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Occurrence and Mobility of Mercury in Groundwater

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1. Introduction

1.1. Forms, toxicity, and health effects

Mercury (Hg) has long been identified as an element that is injurious, even lethal, to living organisms. Exposure to its inorganic form, mainly from elemental Hg (Hg(0)) vapor (Fitzgerald & Lamborg, 2007) can cause damage to respiratory, neural, and renal systems (Hutton, 1987; USEPA, 2012; WHO, 2012). The organic form, methylmercury (CH₃Hg⁺; MeHg), is substantially more toxic than the inorganic form (Fitzgerald & Lamborg, 2007). Methylmercury attacks the nervous system and exposure can prove lethal, as demonstrated by well-known incidents such as those in 1956 in Minimata, Japan (Harada, 1995), and 1971 in rural Iraq (Bakir et al., 1973), where, in the former, industrial release of MeHg into coastal waters severely tainted the fish caught and eaten by the local population, and in the latter, grain seed treated with an organic mercurial fungicide was not planted, but eaten in bread instead. Resultant deaths are not known with certainty but have been estimated at about 100 and 500, respectively (Hutton, 1987). Absent such lethal accidents, human exposure to MeHg comes mainly from ingestion of piscivorous fish in which MeHg has accumulated, with potential fetal damage ascribed to high fish diets during their mothers' pregnancies (USEPA, 2001). Lesser human exposure occurs through ingestion of drinking water (USEPA, 2001), where concentrations of total Hg (THg; inorganic plus organic forms) typically are in the low nanograms-per-liter range¹, particularly from many groundwater sources, and concentrations at the microgram-per-liter level are rare.

¹ Because many studies report Hg concentrations in units of nanograms per liter, results reported for aqueous samples in other units herein will be converted to nanograms per liter. Contents of solid materials will be reported in megagrams, kilograms and (or) milligrams per kilogram.

1.2. Standards for mercury in water, and other regulations

For drinking water the World Health Organization (WHO) guideline for THg is 1,000 ng/L, a level (in some instances given as 0.001 mg/L or 1.0 µg/L) adopted by the European Union countries, the United Kingdom, Canada, and India (WHO, 1993; NIEA, 2011; Environment Canada, 2010; Srivastava, 2003). These standards are lower than the maximum contaminant level (MCL) adopted by the U.S. Environmental Protection Agency (USEPA), which is 2,000 ng/L (USEPA, 2001a). The USEPA has also adopted a reference dose (RfD) for MeHg in drinking water of 0.1 µg/kg bw/day (or 100 ng/kg bw/day, where bw = body weight) (USEPA 2001b).

Measures, such as regulations to restrict commerce in Hg, have been taken to reduce the amount of elemental Hg available globally. The amount mined in 2010, for example, was estimated at 2042 megagrams (Mg; or 2250 tons) (Brooks, 2010). In 2007, the European Union passed a ban on the export of Hg(0) and in 2008 this was expanded to include various Hg compounds. The USEPA, in 2008, passed a ban on the export of elemental Hg from the United States (USA), to take effect in 2013 (USEPA 2009). Because the USA is ranked as one of the world's top exporters of Hg (~417 Mg in 2010 (Brooks, 2010)), implementation of the act will remove a substantial amount from the global market, as it is exported to foreign countries where, among other uses it is employed in small-scale gold (artisanal) mining (USEPA, 2012). China, the world leader in Hg production in 2010, plans to lower production of some metals, including Hg, by 2015 (Brooks, 2010).

1.3. Previous studies of mercury in the environment

Given the potentially severe health effects of MeHg, the need to understand the production of MeHg and its bioaccumulation in the food web, as well as the role of atmospheric deposition in supplying Hg to soils and surface water, has led to numerous investigations of Hg inputs and transformations. Hence, the majority of studies and reviews of Hg in the environment focus on atmospheric inputs (e.g., Engstrom et al., 2007; Glass et al., 1991; Pacyna et al., 2006; Schuster et al., 2002) and the fate and transport of Hg in soils, sediments and surface-water settings (e.g., Bradley et al., 2011; Driscoll et al., 1994; Grigal., 2002; Porvari et al., 2003; Rudd, 1995; Shanley et al., 2002; Schuster et al., 2008; Selvendiran et al., 2008; Skyllberg, 2008; Ullrich et al., 2001; Yu et al., 2012). Many of these studies have their emphasis on the production, mobility, and bioaccumulation of MeHg. Far fewer studies have been performed and published on Hg in groundwater. Some of those have shown that Hg concentrations are low, in the nanograms-per-liter range (e.g. Krabbenhoft & Babiarz, 1992). However, other studies have shown that regional levels of Hg in groundwater can be high, in the micrograms-per-liter range (e.g. Barringer & Szabo, 2006), and some show that microgram-per-liter levels of Hg are being found in groundwaters previously not tested (e.g. Khatiwada et al., 2002).

As discussed below, not all contamination with Hg at the land surface causes contamination of groundwater. It is critical to know the complex biogeochemistry of Hg in order to understand how existing important research applies to Hg fate and transport in groundwater systems.

2. Sources and fluxes of mercury

2.1. Mercury in natural materials

Mercury is one of the least abundant elements in crustal rocks. Concentrations in rocks of the upper continental crust typically range from 0.01 to about 2 mg/kg, although concentrations higher by more than two orders of magnitude are reported from igneous and sedimentary rocks of Crimea and the Donets Basin of Russia (Fleischer, 1970). A reasonable estimate of the average concentration of THg is 0.08 mg/kg (Fairbridge, 1972). The most abundant Hg mineral is cinnabar (HgS), which can be found in association with metacinnabar (β HgS—a metastable sulfide). Other Hg minerals, mainly sulfosalts that can also contain arsenic, are not common, and, when found, are generally associated with ore deposits.

Volcanic emissions have been estimated by some researchers to constitute the main natural source of Hg to the atmosphere where Hg is primarily present as gaseous elemental Hg (Martin et al., 2012). Kilauea, in Hawaii, was estimated to produce about 260,000 kg/yr (Siegel & Siegel, 1987). In contrast, Ferrara et al. (2000) suggest that volcanic emissions are not the main natural source of THg to the atmosphere, based on reported estimates of emissions from Mediterranean volcanoes: Vulcano, about 1 to 6 kg/yr; Stromboli, about 7 to 80 kg/yr; and Etna, about 60 to 500 kg/yr.

Volcanic emissions can cause local contamination of soils and surface waters, but, as shown at Mt. Etna in Sicily, concentrations of Hg in local groundwater were typically < 10 ng/L (Martin et al., 2012), indicating that Hg had not been easily mobilized from the land surface. Nevertheless, some of the Hg deposited to soils by volcanic emissions volatilizes and can be re-emitted to the atmosphere (Fig. 1). Further, evasion of Hg(0) from the ocean surface adds substantially to atmospheric Hg (Mason et al., 1994). Characterization of atmospheric THg along the central USA Gulf Coast has shown inputs from sea spray increases atmospheric deposition of THg in coastal regions (Engle et al., 2008).

Mineralization associated with igneous activity has produced volcanic-hosted massive sulfide deposits, in which the ore mineral cinnabar forms (some mined since the third century B.C. (Navarro, 2008)). Such major geologic sources of Hg are found in Spain, Slovenia, China, and the western USA, in California. Volcanically derived sedimentary deposits containing other sulfides also can contain substantial Hg (Navarro 2008).

Associated with igneous activity, circulating geothermal fluids can contribute Hg to groundwater, surface water, and to solids that precipitate around mineral springs, geysers and fumaroles. In Russia, Yudovich and Ketris (2005) report that Hg contents in condensate from fumarole gases ranged up to 0.11 mg/kg at the Kamchatka Peninsula, and even higher (up to 0.40 mg/kg) at fumaroles in Japan and Guatemala. In Yellowstone National Park in the western USA, Hg is present at concentrations of 12 to 640 ng/L in waters of hot springs and geysers (Ball et al., 2006), although Hg minerals were not recognized in precipitates there (White et al., 1970). Saline waters at Sulfur Bank and Wilbur Springs in the California Coast Range contained about 1,500 ng/L of Hg, and cinnabar and metacinnabar precipitate at Sulfur Bank (White et al., 1970).

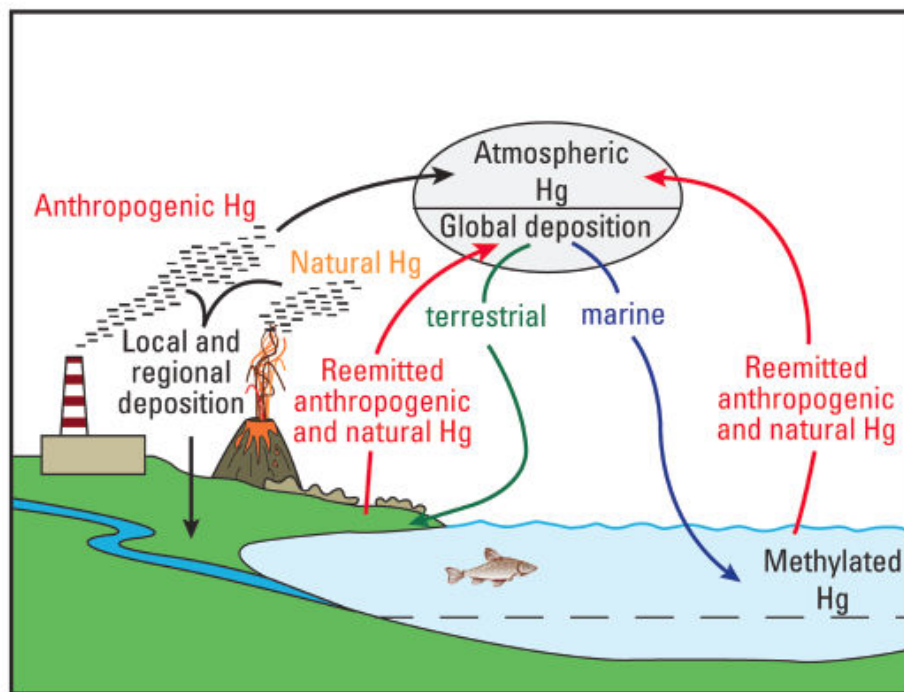


Figure 1. Sources and biogeochemical cycling of mercury between land surface, surface water, and the atmosphere (from Tewalt et al., 2001).

Fleischer (1970) compiled literature values for Hg in crustal rocks, worldwide. Average values for mafic igneous rocks ranged from 0.001 to 0.240 mg/kg, whereas for silicic igneous rock, averages ranged from 0.005 to 0.190 mg/kg, except for igneous rocks from the Crimea and Donets Basin, where the average Hg contents ranged from 0.250 to 17.6 mg/kg. Average Hg contents of sandstones and limestones ranged from 0.018 to 5.70 mg/kg, and in shales from 0.05 to 2.3 mg/kg, with the higher contents typically found in the Russian shales. In metamorphic rocks, contents ranged from 0.060 to 2.50 mg/kg.

Many of the widely used sources of coal contain high concentrations of Hg; these include from China (Pirrone et al., 2010), Ukraine (Kolker et al., 2009), and Texas, USA (Tewalt et al., 2001). Coal burning is a major source of Hg release into the atmosphere (Wang et al., 2004); but potential effects on groundwater are mostly unknown. The Hg content of coals ranges from 0.01 to 1.85 mg/kg, with the highest content found in some Chinese coals (Pirrone et al., 2010 and references therein). Much of the Hg in coals is in associated pyrites, with contents that can be 10 mg/kg or greater (Yudovich & Ketris, 2005). Direct effects from coal seams on groundwater may not be obvious, however. Cravotta (2008) did not find detectable Hg concentrations in samples of waters discharging from abandoned coal mines in Pennsylvania, USA.

2.2. Mercury in atmospheric deposition and its effects

Emissions of Hg to the atmosphere have increased greatly since the beginning of the industrial era, although estimates of the increase in atmospheric levels vary widely—from about 3 to 24 times that of the pre-industrial period (Wang et al., 2004, and references therein). Recently, it

has been estimated that total global emissions account for about 6500 megagrams (Mg) of Hg released annually to the environment. The uncertainty for current estimates is about a factor of two, according to Lohman et al., (2008). Nevertheless, as Gustin et al. (2008) point out, estimates of natural emissions vary widely (volcanic emissions are not constant, for example). Gustin et al. (2008) also note that the range in estimates of anthropogenic releases is small, relative to the range of estimates for natural sources. Coal burning and combustion of other fossil fuels were estimated to constitute about 60 % of the annual amount contributed to the atmosphere from anthropogenic sources (Swain et al., 2007). Total Hg contents of ice-core samples from the Upper Fremont Glacier in Wyoming, USA, when integrated over the past 270 years indicated that anthropogenic emissions accounted for 52%, volcanic events contributed 6%, and background sources supplied 42% (Schuster et al., 2002), and most of the anthropogenic contributions have occurred since about 1850. A current estimate of total annual emissions, both natural and anthropogenic, is about 7,300 Mg (Pirrone et al., 2010) (Table 1), higher than earlier estimates, and also with a higher uncertainty. In terms of regional emissions, those from Asia have increased from 38% to 64% of global emissions over the period of 1990-2007 (Pirrone et al., 2010).

Global production (mining and processing) of Hg has been reduced since the mid 20th century, although present-day production may still contribute about one third of emitted Hg from anthropogenic sources (Hylander & Meili, 2003). Amounts of Hg in atmospheric deposition are declining in some parts of the USA as there have been efforts to curb industrial and power-plant emissions. For example, in a study of Hg loading to Minnesota (USA) lakes, Engstrom et al. (2007) found that inputs, mainly from atmospheric deposition and subsequent soil erosion, peaked in the 1970s, and have declined substantially in recent years. Additionally, in the upper Great Lakes (Superior & Huron) in the USA and Canada, a decline in Hg in fish tissue is noted, although not in the lower Great Lakes (Erie & Ontario) (Bhavsar et al., 2010).

Atmospherically deposited Hg has affected mainly surface water and the organisms that live in water bodies. Hg deposited as Hg(0) may be oxidized to Hg(II), then transformed to MeHg by bacterial activity at and below the sediment/water interface or in algal mats. Low-trophic-level organisms (invertebrates) take up both THg and MeHg (Fig. 1). The concentration of MeHg in organisms increases with each step up the food chain—a process known as biomagnification (Alpers & Hunerlach, 2000; USGS, 2000). During the late 20th century, emissions from coal-fired plants in the Midwest of the USA, which are mainly in vapor (Hg(0)) form (Lindberg, 1987), deposited Hg on surface-water bodies. These emissions and other industrial emanations have resulted in fish consumption advisories because of high levels in the tissues of edible fish (Brooks, 2002). Advisories for non-commercial fish, as of 2006, now extend to freshwaters in 48 USA States, of which 23 are statewide advisories. In addition, 13 States have coastal and estuarine advisories (USEPA, 2010).

Results of two studies suggest that Hg from atmospheric deposition contributes to elevated Hg concentrations in groundwater. Bradley et al. (2012, p. 7507) found that strong hydraulic gradients toward a stream indicated deep groundwater discharge was the primary source of filtered Hg (FTHg) to a Coastal Plain stream, USA. Additionally, higher concentrations

Source	Mercury ^e (Mg/yr)	Year for estimate
<i>Natural</i>		
Oceans	2,680	2008
Lakes	96	2008
Forests	342	2008
Tundra/grasslands ^b	448	2008
Desert/non vegetated areas ^c	546	2008
Volcanoes and geothermal areas	90	2008
<i>Anthropogenic</i>		
Non-ferrous metal production	310	2003-06
Pig iron and steel production	43	2003-06
Cement production	236	2003-06
Caustic soda production (chlor alkali process)	163	2003-06
Mercury production	50	2003-06
Gold production	400	2003-06
Waste disposal	187	2003-06
Stationary (fossil fuel) combustion	810	2003-06
Coal-bed fires	32	2003-06
Vinyl chloride monomer production	24	2003-06
Other	65	2003-06
Biomass burning ^d	675	2008
Agricultural areas ^d	128	2008

^a the mean uncertainty associated with these estimates is + 25% (Pirrone et al., 2010)

^b Includes savannah, prairie, chaparral.

^c Includes metalliferous areas.

^d Amounts may need reconfiguring from Pirrone et al.(2010) category of natural sources, p. 5953, because some burning is caused by humans, agricultural inputs of Hg are anthropogenic, and evasion is amplified by soil disturbance.

^e Values have been rounded to the nearest whole number.

Table 1. Estimates^a of global mercury emissions from natural and anthropogenic sources, and year(s) for which estimate is made. [Mg, megagrams; Data from Pirrone et al., 2010 and references therein]

of FTHg in deeper wells near the stream (compared to shallower wells) and a lack of geologic Hg deposits in soils and sediments were “consistent with atmospheric Hg deposition on the terrestrial landscape as the distal source of FTHg to groundwater.” Barringer and Szabo (2006) contend that Hg deposited from the atmosphere to soils of the Coastal Plain of southern New Jersey, USA, may be mobilized, along with pesticide

residues, to groundwater where Hg concentrations in domestic well water are found to exceed the State and USEPA MCL of 2,000 ng/L.

2.3. Effects of mercury from manufacturing and agriculture on soils, surface water and groundwater

Mercury in consumer products and their manufacture constitutes a source of Hg to aquatic systems. Mercury is used in dry-cell batteries, fluorescent light bulbs and thermostats, and, in the mid-to late 20th century, as a fungicide in paints and in wood preservatives; Hg is also used in dental amalgams (Barringer et al., 1997; Brooks, 2000, 2002; USEPA, 2006). Use of Hg in dentistry has consumed large amounts of the metal (about 63,500 kg in Europe), resulting in emissions as well as constituting a substantial portion of the Hg in municipal waste streams (Hylander et al., 2006; Metro, 1991). Several studies, summarized by Morrison (1981), indicated that subsurface disposal of municipal sewage sludge in the USA resulted in several metals, including Hg, leaching to groundwater. Since the mid 20th century, industrial use of Hg has declined in the USA and elsewhere, however. There are now ongoing attempts in some countries, such as the USA and the United Kingdom, to reduce the amount of Hg used in products; particularly those that are then discarded (Bradley & Journey, 2012).

Groundwater contamination with THg from both inactive and active industrial sources is found in many countries where, in general, the contamination is relatively local. Chlor-alkali plants that once produced chlorine gas and sodium hydroxide using Hg-cell technology have been shown to contribute Hg to surface water, soils and groundwater—up to 22,900,000 ng/L in groundwater at a facility in Sydney, Australia (Orica, 2012). There are numerous such facilities; other examples are chlor-alkali plants in New York State, USA, and in Kazakhstan, which have also produced Hg contamination of surrounding soils and waters (Gbondo-Tugbawa & Driscoll, 1998; Ullrich et al., 2007). The use of Hg-cell technology is being voluntarily phased out in most countries; however, wastes from chlor alkali plants still remain at some locations (Hylander & Meili, 2003).

In some instances, Hg contamination of groundwater is more diffuse, perhaps coming from multiple (potentially small) point sources. Suspected industrial and wastewater discharges have introduced Hg contamination to the surficial alluvial aquifer in urban Madras, India (Somasundaram et al., 1993), where, along with other metals, Hg concentrations are reported to range from 1,000 to 18,000 ng/L in water from wells near the River Cooum in the Madras urban area, mainly exceeding the Indian drinking-water standard of 1,000 ng/L.

In some instances, Hg released from industrial operations results in contamination of soils at the site, but the soil characteristics are such that the Hg is sequestered or attenuated, and does not leach to groundwater, as found, for example, at a site in Trondheim, Norway (Saether et al., 1997). In other instances, Hg contamination of groundwater is noted locally near industrial sites. At a site in southern Germany where “kyanizing” (mercuric chloride (HgCl₂) used to preserve wood from decay) was performed, groundwater in a 1.3-km-long plume was found to be contaminated with Hg at concentrations that reached 230,000 ng/L (Bollen et al., 2008). HgCl₂ is extremely soluble in water, (7.4×10^{10} ng/L; O’Neil, 2006), and thus easily mobilized from inputs at the land surface to the water table.

Mercury has been used in munitions and for other purposes on military bases. This use has, in some cases, led to contamination of soils at the bases (Bricka et al., 1994); with the potential for further contamination of surface and groundwaters. Mercury contamination of soils, surface water and groundwater is found at a former military base in southern New Jersey, USA. The Hg content of soils ranged up to 555 mg/kg, and concentrations in some streamwater and groundwater samples exceeded 2,000 ng/L; determining whether the Hg derives solely from military activities is a part of ongoing investigations there (Barringer et al., 2012).

From the early-to-late 20th century, Hg was used in agricultural pesticides, but use of Hg compounds decreased substantially after 1970 in the USA (Murphy & Aucott, 1999). Mercurial compounds also were once used on golf courses in the USA, being most heavily applied in northern States to control snow mold. On a golf course in New Hampshire, USA, Estes et al. (1973) estimated that annual fungicide applications contributed 2.1 kg of Hg per hectare. In Australia, sugar-cane setts were treated with a fungicide containing methoxymethylmercury chloride before planting; concentrations of Hg from 30 to 670 ng/L were found in groundwater underlying cane cropland, but were interpreted as being within the range of naturally occurring Hg concentrations in area groundwater (Brodie et al., 1984). It is apparent that not all applications of Hg to soils result in groundwater contamination, but there are instances where Hg can be mobilized from soils to groundwater.

In the early to mid-20th century, phenylmercuric acetate was used in orchards; calomel and HgCl₂ were used on row crops; these are known to be used on sandy agricultural soils of the Coastal Plain of southern New Jersey, USA (Murphy & Aucott, 1999). Inputs of Hg would have been high if the federally recommended application rates of 3.4 kg/hectare for highly soluble HgCl₂ were followed (Barringer et al., 1997 and references therein). Mobilization of Hg from applications of mercurial compounds, enhanced by subsequent disturbance from residential development of the land, may be the cause of elevated Hg concentrations on groundwater downgradient from such sources. Water from wells completed in the quartz sand aquifer beneath the former agricultural land contains Hg at concentrations exceeding 2,000 ng/L (Barringer et al., 2005; Barringer & Szabo, 2006).

In addition to pesticides, Hg also could be introduced to soils via fertilizers. A commercial 20-20-20 fertilizer solution prepared according to manufacturer's directions contained 280,000 ng/L of Hg (Barringer & MacLeod, 2001). Mercury was measured in several common fertilizers, with the highest concentration (5.1 mg/kg) found in calcium superphosphate, and a lower concentration (1.2 mg/kg) in 15-5-5 Nitrogen-Phosphorus-Potassium (NPK) fertilizer (Zhao & Wang, 2010). Some States in the USA are acting to regulate the amount of metals permissible in fertilizers and other agricultural chemicals (e.g. ODA, 2002).

2.4. Effects of human activities on naturally occurring mercury

Seawater intrusion along coasts typically occurs because withdrawals of freshwater resources reduce the freshwater hydraulic head, allowing seawater to enter aquifers on land. In southern Tuscany, Italy, the high chloride concentrations brought in by seawater intrusion may have been responsible for mobilizing Hg in the geologic materials to groundwater, perhaps as a chloride complex (Grassi & Netti, 2000; Protano et al., 2000). In Sardinia, dewatering of a lead-

zinc (Pb-Zn) mine resulted in intrusion of deeper saline water that may have been responsible for increased Hg concentrations in shallow groundwater (Cidu et al., 2001). Experiments support these interpretations; Behra (1986) showed that elevated chloride (Cl⁻) concentrations mobilized Hg(II) in columns packed with quartz sand.

Contamination of soils, surface water and groundwater also arises from mining of cinnabar deposits. Mining of other metal ores has also resulted in Hg contamination, such as at the McLaughlin gold-mercury deposit in California (Sherlock, 2005), because of trace amounts of cinnabar or occurrence of Hg with other sulfide minerals. As a result of early 20th century copper mining activities along the Alaskan coast, USA, dissolved concentrations of Hg up to 4,100 ng/L were found in pore waters of sediments affected by mining waste (Koski et al., 2008). In a Canadian gold and silver mine, accessory cinnabar in waste piles oxidized and leached to groundwater, resulting in concentrations that ranged up to 150,000 ng/L (Foucher et al., 2012). Not all mining activities and mining waste disposal procedures result in extremely high levels of Hg in groundwaters, however; concentrations in adit water samples from an abandoned mercury mine in Turkey were still high relative to most waters, but ranged from 250 to 274 ng/L (Gemici, 2008).

The process of amalgamation of silver and gold with Hg was developed in the 16th century and used on an industrial scale into the 19th century in Central and South Americas, primarily to extract silver, and into the 20th century in North America for gold extraction (Nriagu, 1994). Elemental Hg was lost to the environment during the process; Hg losses during gold and silver extraction in the Americas are estimated to be about 240,000 Mg (Nriagu, 1994). Similar extraction activities have taken place in the Philippines, Indonesia, Thailand, Vietnam, Tanzania, and China (Lacerda, 1997), though the scale is not as great as in the Americas. Although some of this mining-activity-related Hg has volatilized, adding to the atmospheric Hg burden, much of it apparently still remains in the areas where metal processing took place. A few of these mining/extraction sites have been studied. In Tanzania and Zimbabwe, Hg sorption to iron-rich lateritic soils appears to have prevented groundwater contamination from Hg in tailings (van Straaten, 2000). Extreme surface-water loads have been documented from many of these mines including the Sierra Nevada gold mines in the USA (Domagalski, 1998), the Idrija Hg mine in Slovenia (Covelli et al., 2007), as well as Hg mining in Spain (Navarro, 2008) among others, with Hg sorption to iron-hydroxide-rich stream deposits a likely mechanism for Hg attenuation in some cases (Rytuba, 2000). Use of Hg in small-scale (artisanal) gold mining operations remains a substantial concern even today (Bradley & Journey, 2012).

3. Biogeochemistry of mercury: Field and experimental studies in soil and surface-water environments

3.1. Impact of mercury reactivity on transport

Oxidation-reduction, precipitation-dissolution, aqueous complexation, and adsorption-desorption reactions will strongly influence the fate and transport of Hg in groundwater, and

in the environment, generally. At the land surface, Hg participates in photochemical reactions (see the review of Zhang, 2006), but these reactions are not relevant to groundwater. Biogeochemical reactions in soils are of great importance to the fate and transport of Hg, however. Characteristics of soils, which include pH, carbon content, mineralogy, drainage properties, slope, and texture, all play a role in Hg retention or mobility and whether THg inputs to the land surface reach the water table. Concentrations of THg typically are higher in organic soil horizons than in the deeper mineral horizons because Hg typically is closely associated with organic matter (Amirbahman & Fernandez, 2012), and Andersson (1979) reports sorption to iron oxides (typical of some temperate-climate subsoils, and also tropical soils) at $\text{pH} > 5.5$. The reactions described below can occur in soils, in the surface-water environment, and, apparently, in groundwater as well.

3.2. Oxidation-reduction and sorption reactions

The three stable oxidation states of Hg in low-temperature aquatic systems are Hg(II), Hg(I) and Hg(0). The mercurous (Hg(I)) species is stable over a more limited range of conditions in sulfidic aqueous systems than it is when sulfur is absent (Hem, 1970). The Hg species vary in their solubility, complexation, adsorption (Stumm and Morgan, 1995) and their availability for microbial processes. Therefore, oxidation-reduction (redox) reactions will have a profound influence on Hg concentrations and mobility in groundwater. Both abiotic and biotic (primarily microbial) processes can drive Hg redox transformations.

Iron geochemistry is intimately associated with that of Hg. Anaerobic column experiments showed transport of Hg(II) retarded by sorption (as a Hg-Cl complex) to pyrite (FeS_2) (Bower, et al., 2008), and Hg(II) has been shown to sorb to iron oxides at $\text{pH} > 5.5$ (Andersson, 1979). Given a positive association of Hg with iron (Fe) in iron-hydroxide-rich sub-soils in the New Jersey Coastal Plain, USA, sorption of Hg to Fe hydroxides appears to be a mechanism for attenuating Hg (Barringer & Szabo, 2006). The same mechanism appears present at some mining sites (Rytuba, 2000; van Staaten, 2000), although formation of aqueous and solid-phase sulfides controls Hg(II) concentrations in tailings-contaminated sediments from California, USA, mines (Rytuba et al., 2005). Fe(II) hydroxides can be reductively dissolved by sulfide, resulting in the release of sorbed Hg. Experiments showed that, in the presence of sulfide (S^{2-}), Fe (III) was reduced and concentrations of dissolved Hg increased (Slowey & Brown, 2007). It appears that these and the experiments of Bower et al. (2008) were not done in the dark, however. Consequently, applicability of results to a groundwater setting is not clear.

Field examples also demonstrate that oxygen-depleted conditions caused by septic-system-effluent releases led to reductive dissolution of Fe hydroxides, resulting in release of sorbed Hg(II) (Barringer & MacLeod, 2001). Further, the Fe(II) generated in such a reaction may adsorb to minerals where it can then reduce Hg(II) to Hg(0) (Charlet et al., 2002). Recent experiments show that Fe(II) in minerals also can reduce Hg(II) to Hg(0). For example, in sealed, dark bottles, magnetite was found to reduce Hg(II) to Hg(0) within minutes (Wiatrowski et al., 2009; Yee et al., 2010). Mercury (Hg(II)) was also rapidly reduced in anoxic solutions by Fe(II) under varying pH conditions, with aqueous $\text{Fe}(\text{OH})^+$ being the species that best described the

electron transfer that occurred in the experiments (Amirbahman et al., 2012). Metals other than iron, such as tin, are also known to reduce Hg(II) to Hg(0) (e.g., Biester et al., 2000).

Natural organic matter has been shown to abiotically reduce Hg(II) to Hg(0) (Allard & Arsenie, 1991). Experiments under dark anoxic conditions by Gu et al. (2011) showed that dissolved organic matter (DOM) reduced Hg(II) to Hg(0) when low concentrations of DOM were present. At higher DOM concentrations, however, complexation with Hg inhibited Hg reduction reactions.

Microbially mediated redox reactions involving Hg also have been demonstrated. Hg(II) was reduced to gaseous Hg(0) by a *Pseudomonas* strain (Baldi et al., 1993). A newly isolated *merA*-carrying *Bradyrhizobium* bacterium recently was found by Wang et al. (2012) to also reduce Hg(II) to Hg(0). The recent work by Wang et al. (2012) shows that Hg inhibits denitrification in groundwater in direct proportion to the concentration of Hg.

3.3. Organic and inorganic complexation

Mercury (Hg(II)) can be present not only as Hg^{2+} , but as $\text{Hg}(\text{OH})_2$, HgCl_2 and other minor OH^- and Cl^- complexes, and in complexes with various organic anions, depending on pH, Eh, chloride concentrations and presence of DOM. Were DOM to be low or absent, then Hg could be present as hydroxide or chloride complexes in fresh waters (Reimers & Krenkel, 1974; Stumm & Morgan, 1995); at low to moderate pH and moderate to high chloride concentrations, chloride complexes would be most likely (Ravichandran, 2004). In the presence of dissolved sulfide, mercury-sulfide species may form (Benoit et al., 2001).

Mercury tends to form strong complexes with S^{2-} and, in DOM, Hg(II) binds preferentially to sulfur-containing functional groups such as thiols (Gabriel and Williamson, 2004; Ravichandran, 2004; Reimers & Krenkel, 1974). In anoxic environments, Hg can form complexes such as dissolved HgS , HgS_2^{2-} , $\text{Hg}(\text{SH})_2$, HgSH^+ , HgOHSH and HgClSH (Gabriel & Williamson, 2004). Although metals typically bind to acid sites (carboxyls, phenols, ammonium, alcohols, and thiols) in organic matter, Hg(II) binds preferentially with thiols and other reduced sulfur groups with which it forms strong covalent-like bonds. These sulfur-bearing groups are found in moderate abundance in organic matter in soils, in some surface water, and in wastewater (Hsu-Kim & Sedlack, 2003; Ravichandran, 2004). When the Hg/DOM ratio is high ($> 10,000$ ng Hg to 1 mg DOM), however, Hg also binds to the more abundant but less Hg-selective oxygen (ie., carboxyl) functional groups (Haitzer et al., 2002). Further, binding of DOM with Hg(II) is less strong at low pH than at high pH (Haitzer et al., 2003); this occurs because the extent of protonation of functional groups serving as Hg(II) ligands on DOM increases as pH decreases. Given the affinity of Hg(II) for thiol groups on DOM, it has been shown that DOM can dissolve cinnabar, inhibiting or preventing precipitation of metacinnabar and aggregation of HgS nanoparticles (Ravichandran et al., 1999; Reddy & Aiken, 2001; Slowey, 2010; Waples et al., 2005).

3.4. Microbial transformations

An important transformation of inorganic Hg involves its methylation to monomethyl- or dimethyl-mercury. Methylation of Hg(II) in soils and surface-water was found to be carried out under anoxic conditions by dissimilatory sulfate-reducing bacteria (DSRBs) (Gilmour et al., 1992). Dissimilatory iron-reducing bacteria (DIRBs) later were found to be able to methylate Hg(II) as well (e.g., Kerin et al., 2006). Populations of both DSRBs and DIRBs have been found to coexist in stream-bottom sediments where fine-grained sediments were “potential hot spots for both methylation and demethylation activities” (Yu et al., 2012).

Further, at low sulfate (SO_4^{2-}) concentrations, the methylating activity of SRBs is stimulated, but at high concentrations the methylating activity is inhibited because precipitated sulfides incorporate the Hg (Ullrich et al., 2001). Concentrations of SO_4^{2-} between 0.2 and 0.5 mM (about 19 to 48 mg/L) appeared to be optimum for promoting Hg methylation in freshwater (Gilmour and Henry, 1991). Barkay et al., (1997) discovered that high concentrations of DOM and salinity inhibited Hg(II) methylation because the Hg was complexed into forms that were not bioavailable to the methylating bacteria. The Hg in aqueous HgS complexes, which form in the presence of dissolved sulfide, was found to be bioavailable to the methylating bacteria, however (Benoit et al., 1999). Recent research shows that, although DOM can inhibit Hg bioavailability by complexing the Hg, DOM can also prevent HgS nanoparticles from aggregating, and thus the nanoparticles are bioavailable (Graham et al., 2012).

Mercury demethylation has also been studied in stream and lake sediments (e.g., Achá et al., 2011; Hintelmann et al., 2000; Pak & Bartha, 1998; Steffan et al., 1988). In experiments using sediments from southern New Jersey lakes, USA, Pak and Bartha (1998) showed that demethylation of MeHg is carried out by sulfidogenic and methanogenic bacteria, which are obligate anaerobes. Although the Hg methylation process was inhibited by low pH (4.4) conditions (which are common in southern New Jersey surface waters and groundwaters), demethylation of MeHg did not appear to be similarly affected for the pH range 4.4 to 8; inhibition occurred at $\text{pH} < 4.4$ (Steffan et al., 1988).

3.5. Colloids and particles

Extensive sorption of Hg(II) can limit concentration and mobility in groundwater unless the Hg(II) binds to colloidal solids under conditions where the colloids are stable and mobile. Colloids (particles $< 1 \mu\text{m}$ in one dimension (Kretchmaar & Schafer, 2005)) in waters provide transport for various contaminants and generally are sufficiently small so as to pass the $0.45 \mu\text{m}$ pore-size filters used by most researchers in collected filtered water samples. Because of their large surface area relative to their volume, small particles and colloids can provide many sorption sites for strongly sorbing contaminants whose mobility would otherwise be minimal through soils and aquifers. Such movement can be triggered by chemical or physical disturbance of soils and sediments. For example, Hg sorbed to particles was released to runoff from boreal forest soils following clear cutting and scarification (Porvari et al., 2003).

Colloids can be formed by clay minerals; oxides and hydroxides of iron, aluminum, and manganese; silica; humic and fulvic acids; carbonates; phosphates (Ryan & Gschwend, 1994),

also bacteria; and viruses (Kretchmaar & Schafer, 2005). Colloids are common in surface waters, soil and sediment porewaters. Colloids are found in groundwater as well. Changes in pH and redox reactions can cause dissolution or precipitation reactions that can form or release colloidal material. Examples are precipitation of colloid-sized minerals such as iron hydroxides when Fe(II) is oxidized, and oxides and carbonates that would precipitate at high pH.

In a southern New Jersey, USA, aquifer with Hg contamination, a study found colloids were more abundant in anoxic groundwater of an undeveloped area than in oxic groundwater (Ryan & Gschwend, 1990). The greater abundance likely occurred because iron hydroxide cements that bound clays to quartz-grain surfaces were being dissolved, liberating both Fe(II) and clay particles to solution (Ryan & Gschwend, 1994). With fluctuating water tables, some of the Fe(II) could be re-oxidized, forming colloidal precipitates.

In groundwater, colloids are subject to forces exerted by pumping. Sequential sampling of domestic wells in the unconfined aquifer system of southern New Jersey found that particulate Hg concentrations were commonly higher in first-draw water samples than in samples collected later during well purging (Szabo et al., 2010).

4. Background concentrations of THg in groundwater and groundwater/surface-water interactions

“Background” concentrations—that is—naturally occurring concentrations of THg (and MeHg) in groundwater probably depend upon ambient geochemical conditions, which would include pH that favors adsorption or desorption, presence and amount of Fe and DOM, and oxidizing or reducing conditions favorable to mineral precipitation or dissolution or microbial activities, including Hg(II) methylation. Absent known sources of contamination, background concentrations of THg in groundwater in several studies were found to be < 10 ng/L (Andren & Nriagu, 1979; Barringer & Szabo, 2006; Krabbenhoft & Babiarz, 1992; Kowalski et al., 2007). Total mercury concentrations in other groundwater studies, depending on filtration or lack thereof, ranged from <5 to 210 ng/L (Wiklander, 1969/1970; Reimann et al., 1999), with concentrations generally higher in unfiltered samples because of particulate material².

Relatively few studies have examined interactions between groundwater and surface water. In the Everglades swamp area in Florida, USA, groundwater pumping, dredging of canals, levee construction, and land subsidence have altered area hydrology (Harvey et al., 2002). In the surficial aquifer, THg, which is an element of concern because of severe MeHg impacts on Everglades biota, is recharged from surface water to groundwater, with higher concentrations (0.8 to 2.7 ng/L) tending to be in recharge from agricultural areas. Methylmercury (0.2 ng/L) was found only in groundwater recharged from agricultural areas and was not detected in groundwater elsewhere (Harvey et al. 2002). In a study of Hg inputs to Lake Superior, USA,

² An issue with studies of low concentrations of Hg historically has been sample contamination. Studies since the early 1990s have used sampling protocols that typically obtain reliable samples; e.g. Krabbenhoft and Babiarz, (1992).

however, groundwater was found to be an important source of MeHg to the lake, with concentrations as high as 12 ng/L in a hyporheic-zone sample (Stoor et al., 2006).

At a lake in glacial outwash (Wisconsin, USA), groundwater (sampled by piezometers and dug wells) both discharges to the lake and receives recharge from lake waters. Mercury enters from atmospheric deposition to the lake, and, apparently, through soils to groundwater. Mercury concentrations in groundwater discharge (mean 12 ng/L) to the lake was higher than that of water from nearby wells (mean 2.8 ng/L), showing the importance of reactions near and at the sediment/water interface (Krabbenhoft & Babiarz, 1992). In a New Jersey, USA, Coastal Plain watershed, groundwater discharging to a major river contained concentrations of THg in urban areas (some mainly in particulate form) that were higher than those in forested wetlands areas. Concentrations of THg in unfiltered water were 36 and 177 ng/L in discharge to the river at two sites in an urban area (Barringer et al., 2010a) and were not representative of background concentrations for that aquifer, which typically are <10 ng/L (Barringer & Szabo, 2006). Bradley et al. (2012) also found Hg in groundwater discharge to be an important input to a southern USA Coastal Plain stream, although the THg concentrations in the groundwater were an order of magnitude lower than the concentrations in urban groundwater discharge in the study of Barringer et al. (2010a).

5. Biogeochemical processes and mechanisms for mobilizing mercury in groundwater — Case studies

5.1. New Jersey Coastal Plain, USA

At more than 70 residential sites underlain by an areally extensive (7,770 km²) unconfined non-calcareous quartz sand aquifer system in the Coastal Plain of New Jersey, USA, water from domestic wells has been found to contain Hg at concentrations that exceed the State MCL of 2,000 ng/L. In the same aquifer system, background levels of THg in the groundwater in neighboring forested areas and unaffected residential areas are <10 ng/L (Barringer et al., 1997; Barringer & Szabo, 2006). This highly permeable system is vulnerable to contamination, with a water-table depth commonly less than 7 m below land surface. Past agricultural use of mercurial pesticides and atmospheric deposition are two likely sources of THg to the aquifer. Currently, about 700 wells are known to have withdrawn water containing THg at concentrations ranging as high as 80,000 ng/L (Dr. Judith Louis, New Jersey Department of Environmental Protection, 2010, oral commun.); the New Jersey Department of Environmental Protection supplies treatment systems or connections to public supplies for the affected households. A small number of public-supply wells have also been affected in urban/suburban areas (Fischer et al., 2010). Groundwater contaminated with THg was found in a similar Coastal Plain aquifer in the neighboring State of Delaware (Koterba et al., 2006).

Redox reactions were found to be important in explaining the mobility of Hg in the New Jersey Coastal Plain aquifer system. Septic-system effluent discharges, which were ubiquitous in the unsewered residential areas with Hg-contaminated well water, apparently drove redox

reactions that influenced THg mobility in the aquifer. Discharges with elevated concentrations of electron donors promoted reductive dissolution of Fe hydroxide coatings on subsoil and aquifer sediment grains and sorbed Hg (presumably as Hg(II)), was released to groundwater (Barringer & MacLeod, 2001; Barringer et al., 2006; Barringer & Szabo, 2006). Septage and leach-field effluent contained THg concentrations in the range <20 to 60 ng/L. Therefore the effluent is seen, not as a prominent source of Hg, but as a source of electron donors (or reduced solutes) capable of driving redox reactions, such as dissolution of Fe hydroxides and reduction of Hg(II) to Hg(0), that favor increased concentrations and mobility of Hg.

The THg in New Jersey groundwater is hypothesized to be mobilized from soils. The mobility of Hg in soils was tested during U.S. Geological Survey (USGS) studies by pulsed leaching of samples of disturbed subsoils with de-ionized water, with artificial road-salt solution and with 20-20-20 fertilizer solution. In all cases the Hg removed was particulate, and was associated with removal of particulate Fe, indicating that the most likely mode of transport for the THg from the mineral soil horizons was in association with Fe hydroxide particles (Reilly et al., 2012; Barringer et al., (2012)). In the Fe hydroxide-rich subsoils, the introduction of septic systems, and onset of reducing conditions in some instances provided the conditions for reductive dissolution of hydroxides and release of sorbed Hg(II) to the water table. From the water table, gradients toward numerous pumping domestic wells brought mobile Hg to levels in the aquifer where drinking-water supplies were impacted. The question then arises—in what form is the Hg mobile?

Although well-water samples were not analyzed for Hg(0) in the USGS studies in the New Jersey Coastal Plain, geochemical modeling results indicated that Hg in the groundwater could be reduced and that Hg(0) would be a likely species in the groundwater (Barringer & Szabo, 2006). The presence of Hg(0) in water from the Coastal Plain aquifer system has been shown by sampling at the military base mentioned previously, where reducing conditions are present in DOM-rich wetland areas (Barringer et al., 2012). As mentioned earlier, experimental studies have shown that reduction of Hg(II) to Hg(0) by sorbed Fe(II) is sufficiently fast to promote mobilization as Hg(0) (Amirbahman et al, 2012; Charlet et al., 2002). Because Hg(0) is slightly soluble in water (56,000 ng/L at 25° (O'Neil, 2006)), it is likely that, in parts of the aquifer system affected by effluent discharges, Hg(0) could form and be mobile as dissolved Hg within the aquifer.

Mercury in the New Jersey Coastal Plain aquifer also appears to be mobile in particulate and colloidal form. The differences between unfiltered Hg concentrations and filtered concentrations (passing 0.45- μ m pore-size filters) is large for some groundwater samples; the magnitude of this difference is interpreted as the concentration of particulates greater than 0.45 μ m in diameter (Barringer et al., 2006; Barringer & Szabo, 2006). The finding of Hg on particulates/colloids indicates presence of THg, either as oxidized Hg(II) or as reduced Hg(0) (Bouffard & Amyot (2009) sorbed to the mobile particles. Currently (2012) in New Jersey, the composition of the particulates is not known at the various residential Hg contamination sites—they could be Fe hydroxides (Ryan & Gschwend, 1990), clay minerals (Ryan & Gschwend, 1994), organic material (Hurley et al., 1998), mixed organo-oxide colloids (Chadwick et al., 2006), or sulfide particles (Slowey et al., 2005), depending on the geochemical environment in which they form.

The presence of particulates indicates that the dissolved THg concentrations measured in the New Jersey Coastal Plain groundwater represent only some fraction of the total pool of THg present in parts of the aquifer system

5.2. Nepal

An incidence of Hg in groundwater in Nepal bears some resemblance to the New Jersey Coastal Plain contamination. In Nepal, public supply wells, deep private wells, and shallow dug wells, hand pumps and spouts completed in gravelly unconfined and confined aquifers were sampled. Twenty-three of the samples from 31 sampling sites contained Hg at concentrations that exceed the WHO Guideline of 1,000 ng/L; the highest concentration measured was about 300,000 ng/L in water from a dug well in an urban area. Concentrations of nitrogen species (NH_3 and NO_3^-) and dissolved organic carbon (DOC) were particularly high in several of the well water samples (ammonia (NH_3), up to 62 mg/L as N; nitrate (NO_3^-), 25 mg/L as N; and DOC, 63.6 mg/L), and reducing (anoxic) conditions were apparent in the confined aquifer (Khatiwada et al., 2002). No suggestions as to the source of the Hg were given, but the elevated nutrient and organic carbon levels are suggestive of anthropogenic inputs such as sewage that either include Hg, or that mobilize naturally occurring Hg, presumably under reducing conditions.

5.3. Cape Cod, Massachusetts, USA

The importance of redox conditions in Hg release and mobility also is demonstrated in recent research at the USGS research site downgradient from the Massachusetts Military Reservation on Western Cape Cod. Land disposal of treated wastewater to the unconsolidated sands and gravels of the shallow aquifer from the 1930s to December 1995 resulted in development of a plume of contaminated groundwater that has been investigated since the early 1980s (LeBlanc, 1984). In addition to standard monitoring wells, the area affected by the plume has been instrumented with numerous multi-level samplers (MLS) (LeBlanc et al., 1991). These MLS allow collection of point samples from distinct biogeochemical zones, which would otherwise be difficult owing to steep vertical gradients in groundwater chemistry in the plume. An extensive suboxic zone with elevated nitrate concentrations and denitrification, and an anoxic zone with dissimilatory iron reduction (DIR) have persisted for more than 15 years following cessation of inputs from the source (Repert et al. 2006; Savoie et al., 2012). A recent study that examined Hg fate and transport within the plume found that $\text{Hg}(0)$ constituted > 50% of the Hg present in the DIR zone near the source. About 1-2 km downgradient from the source, the anoxic zone had essentially no dissolved iron, but concentrations of both ammonium (NH_4^+) and NO_3^- were high. Methylmercury comprised nearly 100% of the dissolved THg present in some samples from this region of the plume. Under the original infiltration beds, THg concentrations ranged up to about 200 ng/L (1,000 pM), but concentrations were rapidly attenuated with distance downgradient from the beds. Concentrations of dissolved THg in the oxic, uncontaminated groundwater, where pH values ranged from 5.0 to 5.6, were about 0.2 ng/L. The study shows there are at least two distinct redox environments and two different microbial regimes operating within the plume. However, the distribution of dissolved THg

suggests that downgradient from the source, dissolved THg has been mainly mobilized from the non-calcareous, quartzitic aquifer sediments rather than being transported long distances in the wastewater stream (Carl Lamborg, Woods Hole Oceanographic Institution & Douglas Kent, USGS, 2012, written commun.).

5.4. Maine, USA

Crystalline rocks can contain Hg that may become mobile. Mercury in water from domestic wells completed in fractured rock aquifers of the Waldoboro pluton complex in Maine, USA, exceeded the USEPA drinking water standard of 2,000 ng/L (Sidle, 1993). Most high Hg concentrations were found in water from granitoid rock aquifers that contain several joint sets as well as cataclasite-fault breccias zones and shear-mylonite zones. Mineral-rich pegmatite dikes follow one of the joint sets in the Waldoboro pluton. A few anomalously high concentrations occurred in water from wells completed in associated metamorphic rock aquifers (gneisses and amphibolites) of the Bucksport Formation.

The Hg content of the rocks varied substantially, from 0.005 to about 500 mg/kg, with a median content of 78 mg/kg. Mercury concentrations in well-water samples ranged from 40 to 6200 ng/L. Mercury in surficial sediments, which contained glacially-derived deposits, ranged up to about 0.100 mg/kg. The presumption is that the Hg derived from the geologic materials, and that the fracturing aided in transporting Hg-rich water through the aquifers. There were no other chemical data reported for the domestic wells, and therefore it is not clear whether natural weathering of the Hg-enriched rocks was the cause of the high THg levels measured in well water, or whether inputs of anthropogenic chemicals could have mobilized Hg from the geologic substrate.

5.5. Groundwater discharge to coastal areas

Largely within the last decade, researchers have turned to an examination of the impacts of fresh groundwater inputs on coastal waters. Groundwater that discharges to bays and estuaries has been found to contribute nutrients to coastal waters (e.g., Slomp & van Cappellen, 2004), and recent research has expanded to examine contributions of trace elements from this source. Within the past 5 years, at the volcanic island of Jeju, south of Korea, on the south coast of the English Channel at Caux, France, and along both east and west coasts of the USA, submarine groundwater discharge (SGD) of Hg and MeHg to estuaries and bays has been investigated (Black et al., 2009; Bone et al., 2007; Ganguli et al., 2012; Laurier et al., 2007; Lee et al., 2011).

Mass balance indicated that Hg in SGD at Jeju Island constituted 34 and 67% of the total Hg annually in waters of two bays, whereas atmospheric deposition contributed from 23 to 25% of the Hg. Methylmercury in SGD at the island also constituted the majority of MeHg in the coastal waters (Lee et al., 2011).

At Waquoit Bay in Massachusetts, USA, sampling of SGD showed that Hg concentrations in groundwater ranged from <0.64 ng/L to 52.4 ng/L, and that daily discharge of Hg was from 94 to 380 ng/m² (Bone et al., 2007). Further, total dissolved Hg and DOC were not correlated, a

lack of relation that was also observed in some of the New Jersey, USA, Coastal Plain studies, particularly at THg concentrations much higher than those found in waters discharging to Waquoit Bay.

At Caux, France, the Hg concentrations in tissues of blue mussels (*Mytilus edulis*) were higher than elsewhere along the coast, prompting an investigation of Hg in SGD. Although the total Hg concentrations were not greatly elevated at Caux (a mean of 0.73 ng/L), they were higher than in the nearby industrialized Seine estuary (mean of 0.32 ng/L) and the dissolved Hg likely represented a source of bioavailable Hg to the mussel population. Dissolved MeHg concentrations at Caux constituted from 2.4 to 7.8% of the total Hg present in SGD (Laurier, et al., 2007).

On the west coast of the USA, north of San Francisco, SGD contributed from 0.24 ng/L to 5.7 ng/L to California coastal waters; the Hg concentrations were significantly correlated with NH_4^+ and silica (SiO_2) (Black et al., 2009). Farther south, at Malibu Lagoon, SGD also transported Hg and MeHg to coastal water. Mixing between groundwater and seawater was inferred. MeHg concentrations in seawater increased at low tide, as did filtered Hg concentrations; inputs from SGD were thought to change Hg partitioning and solubility in the seawater (Ganguli et al., 2012).

6. Conceptual model for processes influencing mercury fate and transport in groundwater

Overall, the studies of the Hg-contaminated groundwater in New Jersey and Cape Cod, in particular, have provided opportunities to investigate mechanisms for releasing Hg from the land surface to the water table, and to suggest further avenues to explore biogeochemical reactions that mobilize Hg from the subsurface and within aquifers. A conceptual model for Hg mobilization has been developed by New Jersey researchers (Reilly et al., 2011) and is shown in figure 2.

Mercury, either naturally occurring, of anthropogenic origin, or both, is released to the water table as Hg(II) from surface soils and subsoils by weathering or by inputs of anthropogenic chemicals such as road salt or fertilizers, or by subsurface inputs of septic-system effluent. Under oxidizing conditions, dissolved THg is mobile as a complex with DOM, and sorbed Hg(II) is mobile on Fe hydroxide particles. Effluent discharges provide electron donors and sorbed Hg(II) is released as Fe hydroxides reductively dissolve, and Hg(II) may be reduced either by DOM or by Fe(II). Where anoxic conditions are present, sulfate reduction is an important terminal electron accepting process, and methylation may take place. Additionally, sulfides may precipitate, removing Hg from the aqueous phase. Hg(0) may be re-oxidized to Hg(II) should groundwater become more enriched in oxygen farther down a flowpath.

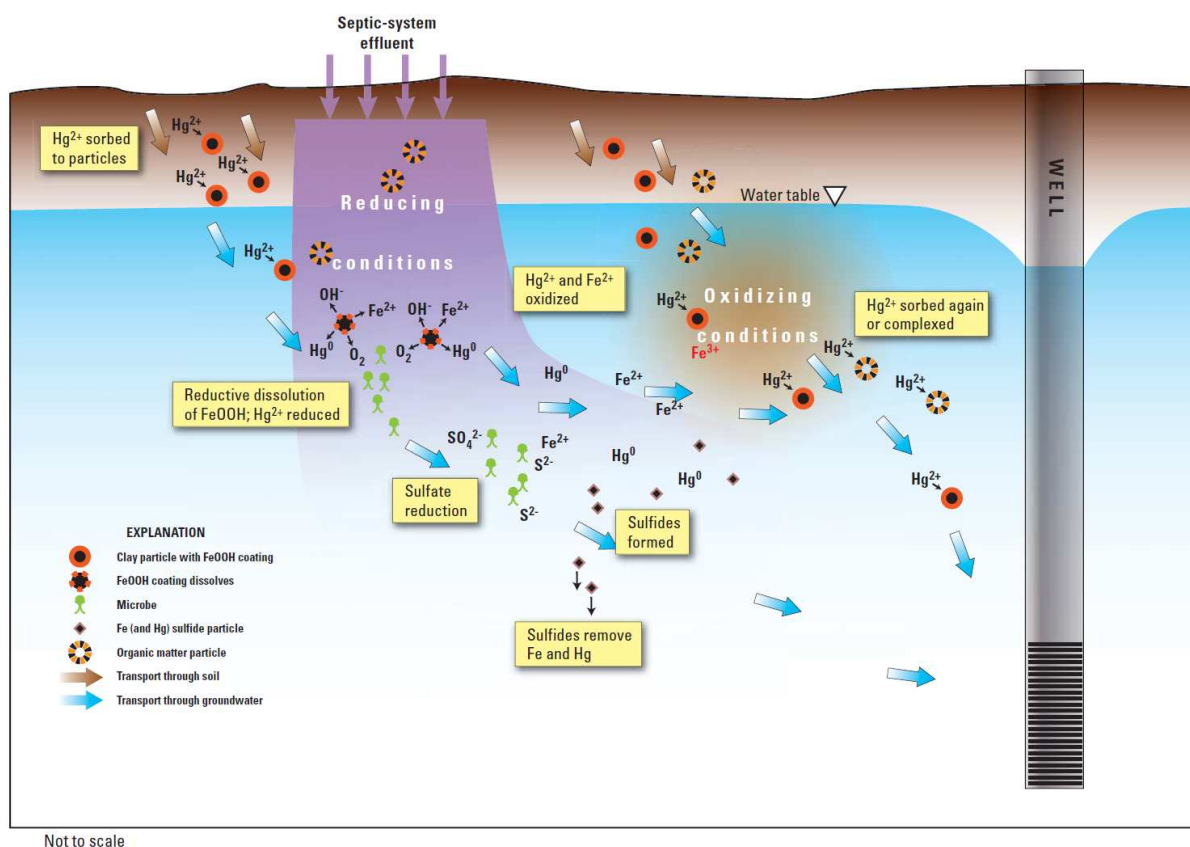


Figure 2. Mobilization of mercury from land surface to groundwater and biogeochemical transformations along flow paths in an unconsolidated sandy, acidic aquifer.

7. Conclusions

Mercury is relatively rare compared to most other elements, but owing to its toxicity at low concentrations, Hg is an important potential contaminant. There is a large reservoir of inorganic Hg in the environment—much of it derived from human activities, most associated with industrialization. Some of that Hg enters freshwater supplies where conditions may be conducive to methylation and thus the production of MeHg that readily bioaccumulates. Relatively less Hg is mobilized to groundwater than to surface water, in part because Hg can be attenuated by sorption to clays, iron oxides, and residual soil organic matter. Studies of the fate and transport of Hg in the subsurface are beginning to reveal how transport from land surface to groundwater might occur and how Hg remains mobile within aquifers.

In none of the above studies of Hg discharge to coastal waters have the sources of the Hg in SGD been identified, nor have the mechanisms for maintaining Hg mobility in groundwater discharging to the coasts been discerned. Given the recent discoveries of Hg and MeHg inputs from SGD, there clearly are avenues for further investigations into this phenomenon. Uptake into estuarine biota in the biodiverse and biomass rich estuarine and coastal waters is of key concern for these sensitive ecosystems and for human health, given the great potential for biomagnification. The importance of groundwater inputs thus cannot be ignored.

Studies in New Jersey and Cape Cod, USA, have investigated processes leading to Hg mobility in groundwater in settings that involve inputs from sewage to the subsurface. Given that sewage effluent contains materials that can fundamentally alter biogeochemical environments, mobilization of metals such as Hg, whatever their origin, may be an ever increasing process as humans continue to develop their surroundings. It is hoped that the research, past and ongoing, that is discussed herein will be of use to readers who seek to understand, to prevent, or to mitigate Hg contamination of groundwater supplies.

(Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.)

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