential extraction techniques have shown isotopic differences between labile, organically- bound, and mineral phases of Hg in sediments (Grigg et al., 2018) and soils (Yin et al., 2013a), indicating the pools of inorganic Hg available for methylation may also diverge from the total isotopic measurements. Further research is needed to definitively track Hg sources through the bioaccumulation process and understand the connection between matrices such as sediments and higher trophic level biota. Despite all of these potential fractionation processes during bioaccumulation, recent research has shown that isotopic compositions in fish tissue are predominantly tied to factors such as land use and proximity to industrial Hg sources(Janssen et al., 2019). The preservation of isotopic signatures in biota potentially allows for the identification of bioaccumulated Hg sources based on comparison of fish populations from impacted and unimpacted sites, rather than previous attempts of comparing sediments to fish. Overall the application of Hg stable isotopes has proved useful in source attribution and has provided insights to Hg cycling and bioaccumulation.. With further application, isotope techniques may prove vital to policy and remedial decisions at impacted sites by providing quantitative information on the relative contributions and spatial extent of Hg contamination from specific industrial soruces.

2.3. Mercury speciation, fractions and bioavailability

While many regulatory criteria are based on THg concentrations, it is often important to also measure MeHg concentrations during site assessments because MeHg accumulated in fish and wildlife tissue is often the largest driver of human and ecological health risk. Pre- and post-remediation site monitoring for changes in MeHg and %MeHg of THg in water, sediments, and biota can provide a useful measure of the project success (Matthews et al., 2013).

In addition to THg and MeHg measurements, which are relatively well established at many contaminated sites, it can also be useful to better understand form and speciation of Hg_i, which can impact Hg mobility, toxicity, and availability for methylation. Inorganic Hg (Hg_i) speciation typically consists of Hg^0 and Hg^{2+}, with the latter occurring as various compounds such as Hg bound to NOM, sulfur-based minerals, or chloride (see Table S1 for additional examples). Differences in Hg_i have been incorporated into regulatory criteria/ toxicity values, and have been utilized to focus remediation efforts on the more available and mobile Hg forms(California Department of Conservation, 2003; Ecology and Environment, 2015; US EPA, 2018a). For example, mineral-bound and strongly-complexed Hg (like sulfide and iron-oxyhydroxide complexes) have relatively low bioavailability, are less reactive, and tend to be the dominant forms at contaminated sites, specifically mining sites (Kim et al., 2000). However, even though bioavailable/mobile fraction may be a relatively small percent of the total, their absolute concentration may be significantly elevated above background (Marvin-DiPasquale et al., 2009). While some general predictions can be made about the Hg forms at a site based on the type of industrial activity and equilibrium modeling(Jiang et al., 2018), it is useful to directly quantify different Hg_i forms because of their role in effecting bioavailability, reactivity and mobility in the environment. Solid-phase characterization, chemical extractions, thermal programmed decomposition, and porewater measurements can be used to identify these subfractions of Hg.

2.3.1. Solid-phase mercury speciation—Solid-phase Hg speciation can help with predictions of the mobilization, transformation and bioaccumulation of Hg. One solid-phase Hg characterization technique is X-ray absorption fine structure (XAFS) spectroscopy(Andrews, 2006; Skyllberg, 2010). XAFS is a non-destructive element specific technique; the spectra are especially sensitive to the formal oxidation state, coordination chemistry/environment, interatomic distances, and coordination number of atoms surrounding the element of interest (Bunker, 2010; Teo, 1986).

One drawback of spectroscopic techniques is that a concentration of ~100 $mgkg^{-1}$ is often needed to obtain a good quality signal (Kim et al., 2004), though recent studies using the near edge portion of the spectra have collected data at concentrations as low as 1 $mgkg^{-1}$(Chiarantini et al., 2017). While concentrations in this range are commonly encountered at contaminated sites, downstream concentrations are often below the levels needed for detection. Micro-focused techniques may be used to study Hg at lower concentrations (e.g. 0.1 $mgkg^{-1}$) by using a narrowly focused beam, but this may miss compounds that are more widely dispersed in a sample(Bernaus et al., 2006; Santoro et al., 2010).

XAFS research at abandoned mine sites has shown that metacinnabar (β-HgS)and cinnabar(α-HgS) are the two most commonly identified Hg species found in calcined waste rock (Esbri et al., 2010; Kim et al., 2000; Lowry et al., 2004; Rimondi et al., 2014; Yin et al., 2016b). In addition, XAFS also identified the presence of less abundant components that include more soluble phases of Hg such as schuetteite ($Hg_3(SO_4)O_2$), Hg chlorides ($HgCl_2$ and Hg_2Cl_2) montroydite (HgO), $HgSO_4$, and Hg^0(Bernaus et al., 2005; Esbri et al., 2010; Kim et al., 2000; Lowry et al., 2004; Rimondi et al., 2014; Yin et al., 2016b).

XAFS research has also identified that geology as well as industrial processing (e.g. ore roasting) both influence the speciation of Hg calcined mine wastes (Esbri et al., 2010; Kim et al., 2004). For example, the impact of geological setting on Hg speciation has shown that Hg from hot spring deposits has a greater abundance of Hg-chloride phases compared to silica carbonate Hg deposits (Kim et al., 2004). In terms of industrial processes, the roasting of the ore resulted in the transformation of cinnabar to metacinnabar, which is the primary phase of particulate bound Hg transported downstream from mine sites(Kim et al., 2004; Lowry et al., 2004). Lower Hg-ore roasting temperatures result in an increase in more soluble Hg-chloride phases present in the tailings, which were more leachable relative to other Hg forms (Esbri et al., 2010). These results are important in identifying the relative solubility and bioavailability of Hg once it is mobilized downstream from a contaminated site.

Studies conducted at gold mines and chlor-alkali facilities that used Hg^0 during processing have shown Hg^0 is transformed over time to more recalcitrant forms such as cinnabar, metacinnabar, schuetteite, and cordierite ($Hg_3S_2Cl_2$)(Kim et al., 2004; Santoro et al., 2010; Terzano et al., 2010). While these tend to be the dominate phases at these types of contaminated sites, significant amounts of more soluble Hg phases such as including HgO and $HgSO_4$ have also been observed(Bernaus et al., 2006).

Several studies have shown that Hg forms/speciation can change in response to soil properties and redox conditions in ways that impacts its mobility and bioavailability. For example, lab-based experiments have shown that additions of thiol-bound Hg to soils can rapidly polymerize to form Hg sulfide clusters, which have reduced mobility and bioavailability (Manceau et al., 2015). A different study showed that under reducing conditions metacinnabar can become mobilized as aqueous Hg^0(Poulin et al., 2016).

2.3.2. Understanding mercury species through chemical extractions and thermal decomposition—

While techniques like XAFS identify the species of Hg present in a source, chemical extraction and thermal decomposition techniques categorize Hg into behavioral classes that inform our understanding of bioavailability. In general, these methods provide a measure of Hg “extractability” using a series leaching or heating treatments. The specific extraction solutions and temperatures are often proxies for anticipated environmental and biological conditions. Hg chemical and thermal extraction measurements have been conducted as part of the assessment of many contaminated sites(Ecology and Environment, 2015; U. S. EPA, 2015; US EPA, 2017); however, there remains a lack of direct connection between these measures and MeHg production.

Extraction techniques can involve one or multiple steps to provide information on Hg forms present in a sample. Single point extractions include synthetic precipitation leach procedure (SPLP), toxicity characteristic leaching procedure (TCLP), invitro bioaccessibility (IVBA), thiol-based extractions, and reactive Hg measurements. The SPLP procedure can be customized to simulate site-specific precipitation pH levels, but a commonly applied pH level is 4.2 using nitric/sulfuric acid(Xin et al., 2006). The TCLP method simulates the chemistry of landfill leachate and uses an acetic acid solution with a pH of 4.93. The IVBA method is designed to simulate bioavailability of metals from ingestion. An extraction solution of glycine with a pH of 1.5 is used and the extraction is carried out at 37 °C to simulate stomach fluid conditions. This technique was developed and is mostly applied for lead contamination, but has also has some limited use at Hg contaminated sites (Gray et al., 2010). The thiol-based extraction and reactive Hg techniques are distinct from these other measurements in that they focus on identifying the subfractions of Hg that are available for methylating organisms and are based on glutathione-based extractions and tin-reducible fractions respectively (Marvin-DiPasquale et al., 2014; Ticknor et al., 2015).

Other chemical extraction techniques use multiple steps to estimate several biogeochemically relevant Hg fractions. A common(and commercially available) technique based on the methods described in Bloom (2003)) is often referred to as selective sequential extraction (SSE, see Table S1 in the SI). Different extraction solutions are used to estimate six Hg fractions. Fraction-0 (F-0) indicates the presence of Hg^0; fraction-1 (F-1) estimates water-soluble Hg; fraction-2 (F-2) estimates human stomach acid soluble or other acid environments; fraction 3 (F-3) estimates NOM complexed Hg; and fractions 4 and 5 (F-4, F-5) estimate mineral-bound and other strongly complexed Hg. Fractions 0–3 can be interpreted as environmentally available forms of Hg; whereas F-4 and 5 are more recalcitrant and can be considered not environmentally available. Comparisons between SSE and XAFS show good agreement between recalcitrant fractions (F-5) and cinnabar and metacinnabar, but are more divergent in identifying soluble forms (Bernaus et al., 2006; Kim et al., 2003; Terzano et al., 2010). The SSE fractions can be linked to exposure pathways with associated toxicity criteria in risk assessments (Table S2 in the SI). However, risk assessments need to consider the potential transformation between forms, particularly F-0 to F-3. SSE (as well as XAFS analysis) can be performed on sieved samples to identify how Hg speciation changes with gain size, as well as the mobility of different forms of Hg for offsite transport (Lowry et al., 2004).

Instead of chemical extractions to identify Hg fractions, thermal programmed decomposition/desorption (TPD) relies on differences in the thermal stability of specific Hg phases at different temperatures to identify solid-phase speciation (Biester and Scholz, 1997; Lopez-Anton et al., 2011; Rumayor et al., 2016; Saniewska and Beldowska, 2017; Windmoller et al., 1996; Zagury et al., 2006). This technique has been successfully used to speciate Hg compounds at several contaminated sites (Biester et al., 1999; Liu et al., 2006; Rezende et al., 2018; Zagury et al., 2006). For example, Biester et al. (1999) used TPD to show how the age of tailings piles in Slovenia impacted the Hg speciation, and Liu et al. (2006) used TPD to determine the more volatile and non-mineral components of Hg near the US Department of Energy Oak Ridge Reservation in TN, USA. One potential issue with TPD is the possibility of the desorption signal being suppressed in minor phases and overlapping desorption/decomposition signals (Rumayor et al., 2013).

Overall, information on Hg speciation and forms from chemical extractions, thermal desorption, and XAFS analysis can support contaminated site management decisions by targeting specific areas where Hg is more bioavailable and soluble (Fernandez-Martinez, 2019). Chemical extraction data obtained from tests like TCLP are routinely used to determine whether on-site or off-site disposal is needed, as well as whether repositories should be lined or un-lined. In addition, because there are large differences in the toxicity of mercuric chloride versus Hg sulfide, information on Hg forms from SSE and XAFS analysis have been used to calculate exposure risks as part of human health risk assessments(US EPA, 2017; US EPA, 2018b). While the cost of chemical extraction and solid-phase speciation analysis can be relatively large, this information has the potential to greatly reduce remediation costs if large fractions of the Hg are present in recalcitrant forms.

2.3.3. Porewater and diffuse gradient in thin-film (DGT)measurements— Instead of chemical extractions techniques, measurements of porewater provide a direct measure of the fraction of Hg in sediment that may be more available for methylation and more available to flux into the overlying water and accumulate in biota (Bloom et al., 1999; Buckman et al., 2015; Cesario et al., 2017; Covelli et al., 1999; Drott et al., 2007; Eckley et al., 2017; Turner et al., 2018). Multiple methods have been utilized to measure porewater, including piezometers, Rhizons®, centrifuged sediment, and diffuse gradient in thin-film (DGT) samples(Johnson et al., 2016; Mitchell et al., 2009; Noh et al., 2016). DGTs can also be used to help identify bioavailable fractions of Hg in surface water and uptake of Hg_i by DGTs has been shown to correlate with MeHg production (Ndu et al., 2018). Clean-up goals based on porewater concentrations need to consider that different measurements techniques may differ in how the “dissolved” phase of Hg is determined.

Porewater measurements provide unique information because the concentration of Hg in the porewater is often not proportional to the bulk sediment concentrations at contaminated sites. For example, several studies downstream of abandoned Hg mines have shown that the sediments with the highest THg concentrations had lower porewater THg concentrations because the Hg was tightly bound in the solid phase as cinnabar or other mining related forms (Covelli et al., 1999; Eckley et al., 2017; Hines et al., 2000). Distribution coefficients (K_d) are a measure of the concentration of Hg in the solid phase to the porewater phase, and are influenced by the form/speciation of Hg that is affected by the type of contaminated sites; however, they are also affected by other environmental conditions such as the organic carbon, grain size and sulfur/sulfide content of the sediment(Bailey et al., 2017; Marvin-DiPasquale et al., 2009; Schartup et al., 2014). Porewater measurements provide a direct measure of the sub-fraction of Hg that is more likely to be methylated and/or mobile; however, they can require significant additional effort in the field to collect and provide limited insights into the properties of Hg that remains associated with the solid-phase.

2.3.4. Identifying the rate limiting variables for mercury methylation—MeHg production can be impacted by many variables, including the bioavailability of Hg_i and factors that affect the abundance and activity of the microbial community capable of methylation (Marvin-DiPasquale et al., 2014). Both the availability of Hg_i and microbial community can be impacted by multiple environmental parameters, such as Hg_i speciation, the amount and quality or organic carbon, amount and speciation of sulfur compounds, and redox conditions and the associated concentrations of terminal electron acceptors (e.g. SO_4^{2-}, $Fe^{2+}Mn^{4+}$, etc) which can affect the activity of methylating organisms and competition from non-methylating organisms (Hsu-Kim et al., 2013; Vlassopoulos et al., 2018). Hydrological conditions can impact several of these variables, such as redox conditions and microbial activity (Hsu-Kim et al., 2018). The complexity of MeHg production requires extensive assessment to adequately understand the controlling variables; however, the complexity of MeHg production has the benefit of allowing site managers multiple options for reducing MeHg levels which may or may not be directly related to Hg_i source control.

Before an effective management action can be taken to reduce MeHg, there needs to be an understanding of what variables are limiting/controlling the amount of MeHg produced. This is particularly important at contaminated sites where the bulk sediment or whole water THg concentrations are elevated and less likely to be a limiting factor in the amount of MeHg produced. However, even in areas with high bulk phase THg concentrations, it is possible that the small subfraction that is bioavailable for methylation may still be a factor limiting the rate of MeHg production (Eckley et al., 2017).

An experimental approach used to identify variables limiting MeHg production involves performing factorial sediment or water incubation experiments where constituent concentrations of interest are varied (e.g. organic carbon, SO_4^{2-}, Hg_i, etc) and/or redox conditions are varied and/or different microbial communities are inhibited(Acha et al., 2012; Graham et al., 2012; Mauro et al., 2002). The effect of each of these experimental manipulations on MeHg production is monitored and can provide information on which variables/conditions have the largest impact of methylation rates. These experiments are typically performed using enriched Hg stable isotope tracers that can be used during short-terms (typically <24 hour) incubations. The added Hg_i tracer can have different bioavailability compared to the ambient Hg_i present at a contaminated site, and therefore are better at providing information about limiting variables other than the Hg_i concentration. However, correlations of the isotopic tracer methylation rate relative to the %THg/MeHg of ambient Hg can be used to provide insights into the relative bioavailability of ambient Hg in the system(Eckley et al., 2017; Lehnherr et al., 2012). An alternative to short-term Hg isotope addition incubations, longer-term mesocosm/test plot manipulation experiments (typically lasting >30 days and often occurring in the field) can be conducted to monitor ambient MeHg in response to different experimental manipulations (e.g. changes in carbon, nutrients, etc) (Jordan et al., 2019; Mitchell et al., 2008). While these experiments have the benefit of being a better surrogate for real-world conditions, they tend to be more time/resource intensive than shorter-term stable isotope methylation assays.

3. Identifying pathways of mercury release from contaminated sites.

Some Hg contaminated sites received direct Hg discharges into a receiving water body that resulted in elevated fish Hg concentrations. Examples of this include the direct releases of Hg into Minamata Bay, Japan from an acetaldehyde production facility, the Wabigoon-English River, Canada from chlor-alkali and paper production facilities, and Lake Onondaga, USA, from chlor-alkali and other chemical manufacturing. At many other Hg contaminated sites, Hg is mobilized into aquatic systems via surface runoff and groundwater transport or is released to the air via volatilization. In general, contaminated sites in temperate and humid regions have greater releases of Hg to adjoining waterways, whereas arid regions have larger fluxes to the atmosphere(Gray et al., 2002; Kocman et al., 2013).

3.1. Mercury fluxes to water from contaminated sites

The release of Hg from a contaminated terrestrial site into adjoining waterways is a major concern due to the potential for methylation and bioaccumulation in downstream aquatic food webs. Many abandoned Hg, gold and silver mine sites are located in mountainous terrain where conditions near the contaminated area are not conducive to methylation because the soils/tailings are unsaturated and the high gradient streams are well oxygenated. Furthermore, many abandoned mines lack vegetation which also contributes to low organic carbon levels and limited microbial activity relative to conditions further downstream. As such, the release of Hg to downstream waterways is a primary concern at many Hg contaminated sites.

Mercury exports in streams draining undisturbed catchments are typically less than a few $\mu g m^{-2} y^{-1}$, and runoff yields (the ratio of atmospheric deposition to Hg in stream water) are typically <0.06 (i.e. less than 6% of Hg deposited in a catchment is exported in runoff). In contrast, catchments containing a Hg contaminated site can have exports of hundreds of $\mu g m^{-2} y^{-1}$, runoff yields that can be >10largerthan undisturbed catchments(Domagalski et al., 2016; UNEP, 2013). Mobilization to streams is enhanced once contaminated materials have become saturated and overland flow erodes contaminated soils into tributaries. The source of Hg mobilized during periods of elevated discharge can be from newly eroded material from the contaminated site, but also from the re-mobilization of Hg in the downstream riverbed and river banks (Carroll et al., 2004; Kocman et al., 2011; Wang et al., 2004).

The export of Hg from contaminated sites can be highly variable, with concentrations during stormflow conditions being several times higher than during baseflow.Fig.2 shows an example from a stream flowing through an abandoned Hg mine (Black Butte mine, USA). During stormflow the whole water THg (THg-W) and dissolved THg (THg-D—<0.45μm) concentrations increased 14- and 17-fold respectively. Similar magnitudes of increases in THg-W and particulate-bound Hg (THg-P) concentrations have been observed during periods of increased discharge in other contaminated site studies, but often the changes in THg-D are smaller (Morway et al., 2017; Riscassi et al., 2016).

Because THg concentrations increase with discharge, annual loads of Hg transported from contaminated sites can be dominated by a few large, but temporally limited, storm events. For example, in the section of the South River downstream of a historical industrial Hg source, 84% of the annual Hg load was transported during a few storm events (Flanders et al., 2010). Similar results have been observed in other watersheds containing Hg contaminated site (Carroll et al., 2004; Lin et al., 2011). As such, when determining annual Hg loads from contaminated sites, it is critical that high flow events are captured and included in loading estimates. When determining the effectiveness of a remediation action at a site it is important to normalize the loads to account for differences in hydrology between pre- and post-remediation sampling (Kirchner et al., 2011).

One reason there is such a large change in concentrations with discharge downstream of Hg contaminated sites—particularly mining sites—is that >85% of the Hg is often bound to coarse-grain sized particles that are only mobile during higher flows (Fig.2b) (Hines et al., 2000; Horvat et al., 2003; Kirchner et al., 2011; Lin et al., 2010; Morway et al., 2017; Rajar et al., 2007; Zhang et al., 2010). Many studies downstream of contaminated sites have observed a significant positive relationship between THg and total suspended solids (TSS) (Fig.3). Despite large differences in the types of contaminated sites summarized in Fig.3, most TSS versus THg regression slopes are not significantly different. In contrast, most of the intercepts and least-square mean (LSM) concentrations are significantly different and are correlated with the distance downstream from the contaminated source area (Fig.3 insert). These results show that THg concentrations can be elevated above commonly applied aquatic life water quality criteria (e.g. 12 ngL^{-1} in many US waters) up to 100 km downstream of a contaminated source area. Compared to TSS, the relationship between THg and dissolved organic matter (DOM) at contaminated sites is much weaker and is discussed in the SI and Fig. S2.

Many Hg mines performed on-site ore processing that resulted in significant emissions to the air and enhanced deposition to the surrounding landscape. Unlike the mineral-bound Hg found in some mine wastes, this deposited Hg is more likely to be bound to NOM and may be more available for downstream methylation(Baptista-Salazar and Biester, 2019). Unlike coarse-grained high Hg content particles which are only mobile during episodic periods of elevated discharge, the smaller NOM particles or dissolved phases of Hg continue to be mobile over the full range of hydrological conditions, including baseflow(Baptista-Salazar and Biester, 2019). Even though dissolved phase concentrations of Hg may be orders of magnitude lower than whole water or particulate bound concentrations, they may be disproportionately important when determining the impacts on downstream MeHg concentrations in fish.

In watersheds without contaminated sites, MeHg typically makes up 5–20% of the THg in stream water; however, this percentage is often significantly lower in streams impacted by contaminated sites (Kocman et al., 2011; Scudder, 2009) (Fig.4). The lower %MeHg may result from contaminated site Hg being less bioavailable (more likely to be bound to particles) than Hg from atmospheric origins. Also, in the areas with high Hg concentrations, other variables such as organic carbon or terminal electron acceptors (e.g. sulfate, ferric iron, etc) may become the limiting variables that constrain MeHg production. Other landscape variables (reduced wetland coverage, high gradient streams, etc) maybe other contributing factors resulting in a lower potential for methylation close to the contaminated source areas (Fig.4 insert). While THg concentrations typically increase with discharge, MeHg concentrations do not always show this trend and several studies have observed that MeHg concentrations are higher during baseflow conditions (Eckley et al., 2015b; Morway et al., 2017). This behavior may be more impacted by differences in temperature (methylation increases with temperature) than discharge if most of the MeHg load is from production within the waterbody(Flanders et al., 2010) and the baseflow conditions are occurring during the warmer months.

While the %MeHg in waterways draining contaminated sites is typically very low; the absolute MeHg concentrations reported in the literature for some of these sites is very high (see Fig. S2 in the SI). For example, the Azogado Creek downstream of the Almaden Hg mining district in Spain had MeHg concentrations up to 30 ngL^{-1}, even though this was <0.3% of the THg present(Gray et al., 2004). Similarly, the Carson River downstream of the

Comstock silver mining district reported elevated MeHg concentrations up to 22 ngL^{-1}, though this also represents a very small percent (<0.1%) of the THg (Morway et al., 2017). In both studies the THg concentrations in the water were >10,000 ngL^{-1}. At Hg contaminated sites where elevated MeHg concentrations are reported, but are <1% of the THg, there is the potential for significant elevation of the MeHg due to artifact formation of MeHg during aqueous distillation step that is often utilized during analysis (e.g. following EPA Method 1630)(Bloom et al., 1997). Alternative extraction techniques have been shown to decrease artifact formation of MeHg and should be considered when sampling for MeHg at sites with high THg (Bloom et al., 1997). In general, the analysis of MeHg in complex matrices often encountered at contaminated sites has a history of difficulties and various extraction and distillation chemistries have been applied to address this. As such, consideration of the method used for MeHg analysis should be based on evaluation of spike recovery and interferences in the local matrix and laboratory intercalibration studies should be performed to ensure consistent and accurate results (Creswell et al., 2015).

In addition to surface processes, there is potential for groundwater contamination from Hg contaminated sites. At abandoned mine sites, the flux of Hg to surface water is often larger than the flux to groundwater because the majority of Hg is bound to particles which are not very mobile in groundwater (U. S. EPA, 2015). However, given the very high Hg concentrations associated with some contaminated sites, even if a small fraction became oxidized and leached into the groundwater it can result in some proximate areas having concentrations exceeding drinking water standards (typically 1000–2000ngL^{-1}) (Porcel et al., 2015). At industrial sites such as chlor-alkali and former wood treatment facilities, Hg pollution is often in more soluble or mobile forms (e.g $HgCl_2$, Hg^0), and a larger portion may be available for release into groundwater resulting in highly elevated concentrations (>200,000 ngL^{-1})(Bollen et al., 2008). The mobilization of Hg to and within groundwater tends to be higher in sandy low organic carbon soils and lower in areas with high organic content because of the Hg binds to sulfur containing functional groups in the soil matrix that inhibits mobility (Biester et al., 2002; Lamborg et al., 2013). Mobility of Hg in groundwater can be facilitated in areas where the groundwater redox conditions promote the conversion of oxidized Hg species to Hg^0 or MeHg, which are less prone to solid phase sorption (Lamborg et al., 2013). In addition, areas contaminated by Hg^0 spills, can result in Hg present as an immiscible dense non-aqueous phase liquid (DNAPL) that can migrate deep below the surface due to its high density, surface tension, and low residual saturation (Sweijen et al., 2014).

3.2 Mercury fluxes to the air from contaminated sites

Fluxes to water are often the primary focus of Hg contaminated sites because of the direct links to methylation and bioaccumulation in downstream waterbodies. However, fluxes of Hg also occur to the air via the volatilization of Hg^0 as well as through wind entrainment of Hg bound to dust particles (often referred to as fugitive dust emissions). The relative magnitude of these two types of Hg emission sources varies depending on the site-specific conditions. However, due to the long atmospheric lifetime of Hg^0, these emissions mostly contribute to the global pool of Hg, whereas the fugitive dust emissions impacts are more local(Eckley et al., 2015a; Kocman and Horvat, 2011). Globally, the average flux of Hg from contaminated sites to the air is estimated to be of similar magnitude as the flux to water (82 and 116 $Mgyear^{-1}$ respectively) (Kocman et al., 2013).

Volatilization of Hg from contaminated sites has been shown to result in increased Hg concentrations in the ambient air(Eckley et al., 2013). These concentrations are typically below acute inhalation criteria levels (e.g. <50,000 ng m^{-3}), but in some extremely contaminated areas, air Hg concentrations due to surface volatilization can be above chronic inhalation criteria levels(e.g. <300 ngm^{-3}) (Hagan et al., 2013; Robins et al., 2012). Emissions from contaminated sites remain a concern even when below direct inhalation levels because they contribute to the actively cycling global Hg pool(Eckley et al., 2011b; Kocman et al., 2013), which will eventually be deposited, methylated, and accumulated in aquatic biota.

In general, Hg^0 emissions from undisturbed non-geologically/thermally enriched areas are <1 $ngm^{-2}h^{-1}$(Agnan et al., 2016; Hartman et al., 2009); whereas fluxes from contaminated sites can be several orders of magnitude higher >5,000 $ngm^{-2}h^{-1}$(Agnan et al., 2016). For contaminated sites that cover large spatial areas (such as mining operations), the annual emissions from the entire surface area have been shown to range from 19 to 105 $kgyear^{-1}$ from active industrial gold mines (Eckley et al., 2011b) and 51 $kgyear^{-1}$ from a large abandoned Hg mining area (Kocman and Horvat, 2011).

While many variables affect the magnitude of surface-air Hg^0 fluxes, variations in soil Hg concentration, solar radiation, temperature, and soil moisture have been shown to be relatively good predictors of Hg fluxes and equations relating these variables to Hg fluxes have been developed for spatial and temporal scaling(Eckley et al., 2011b; Hartman et al., 2009; Kocman and Horvat, 2011). Other factors influencing the Hg surface to air fluxes include the Hg speciation in the soil (Fig. 5), soil organic matter content, microbial activity, grain size, wind speed and air Hg concentrations(Eckley et al., 2011a; Eckley et al., 2016; Gillis and Miller, 2000; Osterwalder et al., 2019). In general, the processes affecting fluxes from contaminated sites are the same as observed in undisturbed soils(Gustin et al., 2000). However, there are also some unique factors at contaminated sites that can contribute to emissions. For example, at industrial mining sites operating in Hg enriched regions, both heap leaches and tailings ponds have significantly higher fluxes than other surfaces with similar Hg contents. The higher fluxes are associated with increased moisture content in tailings ponds and increased dissolution and release of ore-bound Hg into the leaching solutions(Eckley et al., 2011a).

Whereas point source emissions are immediately reduced after an industry closes or installs emission controls technology; releases of Hg from contaminated soils can continue for decades/centuries after initial industrial activity has ceased (Kocman and Horvat, 2011; Nacht et al., 2004; Robins et al., 2012; Zhu et al., 2018).

4. Contaminated site remediation

Remediation techniques to address Hg contaminated sites can include the removal or containment of Hg contaminated materials, the application of amendments to reduce mobility and bioavailability, landscape/waterbody manipulations to reduce MeHg production, and food web manipulations to reduce MeHg accumulated in desired fish species. These approaches can utilize physical, chemical, thermal, and biological methods.

4.1. Remediation options for removing and containing total-mercury

There are a wide range of options for the remediation of sites with Hg contaminated soils, sediments, and water that are primarily aimed at removing or containing THg (Table 1; summary of case studies provided in the SI). Some of these approaches are well-established and have been utilized to remediate sites; while other techniques are emerging and have primarily been explored in laboratory and test-plot experiments.

Where sufficient resources are available, the excavation, removal, and off-site storage of Hg contaminated materials is a commonly selected remediation approach. For example, in 2015 over 5 million kilograms of Hg-contaminated soil were transported over a thousand kilometers to a hazardous waste disposal facility as part of a multimillion-dollar cleanup of a former chlor-alkali facility (Maine, USA). Such efforts can be very effective in reducing Hg levels and fluxes at a site. However, because of the large costs, alternative techniques are often utilized, or off-site removals are focused specifically on areas with the highest concentrations (or bioavailable fractions) and/or potential for mobilization in runoff.

Instead of removing soils with elevated Hg concentrations from a contaminated site, there are some techniques available that aim to remove the Hg directly from the soil. For example, electrokinetic remediation technology involves the application of low-intensity direct current across electrodes to drive migration of charged Hg molecules to the opposite sign electrode and typically requires the use of a mobilizing solution such as iodine/iodide (Reddy et al., 2003a; Reddy et al., 2003b; Shen et al., 2009). Removal of Hg from soils can occur *in situ*, or alternatively several methods have been developed to removed Hg from the soil matrix after it has been excavated, such as soil washing or thermal desorption, which can occur using on or off-site equipment (Busto et al., 2011; Chang and Yen, 2006; Defregger, 1995).

On-site storage in containment repositories can significantly reduce costs relative to off-site disposal and can be combined with solidification/stabilization technologies to reduce mobility and the potential for off-site transport. On-site repositories, as well as other areas with elevated Hg concentrations, are often capped with low Hg soils and/or even synthetic liners to reduce exposure to the Hg and the potential for off-site transport in surface or groundwater. Capping contaminated soils can also eliminate the photoreduction process that convert the more stable Hg^{2+} forms to the more volatile Hg^0(Carpi and Lindberg, 1997). As a result, surface emissions have been shown to decrease by 50 to 100% after covering contaminated soils with a low Hg content cap(Eckley et al., 2011a; Miller and Gustin, 2013). Similarly, spraying surfaces with a sulfide-based Hg control reagent also has the potential to reduce surface emissions (Miller and Gustin, 2013).

In sediments, capping Hg contaminated areas with a layer sand or clay has been utilized at many contaminated sites. However, because these materials have a relatively weak affinity for Hg and MeHg, there is the potential for migration through the cap via porewater pathways. In particular, due to the low organic carbon content of sand caps, the flux of

MeHg into overlying water and benthic organisms has been enhanced in mesocosm experiments where sand has been mixed into the sediments(Curtis et al., 2019). Incorporating sorbent materials such as activated carbon (AC) or biochar into these caps can reduce this flux through the cap into overlying water.

Soil and sediment characteristics can have a large influence on the effectiveness of a selected remediation approach. For example, the efficiency of solidification/stabilization (S/S) and thermal methods is reduced when fine particulate matter coats the waste particles and weakens the bond between the waste and the binder(Conner and Hoeffner, 1998)or when large aggregates in the waste affect the operation of the mixer (Kalb et al., 2001). Soil moisture content and permeability can also impact the effectiveness of certain soil S/S methods (Timmerman and Zintak, 1998). For bioremediation methods, a high soil moisture content and generally neutral soil pH is typically required (De et al., 2014; Wagner-Döbler, 2013). As such, it is important to characterize site soil particles and bulk densities, as well as other factors that may affect the decision on remedial options.

An *in situ* remediation approach utilized at some sites is phytoremediation. Phytoremediation is an umbrella term for several technologies that can be implemented utilizing plant growth in contaminated areas that include: phytostabilization, phytoextraction, and phytovolatilization. At abandoned mine sites where the soil conditions are not conducive to vegetation growth, the addition of organic matter to tailings materials has been proposed to reduce surface erosion into adjoining waterways(Peltz and Harley, 2016). However, the addition of organic matter has been shown to increase Hg dissolution and promote methylation(Ravichandran et al., 1998; Waples et al., 2005). These undesirable outcomes could exacerbate the issues with Hg pollution associated with the site need to be taken into consideration and studied prior to implementation.

Downstream of historical gold and Hg mining operations, coagulation techniques using polyaluminum chloride and ferric sulfate coagulants have been applied to constructed wetlands with the objective of reducing THg and MeHg from water (Ackerman et al., 2015; Bachand et al., 2019). These efforts have been successful in reducing THg and MeHg concentrations between 50 and 97% compared to untreated waterbodies(Ackerman et al., 2015; Henneberry et al., 2011). The coagulants use charge neutralization, adsorption, and flocculation to transfer Hg in the dissolved phase (often associated with DOM) into colloidal and particulate forms and increase the particles sizes of existing THg-P that can result in higher settling velocities and transfer of the Hg to the sediment. While this technique reduces Hg concentrations in the water column, the transfer of Hg to the sediment may not be a desired outcome for the remediation of some contaminated sites. In addition, because wetlands are highly effective at producing MeHg, the construction of wetlands to induce particle settling has the potential to increase MeHg related to free-flowing waterways (Ackerman et al., 2015). Furthermore, additions of sulfate or ferric iron-based coagulants should be approached cautiously because both constituents can be terminal electron acceptors for microorganisms associated with MeHg production. However, the reduced byproducts of this process (e.g. sulfide) have also been shown to decrease MeHg production(Marvin-DiPasquale et al., 2014); therefore, the specific outcomes may depend on site-specific conditions.

There are many other technologies used to remove/absorb Hg from water using nanoparticles, many of which involve different types of sulfur functional groups associated with different materials (Fryxell et al., 2007; Fu et al., 2018; Hadavifar et al., 2014; Patel et al., 2018); whereas other nanoparticles rely on Hg absorption to hydroxyl function groups on iron oxide and carbonate (Davodi et al., 2017; Zhang et al., 2018). Many of these technologies have been shown to be effective in bench-scale studies using Hg_i ions, and they may be less effective at reducing Hg in environmental samples that are absorbed to particles or DOM. In addition, the cost associated with many of these technologies may prohibit widescale application and the long-term stability under environmental conditions remains uncertain.

While the remediation approaches mentioned above can be effective at decreasing THg concentrations in highly contaminated source areas; the impact that these actions have on proximate or downstream fish MeHg concentrations can be difficult to predict because of the multiple variables and complex relationships influencing MeHg production and bioaccumulation. Despite this complexity, there are numerous examples where remediation activities targeting THg source reductions have resulted in substantial decreases in fish MeHg concentrations (Fig. 6). The impact of remediation activities on fish Hg concentrations is highly variable between different contaminated sites and is influenced by both the effectiveness of the selected remediation action as well as the amount of time post-remediation that the fish monitoring occurred. For example, the post-remediation data from Lake Onondaga presented in Fig 6 represents fish collected just a few years after dredging activities occurred (other remediation actions are on-going), and the full impact of the remedial action(s), especially on longer-lived species, will require longer-term monitoring. In addition to differences between sites, several sites include samples from multiple fish species (e.g. Lake Pinchi, Ball Lake, and Lake Onondaga in Fig. 6) showing that there can be large differences in pre- and post-remediation concentrations between species due to differences in trophic position, life-span, foraging behavior (benthic versus pelagic), and the degree to which their home-range overlaps with the area of contamination.

Despite significant reductions in fish Hg concentrations following remediation actions at some sites (Fig. 6), post-remediation fish Hg concentrations (particularly for higher tropic-level sportfish) often remain above the targeted criteria concentrations (e.g. 0.3 mg/kg in the US). Additional/multiple remediation actions may be necessary to reduce fish MeHg levels to point where consumption advisories are lifted. Examples of remediation options beyond THg source control are discussed in the following sections (4.2 to 4.4).

4.2. Remediation options to reduce mercury mobility and bioavailability using *in situ* amendments

The application of *in situ* amendments is a maturing treatment for hazardous organic chemicals (HOCs); however, it is still evolving for metals including Hg (Ghosh et al., 2011; Kwon et al., 2010). *In situ* amendments have been deployed by mechanically mixing into surface sediments or soils, by thin-capping the surface (also called direct placement), or by mixing into clean capping materials (also called active capping). For HOCs and metals, the goal of these amendments is to transfer contaminants in the bioactive surface layer from soil to sorbent, decreasing bioavailability and efflux, rather than removal of the contaminants. Uniquely for Hg, there is also the potential to design amendments to reduce the Hg_i available for MeHg production. *In situ* amendments offer a potentially less expensive and disruptive approach to mitigating Hg risk than *ex-situ* strategies like dredging(Hou et al., 2016; Patmont et al., 2015).

In situ amendments for Hg and MeHg include biochar, AC, materials modified with thiol and sulfur ligands, and various forms of iron (Hadi et al., 2015a; Li et al., 2013; Meeks et al., 2013; Ting and Hsi, 2019; Wang et al., 2009; Weisener et al., 2005). The effectiveness of the amendments is based on stoichiometric considerations (the amendments active binding sites should be in excess of the sediment Hg) and the amendment's K_d-values for Hg and MeHg since the amendment works by competing for Hg or MeHg against the natural sorbents. Often assessed using an isotherm approach, it's important that the ratio of sorbent to Hg mass reflects conditions in field applications. Thiolated or sulfidized materials, like Thiol-SAMMS™ or sulfidized carbon, have been shown to provide the highest partition coefficients from water, followed by AC, with biochars and organoclays performing less well (Chen et al., 1999; Gomez-Eyles et al., 2013a; Hollerman et al., 1999; Liu et al., 2018d; Muller et al., 2019; Ting et al., 2018).

The kinetics of Hg and MeHg uptake by sorbent materials are generally fast from aqueous solution, with equilibrium achieved in several hours to a couple of days (Li et al., 2013; Sanders et al.; Ting et al., 2018). However, equilibration may be hindered in sediments, or by competing sorbents like DOM(Johs et al., 2019).

The endpoint for assessing amendment efficacy in sediments has often been a surrogate for contaminant availability, such as porewater concentrations or uptake by a passive sampler or organism. Several laboratory-based studies have shown that different types of black carbon-based amendments (e.g. AC and biochar), zero valent iron (ZVI) and Thiol-SAMMS™have the potential to reduce THg and MeHg concentrations in pore waters up to 95% and bioaccumulation of MeHg in worms and snails up to 90% (Gilmour et al., 2013; Lewis et al., 2016; Liu et al., 2017; Schwartz et al., 2019; Ting et al., 2018). In general, the effectiveness of AC amendments has been shown to be more effective at decreasing porewater THg and MeHg concentrations than biochars (Liu et al., 2017; Liu et al., 2018c) (Fig.7). However, biochars often have cost advantages over AC and can provide other benefits like improved soil fertility (Ahmad et al., 2014). The efficiency of all types of amendments can be increased by using smaller grain sizes and sulfidization (O'Connor et al., 2018) (Fig.6).

A few long-term field test-plot/mesocosm studies using in situ amendments for Hg remediation have been conducted in recent years. For example, a field test-plot study in a saltmarsh impacted by a historical chlor-alkali facility (Penobscot, ME, USA) showed that a thin-layer placement of AC-based SediMite™ resulted in a ~70% reduction in porewater THg concentrations after one month of application and then 50–65% reduction after 8 months. The amendment also reduced porewater MeHg concentrations by >90% at one month, and continued to significantly reduce porewater MeHg for about a year (Gilmour et al., 2018). Relative to AC-based amendments, biochar amendments were less effective at decreasing porewater THg and MeHg levels, and other amendments (lime and $FeCl_2$) were ineffective.

In a different field test-plot study located in a marsh impacted by historical industrial Hg releases (Berry's Creek, NJ, USA) several different types of AC applications were assessed. The results showed that over a 2-year period, AC amended sediments had porewater THg concentrations up to 50% lower and caged amphipods up to ~40% lower than unamended control plots. Site heterogeneity between test plots impacted redox conditions and obfuscated the interpretation of the MeHg results(Berry's Creek Study Area Cooperating PRP Group, 2018).

A mesocosm study in a rice paddy impacted by Hg from mining sources in China showed that biochar amendments reduced MeHg in rice grains between ~50–90%, partially due to bio-dilution from the enhanced vegetation growth due to improved soil fertility(Shu et al., 2016).

Field studies have shown excellent retention of thin layer AC placements in marsh sediments. For example, >50% of SediMite™ (pellets formulated from a sorbent plus clays and sand as a weighting agents) applied to a Penobscot River tidal salt marsh was retained over 2 years (Gilmour et al., 2018). In the Berry's Creek field plot trial, retention was roughly 100% over 3 years (Berry's Creek Study Area Cooperating PRP Group, 2018).

Site-specific sediment and soil characteristics have been shown to impact AC and biochar amendment effectiveness. For example, competing sorbents like DOM have been shown to decrease partition coefficients and sorption capacity of amendments(Johs et al., 2019; Sanders, 2018; Schwartz et al., 2019). This decrease in sorption capacity is largely controlled by AC-DOM interactions rather than direct interactions between AC and Hg(Muller et al., 2019; Sanders, 2018; Schwartz et al., 2019).

Early trials of *in situ* amendments tested the idea that amendments could reduce the availability of Hg_i for methylation, in addition to decreasing MeHg availability to organisms. Surprisingly, while sorbent amendments can dramatically increase Hg partitioning to the solid phase, they seem to have less impact on Hg bioavailability for methylation. Lab tests of several sorbents in a Hg-methylating bacterial culture showed no impact of biochar, AC or an organoclay on MeHg production, although all of the sorbents reduced the concentration of filterable Hg_i(Muller and Brooks, 2018). Only long-term (one year) incubation with Thiol-SAMMS® lowered MeHg production. In some studies, carbon amendments have led to increased MeHg accumulation in the solid phase, despite generally decreased porewater concentrations. The increase in MeHg concentrations has been observed more frequently for biochar than AC amendments, and is more common at higher amendments levels (Gilmour et al., 2018; Lewis et al., 2016; Liu et al., 2017). The mechanism appears to be through reduced MeHg degradation rather than increased methylation. The availability of MeHg bound to sorbent amendments is poorly understood and deserves attention

Several types of sediment amendment materials have been shown to leach SO_4^{2-} or other solutes such as Fe that can impact Hg methylation. Sulfate release from an organoclay and carbonized lignin could enhance methylation through stimulation of Hg-methylating microbes(Gilmour et al., 2013; Johs et al., 2019). Some biochars, especially those produced at low temperatures, release DOM, potentially decreasing their ability to sequester Hg (Liu et al., 2018b). There is also potential for sulfide release from sulfidized materials, and subsequent formation of mobile HgS nanoparticle (Ting 2018). As such, the selection of amendments needs to take into consideration the releases of constituents that might impact Hg methylation.

4.3. Remediation strategies to reduce mercury methylation

The abovementioned remediation approaches mostly focus on decreasing Hg_i levels in the environment and/or the availably of Hg_i for methylation. However, remediation options can also focus on decreasing MeHg production and bioaccumulation through mechanisms other than decreasing Hg_i. Because Hg methylation is primarily associated with microorganisms functioning on the lower end of the redox ladder (e.g. iron, sulfate, methane reducing bacteria); efforts to poise the redox conditions, such that these lower redox level microorganisms are not active, can reduce MeHg production. For example, several studies have shown that adding oxygen to the hypolimnion of lakes can decrease MeHg production by not allowing methylation to occur directly in the water column (Dent et al., 2014; Duvil et al., 2018; McCord et al., 2016). The effectiveness of this technique is dependent on how much MeHg is produced in the water column, versus methylation in the sediment or watershed inputs of MeHg. However, increasing hypolimnion oxygen levels has also been shown to have the benefit of decreasing the flux MeHg from the sediment into the overlying water(Duvil et al., 2018). There are multiple ways in which hypolimnion oxygenation can occur, which include oxygen injection, water-lifting aerator systems, or stirrers and these approaches can result in multiple other water quality benefits, such as decreasing the sediment release of other metals and nutrients and improving fish habitat (Dent et al., 2014; Hansen et al., 2017; Munger et al., 2016). Despite clear improvements in MeHg concentrations in bottom waters, hypolimnetic oxygen efforts have been less definitive in decreasing MeHg levels in biota(Beutel et al., 2014; McCord et al., 2016).

Instead of oxygen addition, other studies have shown that the redox conditions can be poised above those favorable to methylation and sediment MeHg release by the addition of nitrate or manganese(Austin et al., 2016; Beutel et al., 2017; Matthews et al., 2013; Vlassopoulos et al., 2018). Nitrate additions can have a dual effect by suppressing the activity of sulfate/iron/methanogenic bacteria involved in methylation, and decreasing the MeHg flux from the sediment into the water by sorption to iron and manganese oxyhydroxides(Todorova et al., 2009). This theory was put into practice in 2011 during a whole-lake nitrate addition in Onondaga Lake (NY, USA) which had received historical Hg discharges from several shoreline chemical manufacturing industries that utilized Hg cells. A liquid calcium-nitrate solution was added directly to the lake's hypolimnion three times per week during summer stratification. This resulted in a 94% reduction in hypolimnetic MeHg concentrations, with increased sorption to Fe and Mn oxyhydroxides in surficial sediments being the primary regulating mechanism(Matthews et al., 2013).

Another option for impacting the microbial activity associated with MeHg production is to reduce carbon source. For example, example studies have shown that vegetation management and/or carbon amendments associated with agricultural activities can have a large impact of MeHg production (Tang et al., 2019; Windham-Myers et al., 2014). Other studies have shown that the manipulation of hydrological variables that affect sediment wetting and drying that can influence redox conditions and the amount of MeHg produced(Eckley et al., 2017; Tanner et al., 2018; Willacker et al., 2016).

4.4. Remediation strategies to reduce methylmercury bioaccumulation

Instead of focusing on THg concentrations and MeHg production, other management options include food web and fish growth manipulations aimed at decreasing MeHg bioaccumulation (Lepak et al., 2012; Lepak et al., 2009). For example, in a whole-lake manipulation study, low-Hg prey fish (rainbow trout, *Oncorhynchus mykiss*) were introduced to a lake to increase the growth and the lower the Hg concentration in northern pike (*Esox lucius*). The results of the study showed that northern pike MeHg concentrations decreased by 50% through an increase in biomass (Lepak et al., 2012)and other studies suggest that reductions in fish concentrations up to 85% are possible through such food web manipulations (Johnson et al., 2015). Without having to address the root cause of the Hg pollution, these studies highlight that large reductions in MeHg concentrations in fish can be achieved rapidly at a relatively low cost (compared to dredging or other source control options). However, such techniques are only applicable to closed systems that are amenable to manipulations and the introduction or removal of fish species would not have a negative impact on native or endangered species.

5. Conclusions

Recent advances in site assessment tools have greatly increased our ability to measure Hg concentrations, forms/speciation, and potential sources. In addition, advances in understanding the variables associated with Hg methylation have also provide site managers opportunities to reduce MeHg levels by targeting pools of more bioavailable Hg_i and/or other factors associated with the methylation process (anoxic conditions, carbon sources, etc). Despite these advances in assessment tools, many novel approaches to site remediation have not moved beyond lab-based or field mesocosm test-plot scale, and their effectiveness during a site-wide application has not been tested. A notable exception to this is the success of nitrate addition/alteration of redox conditions on Lake Onondaga that has reduced fish MeHg concentrations (Matthews et al., 2013). The success observed at Lake Onondaga will hopefully encourage other site mangers to utilize the diversity of novel remediation techniques that have been shown to be successful in laboratory/test plot settings and apply them on a larger-scale.

Hg source reductions at several contaminated sites have shown that decreased MeHg concentrations in biota are possible (Fig. 6)(Fujiki and Tajima, 1992; Kinghorn et al., 2007; Mathews et al., 2015; Southworth et al., 2000). While MeHg concentrations in biota may initially respond relatively quickly to a remediation actionat a highly contaminated site, these levels may still be above targeted criteria concentrations. Further declines in fish MeHg concentrations to meet criteria levels can occur slowly and may take several decades or longer, particularly as the distance from the initial point of release increases. Other contaminated sites have taken actions to successfully reduce hot spots of THg concentrations in sediment/soil and water; however, these actions have not resulted in concomitant reductions in MeHg in biota and/or downstream biota remain significantly elevated above targeted criteria concentrations(Kuwabara et al., 2007; Mathews et al., 2013; Suchanek et al., 2008; U.S. Fish and Wildlife Service, 2011). At these sites, factors other than Hg_i concentrations may be the main drivers of MeHg production. Due to the complexity of Hg cycling and methylation process, remediation solutions can be very site-specific and remediation actions that were successful at one site may prove ineffective elsewhere. As a result, successful remediation actions require a significant investment in research aimed at identifying the sources and mechanisms responsible for contamination. Finally, post-remediation monitoring is critical to determine if a remediation was effective (or not) and can be used to determine if additional actions are necessary to achieve clean-up goals.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments.

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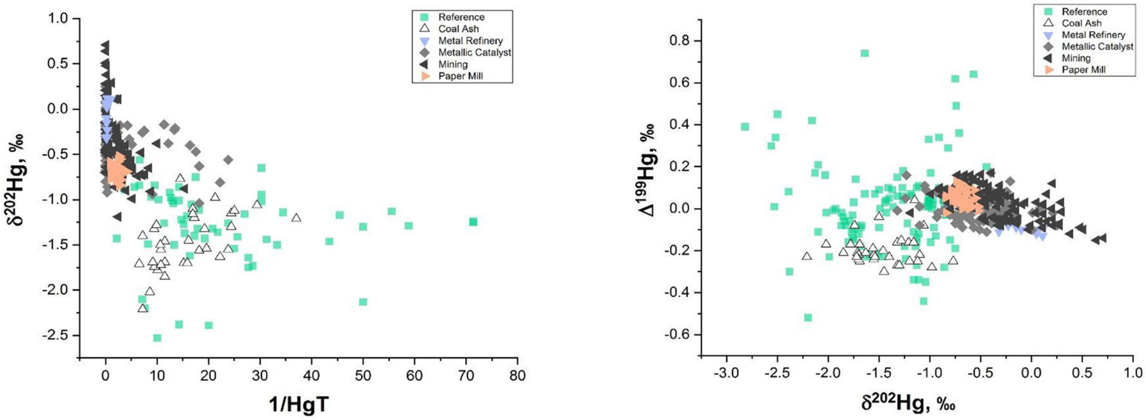

Fig.1.

Mercury stable isotope signatures from different Hg contaminated sites. Mass dependent fractionation—MDF (δ^{202}) as a function of a) concentration and b) Mass independent fractionation—MIF (Δ^{199}Hg) in sediments spanning different industrial sources. Isotopic differences between source types and ranges can be observed for sediments related to mining (Donovan et al., 2013; Foucher et al., 2009; Gehrke et al., 2011a; Yin et al., 2013b), coal ash (Bartov et al., 2012), metallic Hg usage (Feng et al., 2010; Grigg et al., 2018; Mil-Homens et al., 2013; Perrot et al., 2010; Washburn et al., 2018), metal refinery (Sonke et al., 2010), and paper mills (Yin et al., 2016) in comparison to reference sites with no direct Hg discharges or point sources. Overlap exists between some industries including mining and metallic Hg usage (i.e. chlor-alkali) showing the consistency of the industrial Hg signature produced at these types of sites.

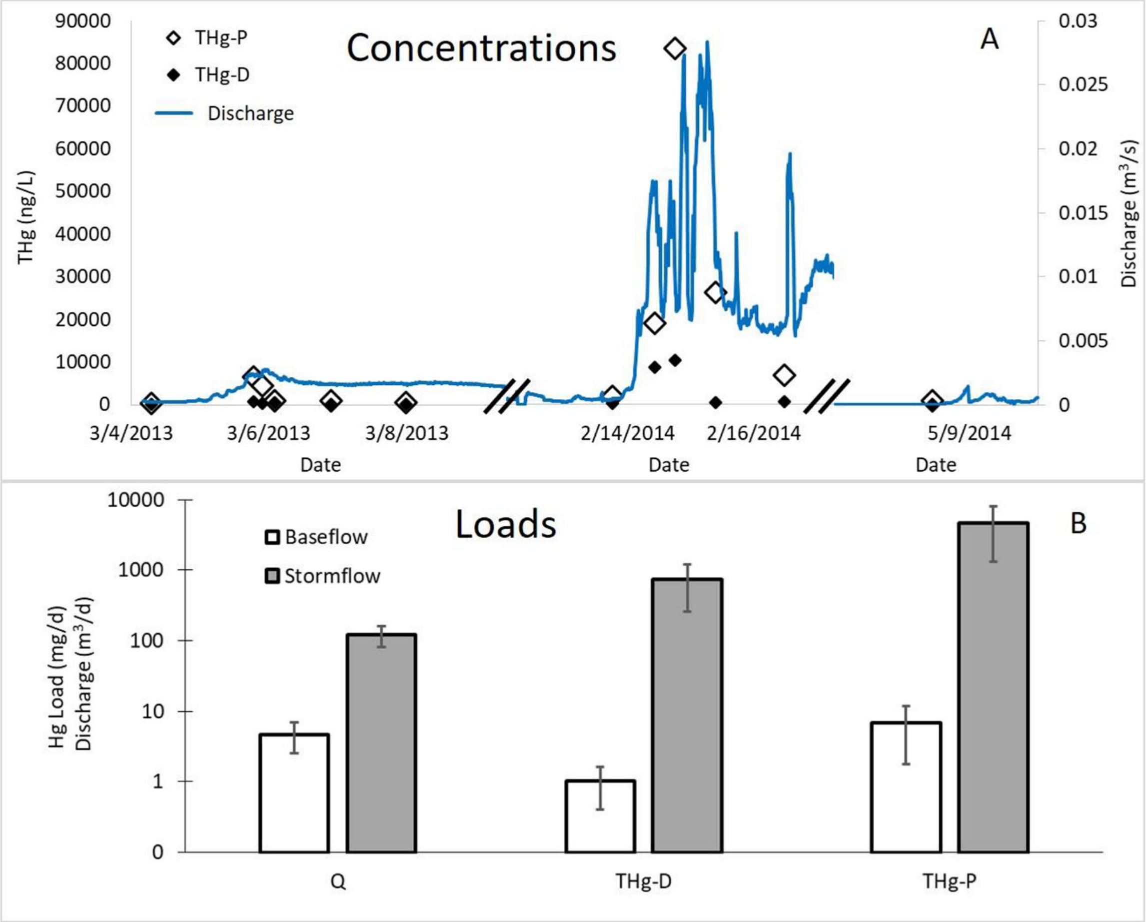

Fig.2.

Data from a creek draining an abandoned Hg mine showing the influence of different hydrological conditions on Hg concentrations and loads. Graph A shows dissolved and particulate bound Hg concentrations during baseflow and stormflow conditions measured during three separate field sampling campaigns (3/2013, 2/2014, and 5/2014). The data from March 6th was collected during a storm event, however the amount of precipitation and discharge during the February 15th storm event was much larger. Prior to rainfall, a baseflow sample was collected on March 4th and February 13th and a separate baseflow sampling event on May 8th. Graph B shows the mean and standard error of discharge and Hg loads from the baseflow and stormflow data shown in graph A. The data in Graph B are plotted on a log-scale y-axis due to the large differences in loads between baseflow and stormflow conditions. All data are from Furnace Creek, which is part of the Black Butte Mine Superfund Site(U. S. EPA, 2015).

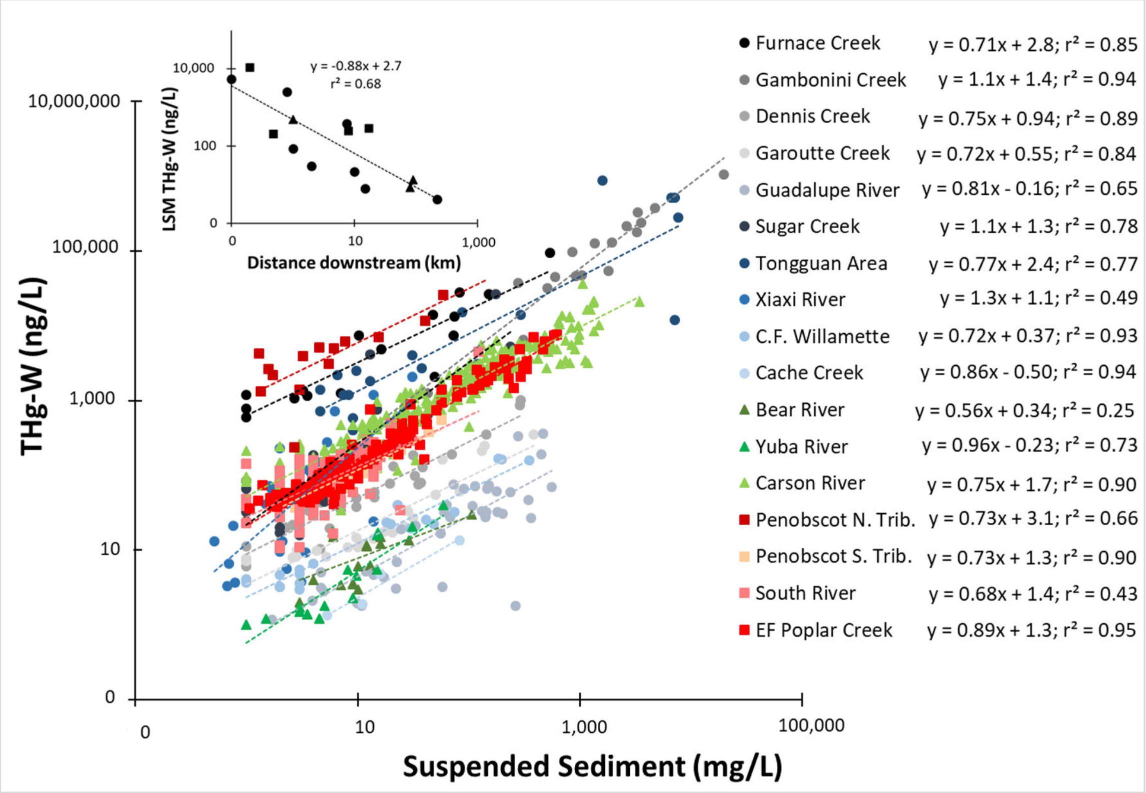

Fig.3.

Correlation between suspended sediment and whole water THg (THg-W) concentrations downstream from 17 Hg contaminated sites. For most sites, the variability in suspended sediment and THg-W were based on repeated measurements from the same location during different hydrological conditions; the two exceptions being the samples from the Xiaxi River and streams in the Tongguan mining area where multiple locations were sampled. The circle symbols represent waterways impacted by Hg mines, the triangles represent waterways impacted by gold mines, and the squares represent waterways impacted by industrial operations. The inset graph shows the least square mean THg-W concentration (all normalized to the covariate mean suspended sediment concentration of 20 mgL^{-1}) versus the distance downstream from the contaminated site where the measurements were conducted (data from Tongguan and Xiaxi not included in this analysis since they were collected at multiple downstream locations). All regressions p-values were <0.05 and are provided in the SI. All data sources are listed in the SI. All data were log (base 10) transformed prior to regression analysis and the regression equations shown are based on this transformed dataset.

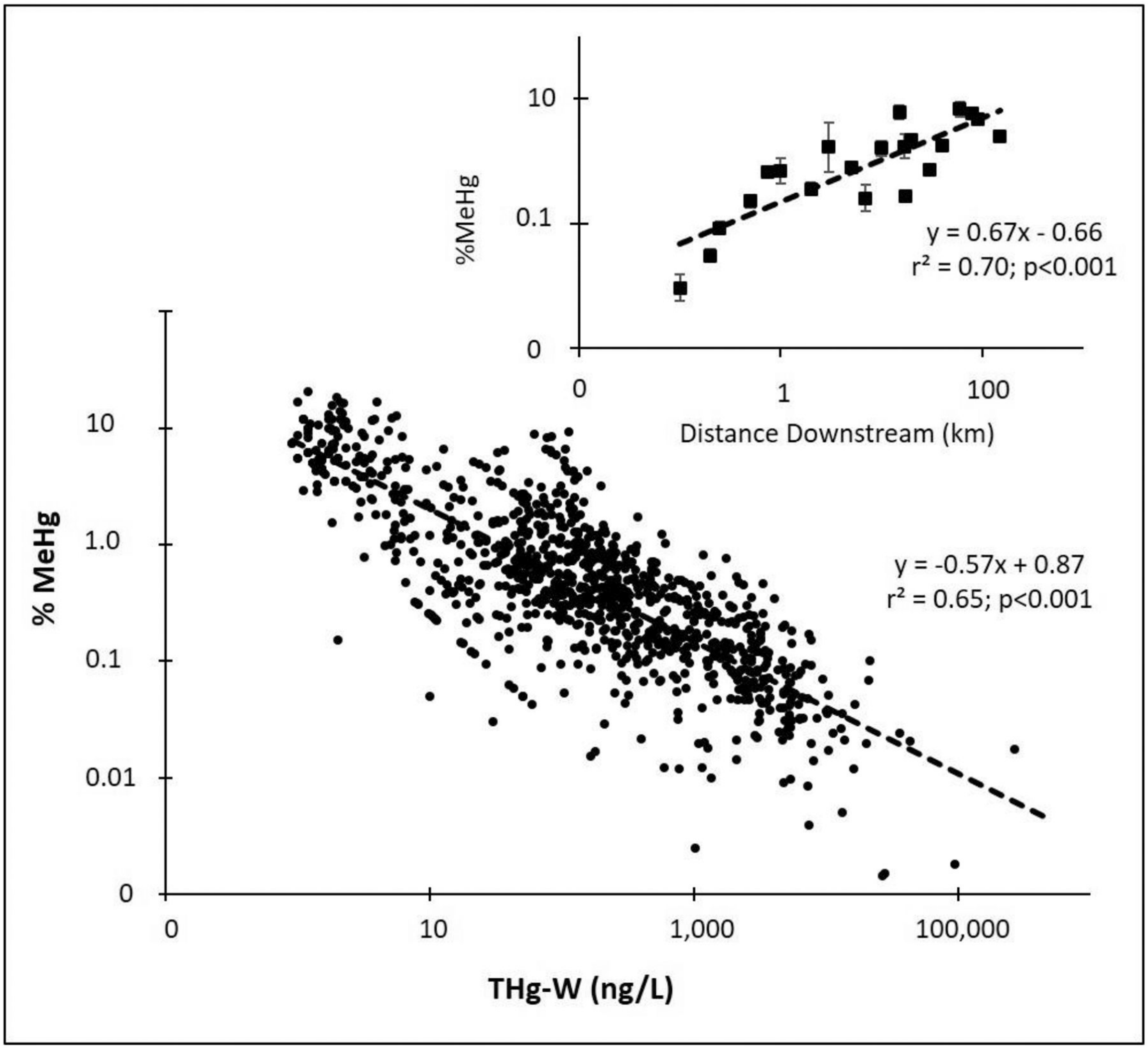

Fig.4.

The main figure shows whole water THg concentration versus the %MeHg in stream and rivers draining catchments containing contaminated sites. While MeHg concentrations tend to increase with the THg concentration (data shown in Fig. S3 in the SI), the %MeHg decreases as the THg concentrations increases. This suggests that the THg concentration may not be a limiting factor for MeHg production at the sites with higher THg concentrations. The inset graph shows %MeHg concentrations averaged (with SE shown) based on the distance the samples were collected downstream of the contaminated site. These results highlight that the methylation efficiency can increase downstream from a contaminated site. The sources of data used in this figure are provided in the SI. All data were log (base 10) transformed prior to regression analysis and the regression equations shown are based on this transformed dataset.

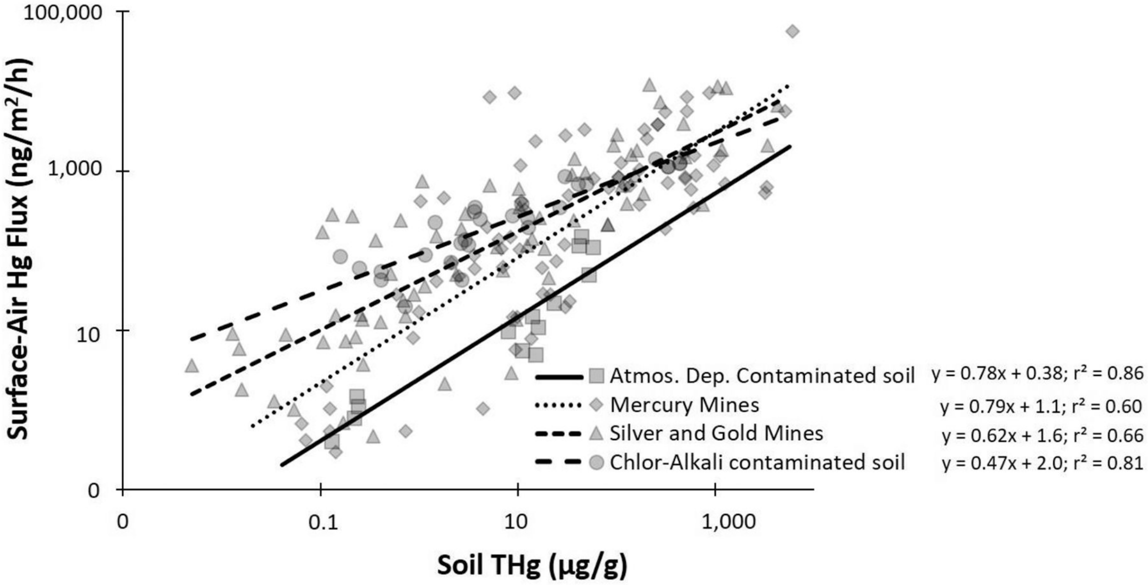

Fig.5.

Graph showing the relationship between soil THg concentrations and surface-air Hg fluxes from different types of contaminated soils. Squares represent data from soils impacted by atmospheric deposition from the Flin Flon smelter in Manitoba, Canada (Eckley et al., 2015a); diamonds represent data from abandoned Hg mines from California, Nevada, and Texas (Coolbaugh et al., 2002; Gray et al., 2015; Gustin et al., 2002; Nacht et al., 2004); triangles represent data from historical gold and silver mining areas in California and Nevada that utilized Hg as part of the extraction process(Coolbaugh et al., 2002; Gustin et al., 2002; Zehner and Gustin, 2002); and circles represent data from soil contaminated by releases from a chlor-alkali plant in Switzerland (Osterwalder et al., 2019). The graph shows that for a similar level of soil Hg contamination, the releases of Hg from soils impacted by atmospheric deposition is lower than soils from abandoned Hg mines and these are both lower than contaminated sites where Hg^0 had been used either for gold/silver amalgamation or chlor-alkali production. All regressions had p-values <0.01. All data were log (base 10) transformed prior to regression analysis and the regression equations shown are based on this transformed dataset.

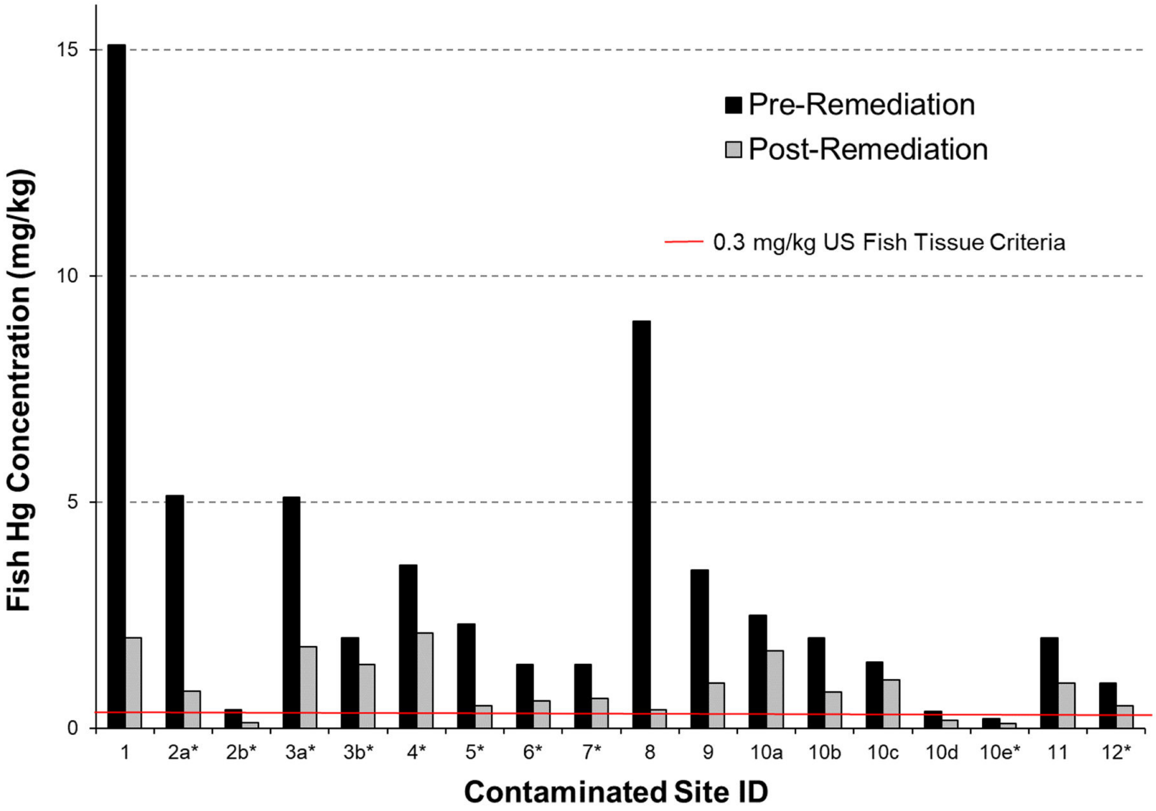

Fig. 6.

Summary of mean and/or median fish Hg concentrations from several contaminated sites before and after remediation actions have occurred. The site ID's are: 1—Clay Lake, Canada (walleye); 2—Pinchi Lake, Canada (a: lake trout, b: lake whitefish); 3—Ball Lake, Canada (a: northern pike, b: walleye); 4—Lake Kirkkojarvi, Finland (northern pike); 5—Lake St, Clair, USA (2alleye); 6—Lake Vanern, Sweden (northern pike); 7—Pena Blanca Lake, USA (largemouth bass); 8—Minamata Bay, Japan; 9—Holston River, USA (rockfish); 10—Onondaga Lake (a: walleye, b: smallmouth bass, c: largemouth bass, d: brown bullhead, e: small prey fish—mostly banded killifish); 11—Poplar Creek, USA (sunfish); 12—Abbotts Creek, USA (walleye). Site IDs 1–7 all had singular source control remediation actions, whereas site IDs 8–12 had multiple remediation actions. Apart from site #8 (Minamata Bay) where the industrial source released MeHg, all the other sites were predominantly contaminated with inorganic Hg. The asterisks (*) next to the site ID represents samples where pre- and post-remediation fish concentrations have been length-normalized. A measure of variability associated with each mean or median value was not included since there was not consistency among all the studies in reporting this information; however, in studies where this is included the variability can be quite large and as a result not all the pre- and post-remediation concentrations may be significantly different. Additional details and references are provided in Table S3 in the SI.

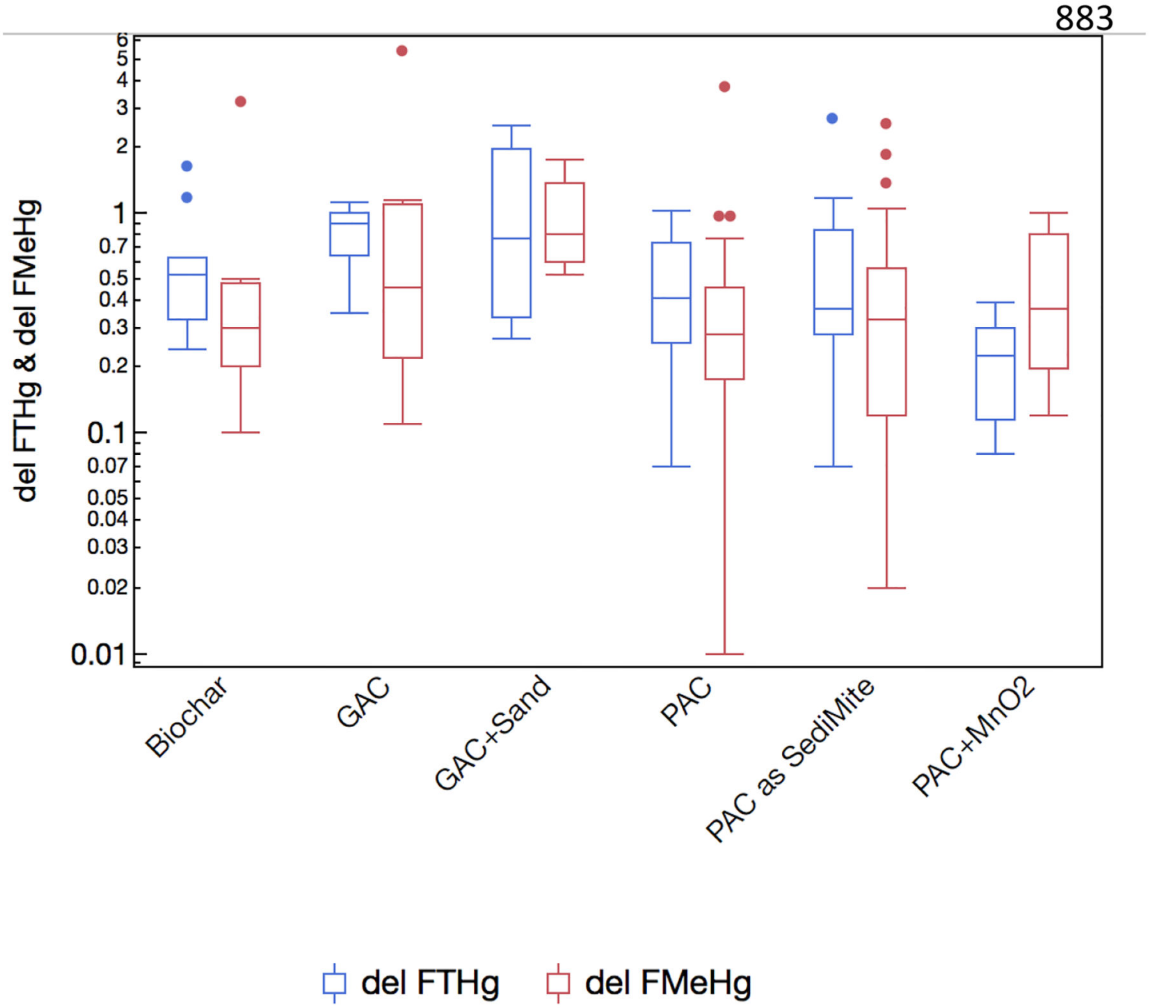

Fig.7.

Reduction in filtered (F) porewater THg and MeHg for different types of sediment amendments. Values are plotted as the ratio of concentration in a treated sample relative to matched unamended controls. A value of one means no change in concentration, a value of 0.1 means that the concentration was reduced to 10% of control concentration. Data were taken from studies that included a variety of dosing levels and incubation times and included field plots studies and lab studies. Data include field studies in Penobscot River saltmarshes (Gilmour et al., 2018), field and laboratory studies in Berry's Creek, NJ marshes(Berry's Creek Study Area Cooperating PRP Group, 2018), and laboratory studies from a freshwater lake and river, an estuarine bottom sediment (Gilmour et al., 2013). N= 85.

Table 1.

Summary of established and emerging technologies for Hg contaminated site remediation.

	Remediation/Treatment Technology	**Soil**	**Waste**	**Sediment**	**Water**	**References**
Established Technologies	Excavation or dredging with removal	♦		♦		Randall and Chattopadhyay (2013); US EPA (2007a); Wang et al. (2004)
	Containment in-place	♦		♦	♦	Liu et al. (2018a); Wang et al. (2004); Xu et al. (2015)
	Ex-situ soil washing	♦				Subires-Munoz et al. (2011); Wasay et al. (2001)
	Solidification/Stabilization	♦	♦			Piao and Bishop (2006); Randall and Chattopadhyay (2004); Zhang et al. (2009)
	Thermal treatment (e.g. batch retorting, ex-situ thermal desorption, in-situ vitrification)	♦	♦			Chang and Yen (2006); Kunkel et al. (2006); Rumayor et al. (2016)
	Pump and treat				♦	US EPA (1996); US EPA (2007b)
	Permeable reactive barrier and/or funnel/gate system				♦	Smyth et al. (2001); Vaselli et al. (2015)
	Adsorption by activated carbon				♦	Di Natale et al. (2011); Hadi et al. (2015b)
	Monitored natural attenuation	♦		♦		Kaplan et al. (2002); Mulligan and Yong (2006)
Emerging Technologies	In-situ thermal desorption	♦				He et al. (2015); Park et al. (2015)
	In-situ flushing/washing	♦				He et al. (2015)
	In-situ electrochemical/ electrokinetic recovery	♦				Niroumand et al. (2012); Reddy et al. (2003b); Suer and Allard (2003)
	Bioremediation: bio-treatment, biofunctionalized zeolite, genetically engineered bacteria				♦	De et al. (2014); Ruiz (2017); Wagner-Döbler(2013)
	Phytoremediation	♦				Chattopadhyay et al. (2012); Marrugo-Negrete et al. (2015); Smolinska and Rowe (2015)
	Nanotechnology	♦		♦	♦	Davodi et al. (2017); Fryxell et al. (2007); Shadbad et al. (2011)
	Precipitation, co-precipitation, chelating agents				♦	Ackerman et al. (2015); Wang et al. (2017)
	Immobilized algae				♦	Bayramoglu et al. (2006); Mokone et al. (2018)
	Biochar			♦	♦	Boutsika et al. (2014); Gomez-Eyles et al. (2013b); Liu et al. (2016)
	Chemical reduction & stripping				♦	Jackson et al. (2013); Mathews et al. (2015)
	Copper or brass shavings				♦	Huttenloch et al. (2003); Richard and Biester (2016)

Note: Soil includes soil, debris, sludge, and other solid phase environmental media; Waste includes nonhazardous and hazardous solid waste generated by industry; and Water includes groundwater, surface water and wastewater.