AVAILABILITY OF ATMOSPHERICALLY DEPOSITED MERCURY TO RUNOFF AND RECEIVING WATERS

Mark C. Gabriel Derek G. Williamson Robert Pitt Department of Civil and Environmental Engineering The University of Alabama, Box 870205 Tuscaloosa, Alabama 35487

ABSTRACT

Current practice in estimating mercury runoff from the watershed in TMDL analysis assumes much of the atmospherically deposited mercury is available for transport to receiving waters; such estimates are overly conservative, and do not reflect the complex nature of mercury surface reactions. The time-dependence of mercury washoff is critical in assessing the variable availability of mercury to the receiving waters. This review illustrates the importance of the relationship between mercury deposition and runoff efficiency for common watershed surfaces. With such fundamental information, better quantitative estimates of mercury loading to marine/freshwater bodies, design of runoff control practices, and land use planning can be developed.

The recent emphasis on mercury depositional impacts on water quality has taken a number of forms including: generating of mercury TMDLs, strengthening a variety of Clean Air Act mercury source regulations, and developing relatively extensive depositional monitoring and modeling programs. However, there has been very little research examining the role of the terrestrial watershed in terms of determining the availability of atmospherically deposited mercury to receiving waters. More specifically, how the biogeochemical characteristics of terrestrial surfaces and dry/wet weather events effect the temporal variation of mercury concentration and chemical form in surface runoff. On the contrary, most TMDLs make the assumption that all mercury deposited on the land surface will be transported through the watershed and into receiving waters. Mercury is deposited onto the watershed through both wet and dry deposition processes and as both reactive gaseous mercury and particulate mercury. To assume uniform availability of all forms of deposited mercury ignores photochemical and biogeochemical processes that will impact mercury fate in the watershed. Transformation processes occurring within the watershed will certainly modify the temporal patterns between mercury deposition onto the watershed and mercury loading into the receiving water. A mass balance approach that accounts for terrestrial transformation processes to determine how much deposited mercury actually washes off into surface water is needed.

Characterization of stormwater runoff has indicated that even hard surfaces (such as pavements and concrete), may retain a significant fraction of heavy metals and prevent

transport in runoff (Pitt, 1987). This lack of availability is especially true for particulate bound toxicants. As vegetated or permeable surfaces are considered, it is possible for the watershed to act as a permanent sink for a portion of the deposited mercury.

The purpose of this review is to illustrate that the availability of atmospherically deposited mercury is a function of watershed characteristics including: terrestrial sorption properties, surface water chemistry, rainfall intensity, antecedent dry weather periods, and photochemical reactions. Using this information and applying it to the interaction of surface types (i.e., paving and vegetation) with deposited mercury during wet/dry weather cycles will allow an estimate of mercury runoff from land cover to receiving waters in a multi-use watershed.



Watershed, mercury transport, terrestrial surfaces, speciation

INTRODUCTION

Mercury contamination from a variety of point and non-point sources, including atmospheric inputs is currently considered the most serious environmental threat to the well being of fish and wildlife resources in the many regions of the United States (Facemire *et al.*, 1995; Mason *et al.*, 1994). More than 16% of all impaired waters in the U.S. on the EPA's section 303(d) list are from mercury contamination (USEPA, 1999). The EPA's section 303(d) list is enforced by the Clean Water Act which requires each state to periodically prepare a list of all surface waters in that state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years. Waters placed on the 303(d) list require the preparation of Total Maximum Daily Loads (TMDLs), a key tool in the work to clean up polluted waters. TMDLs identify the allowable annual total load to an individual source that will result in attainment of the applicable water quality standard (USEPA, 2001A).

The EPA's Receiving Watershed Protection Program currently places mercury in the top 10% of all toxicants that produce impairment to surface waters (USEPA, 2001). As an example, the state of Alabama has 559 acres of impaired surface waters due to mercury alone (USEPA, 2001).

Most U.S. states receive mercury contamination from atmospheric deposition, except for a few locations near major point sources (i.e. hazardous waste combustors) (Bonzongo *et al.*, 1998). As a result, atmospheric deposition is listed as a major source in mercury TMDLs. Current US atmospheric mercury deposition estimates are illustrated in Figure 1.

Figure 1: National atmospheric mercury deposition; USEPA, 1998



BACKGROUND

Mercury Toxicity and Current levels

The issue that drives mercury policy is methyl-mercury bioaccumulation in fish and subsequent fish consumption by humans. The adverse human health effects due to methylmercury have been well documented within the last 30+ years. Methyl-mercury is a neurotoxin and affects the central nervous system (Bonzongo et al., 1998; Lindqvist et al., 1985). Brain damage is the primary adverse affect imposed upon animals and humans (non-infants) from mercury toxicity (Clarkson, 1992). Mercury concentrations above levels that could pose a health risk have been measured in predatory fish from many rivers in the United States (Bonzongo et al., 1998; Facemire et al., 1995). In response, many states have fish advisories for mercury. Many states are particularly vulnerable to mercury contamination in aquatic food chains due to the coexistence of natural (i.e. geologic deposits, volatilization from the ocean) and human-imposed (i.e. chlor-alkali facility) conditions often hypothesized to favor methyl-mercury production. (Bonzongo et al., 1998; Ward et al., 1992; Oremland et al., 1995; Rudd, 1995; Saint Louis et al., 1994, Saint Louis et al., 1996). For instance, in Alabama, total mercury concentrations above the U.S. Food and Drug Administrations safe limit (1 micro-gram/gram wet weight) have been found in some fish species in both Fish River and Mobile Bay (Cooner, 1998). Sediment mercury concentrations as high as 7,500 mg Hg/kg- sediment have also been found adjacent to chlor-alkali facilities (Facemire et al., 1995).

Global Cycling of Mercury

The cycling of mercury through the environment is complex. The current problems associated with mercury in air are largely due to anthropogenic influences. The largest anthropogenic source of mercury, flue gas emissions, generally contains mercury equally divided between two oxidation states, elemental (Hg⁰) and inorganic (Hg²⁺), which is commonly known as reactive gaseous mercury (Lindberg and Stratton, 1998). But due to its high volatility, more than 98% of atmospheric mercury exists as Hg⁰ (Lodenius, 1998; Lindqvist, 1985; Mason *et al.*, 1994). Mercury may be associated with particles or occur as a gas. Pertinent atmospheric processes involve photochemical oxidation of Hg⁰ to Hg²⁺ and reduction of Hg²⁺ to Hg⁰. Atmospheric reduction of Hg²⁺ to Hg⁰ is largely mediated by a reaction with SO₂ (g) or SO₃²⁻ (aq) (Lindberg and Stratton, 1998).

In aquatic systems Hg^{2+} can be reduced to Hg^{0} which is then reemitted to the atmosphere or Hg^{2+} can be methylated to $CH_{3}Hg^{+}$ by microorganisms i.e. sulfate reducing bacteria (Compeau and Bartha, 1985; Watras *et al.*, 1995). Either of these two inorganic forms (Hg^{2+} , $CH_{3}Hg^{+}$) can be removed from the water column and into sediments. In soil environments, mercury is largely fixed in the surface of the soil. (Andersson, 1979; Kim, *et al.*, 1997; Zyrin, 1983). Most mercury in soil is bound to organic matter, therefore, mercury's transport is largely a function of organic material transport (Iverfeldt, 1994). Estimated mobility for mercury in some soil systems is 1-6 µg m⁻²yr⁻¹ (Kim *et al.*, 1997). Transport of mercury through soils at this rate along with atmospherically deposited mercury can be a significant input to aquatic systems. There can be a wide variety of chemical forms of mercury in soil. Three main forms are $Hg(OH)_2$, $HgCl_2$, and HgS(cinnabar) (Kim *et al.*, 1997).

MERCURY IN TERRESTRIAL ENVIRONMENTS

Terrestrial soils are possibly the most significant contributor of mercury to surface water. (Mason et al., 1994). Because soils are a sink for atmospherically deposited mercury, soil mercury levels are increasing and may continue to serve as a long-term source of mercury to surface waters (Johansson et al., 1991). Atmospherically deposited mercury is very effectively fixed in the uppermost layers of soil (top 4 inches) where organic content is high (Andersson, 1979; Kim, et al., 1997; Zyrin, 1983). Mercury may be tightly bound for many years in soil and is slowly transported out (Johansson et al., 1991). In many ways, the top layer of soil may be regarded as a filter. As mercury percolates downward with precipitation it is filtered out. Since most of the soil mercury is organically associated, the organic content of the soils plays a dominant role in the transport of mercury to surface waters (Johansson and Iverfeldt, 1994). The predominant mercury form in acidic soil is $HgCl_2$ and in basic to neutral soil $Hg(OH)_2$ is the predominant form (Kim *et al.*, 1997). These two forms and all others are usually associated with organic and inorganic ligands (Jackson, 1998). The sorption characteristics of soils can also be different for various mercury forms. For instance, it has been shown that sorption of CH₃HgCl and HgCl₂ have different sorption capacities for different soils (Hogg et al., 1978; Biester and Scholz, 1997). The sorption capacity of two different soils differing in clay and organic matter were lower for CH₃HgCl than for HgCl₂. As with many metals, increased transport of mercury occurs through the catchment during high precipitation due to erosion (Johansson *et al.*, 1991; Babiarz *et al.*, 1998).

Even though mercury is a principle metal of concern in urban runoff (EPA, 1983), there is limited research on the sorption of mercury for asphalt/paved surfaces aside from large-scale analyses that considered land use type. Most of the previous research involving the transport of metals on paved surfaces analyzed washoff of toxic metals, such as copper, aluminum, and chromium, during storm events from urban areas (Pitt *et al.*, 1995). These studies concluded that metals are bound to street and parking area particulates and concentration of metals in runoff correlate with sediment concentration. An increase in particle concentration has also been seen to correlate with increased metal concentration (Wilber and Hunter, 1980). In terms of temporal variation with precipitation, metal concentration positively correlates with the peak runoff (Heaney, 1978).

Sorption and Desorption

 Hg^{2+} is rapidly and efficiently removed from solution through sorption by fine suspended matter and sediments (Jackson, 1998). As a rule of thumb, the finest particles, e.g. colloidal clay sized, have the highest sorption capacities. The most important sorbents for mercury are clay minerals, amorphous oxides, hydroxides, oxyhydroxides of Fe, Mn, and Al (i.e. FeOOH), particulate humic substances, and non-humic organic matter (i.e. plankton and biofilms). Out of the above, oxides and humic matter have the highest sorption capacities for Hg^{2+} . Clay minerals follow after oxides and humic matter (Andersson, 1979; Schuster, 1991; Jackson, 1978; Reimers and Krenkel, 1974; Andersson, 1979). The sorption capacity of the three main clay types for mercury are as follows: illite > montmorillonite > kaolinite (Jackson, 1998). Mercury can also be scavenged by co-precipitation with iron sulphide (FeS) (Inoue and Munemori, 1979). Hg²⁺ is most efficiently sorbed by minerals at moderately acidic to neutral pHs and is poorly sorbed under extremely acidic or alkaline conditions (Jackson *et al.*, 1998). Previous work suggests that $HgOH^+$ and $Hg(OH)_2$ are the most efficiently adsorbed species in sediments and soils due to their efficient binding characteristics over a wide range of pHs (Hahne and Kroontje, 1973; Shuster, 1991; Feick et al., 1972; Kinniburgh and Jackson et al., 1978; Chen et al., 1995). Yet, due to their high abundance and polarizing ability, Cl⁻ ions commonly interfere with the binding of the above two and various Hg²⁺ forms with natural sorbents in soil or sediment media. Cl⁻ ions have been seen to release Hg^{2+} ions from binding agents and form stable complexes with the Hg^{2+} ions (Jackson et al., 1998).

Transport and Availability Parameters: Terrestrial Production of Methyl-mercury

In terms of human health risk, the most important form of mercury is mono-methylmercury (CH_3Hg^+) (Jackson, 1998). The case for its importance is due to its high lipophilicity (high fat solubility), which allows it to be easily transported throughout the body (Clarkson, 1992). After long-term exposure to elevated methyl-mercury concentrations in the water column, it is bioaccumulated in fish muscle tissue. Mercury then makes it way up the food chain to humans through fish consumption (Gilmour and Henry, 1991).

Factors controlling mercury speciation in the aqueous environments include: pH, dissolved organic carbon (DOC), suspended particulate matter, colloids, ionic strength and dissolved oxygen (Babiarz *et al.*, 1998; Winfrey and Rudd, 1990). All of these parameters play significant roles in mercury speciation, but DOC and pH are the dominant parameters, therefore they will only be discussed. In many ways, pH and DOC dictate the severity of mercury contamination to a water body (i.e. methyl-mercury formation). DOC and pH are directly related to precipitation and surface type. For instance, the frequency of precipitation and soil type determine the amount of DOC in surface water. High intensity rainfall mixed with soil containing a high organic content results in an increased DOC load to water bodies. Precipitation and soil type also strongly dictate the pH in runoff. For example, existing sulphide compounds in soil and acid rain, by themselves or together, will result in low pH surface water.

In the water column, increased levels of DOC result in lower methyl-mercury formation (Winfrey and Rudd, 1990). The suggested reason for this is that inorganic mercury will bind to DOC ligands, therefore, rendering it unavailable for methylation (Gilmour and Henry, 1991; Barkay *et al.*, 1991). There have been numerous studies that show a strong correlation between mercury and/or methyl-mercury and DOC (i.e. humic matter) and particulate matter in catchment water runoff (Lee and Hutlberg, 1990; Discroll *et al.*, 1995; Johansson *et al.*, 1991). This correlation is observed due to the strong complexation between organic compounds and mercury forms. In many cases mercury will bind and settle out with particulate organic matter. For this situation, methyl-mercury production and later bioaccumulation in the food chain might actually be hindered (Discroll, *et al.*, 1995). Fluctuations in pH may also affect methyl-mercury production and subsequent uptake. When pH is deceased, the increased amount of protons displace Hg^{2+} from binding sites. This then results in free Hg^{2+} that is available for methylation (Lee and Hutlberg, 1990).

There is limited data on the production of methyl-mercury in soils (Kim *et al.*, 1997). Although, a few investigations have demonstrated the production of methyl-mercury in the catchment by the activity of bacteria and fungi in soil (Bringmark, 1997). In many cases, riparian zones were the sites for the high methyl-mercury production. (Lee *et al.*, 1995). An area of terrestrial methyl-mercury production that has been studied extensively is flooded soils. (Kim *et al.*, 1997; Rudd *et al.*, 1992; Louis *et al.*, 1994, Grondin *et al.*, 1995; Winfrey and Rudd, 1990). The anoxic conditions flooded soils produce are ideal for methyl-mercury production by sulfate reducing bacteria (Henry and Gilmour, 1991). In almost all cases, significant methyl-mercury concentrations were found near the soil/sediment –water interface of flooded soils (Winfrey and Rudd, 1990). Aside from this, there still is limited data on the production and transport of methyl-mercury in non-flooded soils (Kim *et al.*, 1997). As a result, it is generally regarded that more research on is needed the fate and production of methyl-mercury in soils (Kim *et al.*, 1997).

CURRENT UNDERSTANDING OF THE TRANSPORT AND AVAILABLITY OF MERCURY IN THE WATERSHED

The majority of mercury deposited from atmospheric sources has its ultimate fate on terrestrial surfaces of watersheds (Mason et al., 1994). Mason et al. 1994 indicated that that 60% of all mercury deposition occurs on terrestrial environments. This is significant considering the terrestrial environment only makes up 30% of the earths surface. The suggested reason for this is that oxidation of mercury in the abundant terrestrial aerosols sequesters mercury rapidly thereby enhancing deposition. In some cases, 75% of the total mercury load to surface water comes from runoff from the catchment (Johanesson et al., 1991). And of this percentage, significant concentrations of methyl-mercury have been observed (Lee and Iverfeldt, 1991; Lee and Hutlberg, 1990; Winfrey and Rudd, 1990, Rudd, 1990). Current practice in estimating mercury runoff from the watershed assumes all atmospherically deposited mercury is available. For example, the mercury TMDLs developed for the Southeast U.S. use a combination of three watershed models to determine the fate and transport of mercury to surface water. The three models are as follows: WASP5, the toxic chemical program TOXI5, and the Watershed Characterization System (WCS). The WASP5 and TOXI5 models are used to simulate mercury in the main stem of surface water (i.e. river). The combined simulation of WASP5 and TOXI5 account for biochemical processes such as Hg²⁺ and CH₃Hg⁺ portioning to solids and DOC, oxidation of Hg^0 , sunlight driven reduction of Hg^{2+} and demethylation of CH_3Hg^+ . and methylation of Hg²⁺ (USEPA, 2001B). These two models account for a large portion of the biochemical mercury processes that occur in the environment but they are only simulated for the main stem and sediment layer of the water body (USEPA, 2001B). The WCS model is used to simulate transport of mercury strictly from the terrestrial watershed. The main driving force of this model is the input of appropriate wet and dry deposition rates for mercury using a comparison between the RELMAP model results as reported in the Mercury Report to congress and the Mercury Deposition Network (MDN) from sample collection sites (USEPA, 2001A). This model calculates the total mercury load as a percentage of the contribution from soil/erosion, runoff, direct deposition and impervious areas. However, the source for its determination is only based upon physical/ hydrological properties of the terrestrial watershed and do not account for the biogeochemical constituents that can significantly alter the temporal variation of mercury concentration from the terrestrial watershed (USEPA, 2001B; Greenfield, 2002). Only assuming physical/hydrological properties can be quite misleading because surfaces in watersheds (i.e. pavement and grass covers) have tremendous chemical sorption capabilities for metals (Kim et al., 1997; Legret and Colandini, 1999). Mercury released from these surfaces can be quite variable through time especially when accounting biogeochemical properties and dry and wet weather cycles. Some estimates show that only 30% of atmospherically deposited mercury actually washes off from terrestrial soils into surface water (Mason et al., 1994). Even hard surface covers have shown the ability to retain between 10-97% of deposited heavy metals; therefore, much less than 100% of the deposited metals may be available to runoff into receiving waters (Pitt, 1987 and 2002).

The US national effort of curbing atmospheric deposition through reducing atmospheric emissions is under way, although, the fate of mercury already present in both sediments and watershed soils remains poorly understood (Kim *et al.*, 1997). There has been very little research, if any, examining the sorption properties of various terrestrial surfaces for total and speciated forms of mercury. Therefore, more research is needed on how mercury is transported through the watershed (Warner, 2002). In many cases, even the science of deposition is still poorly understood. For instance, a recent study in the Florida Everglades indicates that percent of deposited mercury was not only a function of proximity to the source but also of surrounding climate. In addition, global contributions to deposition were seen to outweigh local contributions. This is surprising because it is generally regarded that local source emissions have the largest influence on deposition. As a result of cases such as this, it is generally regarded that more research is needed on atmospheric deposition of mercury and its succeeding fate in the watershed (Guentzel, 2002).

Most of the research involving mercury transport through the watershed has dealt with large-scale analyses where concentration trends have been examined for different land uses and variation from seasonal change (Khalil *et al.*, 2002; Shaley *et al.*, 2002; Krabbenhoft *et al.*, 1995; St. Louis *et al.*, 1996; Sartor and Boyd, 1972; Scherbatskoy *et al.*, 1998; Lawson *et al.*, 2001). Many of these studies only concentrated in certain parts of the country such as Florida Everglades, upper Mid-west, and the Chesapeake Bay Region. (Bonzongo *et al.*, 1998; Vaithiyanathan *et al.*, 1996; Hurley *et al.*, 1998; Guentzel, 2002). In many cases, the sites for these studies were surrounded by sparsely populated areas. Such studies provide invaluable information, but to better assess mercury contamination more research needs to be done in within urban environments.

Surface Water Susceptibility to Mercury Contamination From Terrestrial Runoff

Short periods of high intensity rain are a common occurrence in the U.S., especially during the warmer months in the Southeast. Common effects of the high intensity rain are flooding and excessive erosion. These, as described above, can greatly effect methylmercury production through variation in DOC levels and pH. Typical soil cover for many regions of the US, especially the southeast, involves some clay derivation (Mitchell and Meetze, 1990). As mentioned above, clay can have tremendous adsorption capacities for metals including mercury. This can be beneficial for a region because this can filter out much of the atmospherically deposited mercury on land and retain it in the soil for many years. But during high intensity rainfall, the mercury that has accumulated over long periods of time from dry and moderate intensity wet deposition can be sheared off with terrestrial sediments and be transported through the watershed eventually reaching surface water (Babiarz, et al., 1998). This can pose severe bioaccumulation problems because high concentrations of mercury can be washed off into surface water and bioaccumulate in fish. Even though this is an excepted phenomenon of terrestrial mercury, there are still no detailed studies documenting the washoff properties of speciated mercury forms as a function of variable wet weather events.

It is well known that abiotic speciation of mercury is largely a function of photochemical reactions on land, water, and in the atmosphere (Iverfeldt and Lindqvist, 1986; Lindqvist, 1985; Alberts, *et al.*, 1974, Xiao, *et al.*, 1995). Due to these sunlight-driven reactions, demethylation and reduction of Hg^{2+} can take place. Demthylation and Hg^{2+} reduction further prevent bioaccumulation of methyl-mercury in fish. Baughman *et al.*, 1973 indicated that CH_3Hg^+ complexes may be broken down abiotically to inorganic Hg^0 and other products by photochemical reactions on exposure to sunlight at > 290 nm or UV light at the earths surface. In almost all cases, this process is overlooked when modeling mercury transport to surface water (Kim, *et al.*, 1997). Possible outcomes of neglecting photochemical reactions of mercury form. Up till now very few studies have been conducted on the volatilization of mercury (Hg^0) from soils under field conditions (Johnson and Lindberg, 1995). Many authors suggest that Hg^0 volatization from soils is temperature dependent (Sigel and Sigel , 1988; Xiao *et al.*, 1991; Lindberg *et al.*, 1979).

NEED FOR FUTURE WORK

Mercury's chemical transformation, fate, and transport in atmospheric and aquatic environments have been thoroughly scrutinized for many years. But clearly the link between these two reservoirs, i.e., terrestrial environments, have not received as much attention. In many cases, the terrestrial portion is 95% or more of the watershed surface area. And previous research has found that the size of the terrestrial catchment area greater affects the amount of methyl-mercury accumulation in surface water (Mason *et al.*, 2000; Lee and Hultberg, 1990). This ultimately, stresses the importance of the terrestrial environment during the transport of mercury through the watershed.

With respect to the current knowledge on mercury transport through the watershed, the factors that need further development in the study of mercury transport through the watershed are (1) the chemistry of mercury in soils, especially concerning methyl-mercury production (2) photochemical volatilization dynamics (3) washoff as a function of various weather events (4) mercury deposition and (5) the transport of mercury within soil.

As a result of the lack in information in these areas, current limitations exist in TMDL methods of determining mercury transport to surface water. Some of these limitations arise in estimating temporal variability of mercury fluxes to surface water, runoff efficiency, and the primary mercury form as the total mercury load enters surface water. For example, as already mentioned, current Southeast TMDL methods for determining total mercury concentration from non-point source runoff uses the Watershed Characterization System (WCS). The complexity of this loading function model falls between that of a detailed simulation model, which attempts a mechanistic, time dependent representation of pollutant load generation and transport, and simple export models, which, for example, do not represent temporal variability (USEPA, 2001A). But by not representing temporal variability possible over or underestimates of mercury load to surface water could occur.

CONCLUSION

By understanding how biogeochemical characteristics of terrestrial surfaces (i.e., paving and vegetation), their interaction, and dry/wet weather events effect the temporal variation of mercury concentration and chemical form in surface runoff, better estimates of mercury runoff from land cover to receiving waters in a multi-use watershed can be determined. By doing this, a mass balance can be determined on how much deposited mercury actually washes off into surface waters and is available (i.e. for methylation). This, as already stressed, will develop modeling techniques (i.e. application of more realistic runoff coefficients), improve Best Management Practices (i.e. stormwater control practices), and also allow accurate assessments of potential human health problems.

Determining the primary mercury form in runoff prior to its discharge to receiving waters would also be beneficial because this estimate can provide tremendous information on methyl-mercury bioaccumulation potential in fish and aquatic life. These estimates will eventually aid in design of runoff control practices, such as properly designed drainage systems that have better control of sediment runoff.

In addition, with the information that comes from mercury's transport through watershed surfaces, a variety of Clean Air Act mercury source regulations can be strengthened, existing depositional monitoring and modeling programs can be developed, and ultimately, the understanding of mercury cycling through the watershed can be improved.

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