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*Environmental Assessment Program*

**Technical Memo**

July 29, 2015

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SUBJECT: **Technical Memo: Statewide Atmospheric Deposition Review and Scoping Study**

**EA Activity Tracker Code: 15-041**

**Overview**

Determining the influence that atmospheric deposition of toxics has on surface water quality in Washington State is the impetus for this study. It is a desk study that summarizes the state-of-the-science on the atmospheric deposition of toxics in Washington. A second goal of the study is to outline the necessary scope of a field study to quantify atmospheric deposition at different geographic scales. There are three geographic scales addressed here, roughly defined as local (urban site or reach of a stream), regional (stream or river watershed), and statewide.

Please find the technical memo in the following pages.

# **Statewide Atmospheric Deposition of Toxics Review and Scoping Study**

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Project: 15-041

July 2015

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## 1. Summary

Determining the influence that atmospheric deposition of toxics has on surface water quality in Washington State is the impetus for this study. Information about atmospheric deposition of pollutants can help determine whether pollution controls administered under the Clean Water Act (CWA) would be likely to improve water quality. It would also help define realistic expectations on the extent of improvements that could be accomplished by pollution controls. This desk study was therefore initiated to summarize the state-of-the-science on the atmospheric deposition of toxics in Washington. A second goal of the study was to outline the necessary scope of a study to quantify atmospheric deposition at different geographic scales. There are three geographic scales addressed here, roughly defined as local (urban site or reach of a stream), regional (stream or river watershed), and statewide.

The state-of-the-science on atmospheric deposition of toxics in Washington is scant. Currently, neither the data nor the predictive ability (i.e., models) exists to reliably determine the relative contribution that atmospheric deposition of toxics has on water quality in Washington. From estimates we can say that there is a range of measurable contributions that could be quantified on an annual basis. Washington is not behind in its work on atmospheric deposition; few states have attempted to quantify this contribution with any certainty. There appears to be much greater precedent for the acknowledgment of atmospheric deposition under the Clean Water Act when considering nonpoint sources under the TMDL framework, as opposed to contributions under a NPDES permit (Antony, 2011).

A list of approximately 52 chemicals of concern (not including individual congeners) was identified in this study; however, much of the available atmospheric deposition data focuses on PCBs and mercury. Conceptual models were derived for the transfer of toxics from the atmosphere to land to water at the local (urban) and regional scale. In order to quantify the contribution of atmospheric deposition to a stormwater load or river load, an accurate mass balance must be in place which quantifies other sources. It therefore makes sense to focus any follow-up pilot studies in an area where there is an understanding of the major contributions of toxics.

### ***Local Scale Summary***

- An estimated 15% of the stormwater PCB load on a commercial site in the Duwamish basin could be attributed to atmospheric deposition. A previous scoping study on the Lower Duwamish estimated that 95% of PCBs deposited atmospherically are of local origin.
- Long-term records of mercury at a Seattle sampling station suggest that loading from the atmosphere has remained fairly constant over the last ~20 years. Attempts to parse out regional and local contributions with existing data and literature values were not realistic. Further work is possible with existing Ecology sediment core data to describe the natural background contributions of mercury.
- The degree to which atmospheric deposition influences the discharge or runoff from an urban site will vary with location, season, and land use.
- Models exist for predicting the urban contribution of toxics to stormwater from local emissions and gas phase, but they are not currently used at Ecology.

- The largest flux of toxics in the urban environment is likely from the local atmosphere (airshed) into the organic film on impervious surfaces.
- The atmospheric fluxes of toxics in the densely urbanized areas of the Puget Sound region appear to be higher than surrounding areas and are likely to be source regions for more rural or remote areas. This is a similar finding to other longer term and more comprehensive studies and would likely be the case in other urban areas throughout Washington.

### ***Regional Scale Summary***

- The regional evaluation of atmospheric fluxes of toxics seems achievable based on the work of Colton et al. (2013) and Brandenberger et al. (2010) in the Puget Sound.
- The direct deposition of toxics to waterbodies with large surface areas has been measured and modeled in numerous previous studies, showing that a waterbody can be a sink or source for contaminants like PCBs.
- Atmospheric deposition to the Puget Sound and Lake Washington is a relevant input in the mass balance of toxics.
- Volatilization of toxics from Puget Sound as a loss term appears negligible (<5% for most toxics).
- No work has been completed to evaluate indirect deposition to watersheds and transport of toxics to waterbodies.
- Using published data for PCBs in the Lower Duwamish watershed, it is estimated that the indirect load of PCBs to the river from atmospheric sources is 27%.
- Ecology has a fate and transport model for toxics that incorporates direct atmospheric deposition and an in-stream model for water quality and temperature that would need to be adapted for the fate and transport of toxics. There is currently no watershed hydrodynamic model in-house.

### ***Statewide Scale Summary***

- Wind patterns in Washington suggest that western urban centers could act as potential sources of toxics for eastern Washington waterbodies.
- The assessment of atmospheric deposition of toxics statewide has received no explicit study; however, a number of studies have examined how toxics are accumulating in undisturbed lake biota and sediments. This suggests the spatial patterns present in Washington.
- Mercury in sediment cores suggests that eastern and western Washington have experienced greater deposition of mercury in the last ~ 20 years relative to pre-1900s (3.25 and 7.09 times, respectively). The background flux of Hg from these sediment cores could be used to determine the percent “natural” contribution to Washington once the modern atmospheric fluxes are understood with more certainty.
- PCBs in fish tissues from lakes receiving solely atmospheric inputs have been measured above the concentrations used by Washington to list waters as “impaired” under Section 303(d) of the CWA. It appears that PCBs from local sources in western WA are falling out over the Cascades in precipitation. This finding suggests that understanding the spatial distribution of the atmospheric deposition of PCBs in Washington is worthwhile.
- Ecology does not have the in-house capacity to model the transport and deposition of contaminants statewide.

## 2. Introduction

Under the current water quality standards (WAC173-201A, section 420) Ecology may issue a *variance* to allow for a modification of water quality criteria applicable to an individual discharger or stretch of water. The decision to grant a variance can be informed by information on pollutant sources, including an assessment of sources that cannot be controlled under Clean Water Act (CWA) regulatory programs. Atmospheric deposition is one such source. Information about atmospheric deposition of pollutants can help determine whether CWA-driven pollution controls would be likely to improve water quality. This information can also help define realistic expectations about how CWA-regulated pollution controls affect levels of pollutants entering waterbodies.

Atmospheric deposition of chemicals both directly and indirectly (i.e., to a watershed) to surface waters in Washington has not been an area of active research. Currently, we do not know the extent to which atmospheric deposition of toxics contributes to the contamination of state waters. Isolated studies have been completed (e.g., Brandenberger et al., 2010), but there has been no comprehensive assessment of the contribution atmospheric deposition makes to the loading of toxic chemicals to surface waters. The goals of this project are to:

- Review and assess the state-of-the-science for atmospheric deposition of toxic chemicals in Washington.
- Broadly outline the necessary scope to quantify atmospheric deposition at the local, regional, and statewide scale with enough certainty that results could be used to help support a variance of the water quality standards if that tool is needed.

In general, the toxic chemicals of interest encompass a broad range of inorganic and semi-volatile organic compounds. The initial identification of the chemicals of interest is purposefully broad in this paper, to highlight those toxics that are regulated and could be in the atmosphere. Geographically, the influence of atmospheric deposition will vary at the local (urban site or reach of a stream), regional (stream or river watershed), and statewide scale; therefore, we approach this assessment from these spatial scales.

The importance of atmospheric deposition to the load of toxics in a particular waterbody has been measured and modeled in a number of locations outside the state ([Table 1](#)). In general those studies which address atmospheric deposition do so by quantifying the *direct* deposition of toxics to the waterbody. Furthermore, only those waterbodies with a significant surface area would warrant the calculation of direct deposition (i.e. estuaries, bays, and lakes). It appears that *indirect* deposition to the watershed and then conveyance to surface water has not been reliably quantified in any study, with the exception of a few urban environments in the Great Lakes region (Totten et al., 2006a; Diamond et al., 2010). In this paper we consider the influence of both direct and indirect atmospheric deposition.

This desk study was not intended to provide a comprehensive review of the possible sources to the atmosphere for the chemicals of interest. There are ample reviews and case studies which can provide further details on atmospheric sources of toxic contaminants in Washington (e.g., Brandenberger et al., 2010; Leidos and NewFields, 2013; Shields et al., 2014). In addition, several state agencies oversee the

emissions of toxics as part of the National Atmospheric Toxics Assessment: Ecology, the Puget Sound Clean Air Agency, and the Olympic Region Clean Air Agency. Determining the possible sources of toxics to the atmosphere would be appropriate during follow-up or site specific studies.

This paper aims to:

- Detail conceptual models for the atmospheric deposition and transfer of toxics to surface waters.
- Summarize the available data for Washington, with an emphasis on highlighting previous case studies where the role of atmospheric deposition has been quantified.
- Give an overview of modeling approaches for direct and indirect atmospheric deposition.
- Discuss the uncertainty in measurements of atmospheric deposition.
- Broadly suggest how a project might be designed to address the current data gaps in assessing atmospheric deposition in Washington.

### **3. Policy Background**

There are two aspects from which to approach atmospheric deposition from a regulatory perspective: (1) contributions to waters that receive point source discharges (including direct deposition to waterbodies), and (2) contributions to lands that are sources of non-point source pollution on a larger scale.

#### ***Atmospheric Contributions to Point Sources***

Regulating atmospheric deposition to a point source applies more to the original emission, deposition on a site, entrainment in a stormwater catchment, and conveyance to a receiving waterbody. It is not the regulation of a stormwater point source that incorporates atmospheric deposition from multiple sources to a site. There can also be an influence of upstream contaminants in the receiving waters, which are possibly derived from atmospheric deposition.

Variances issued under the current water quality standards to account for upstream contaminant loads, would apply to receiving waters of NPDES discharges. Quantifying concentrations and loads under this scenario should be relatively straightforward. This paper does not describe the potential for variances under this scenario.

#### ***Atmospheric Deposition to a Non-point Source***

The section of the Clean Water Act which addresses nonpoint source pollution is sec.319. Under this section, states are required to: (1) prepare assessments of nonpoint source problems; (2) develop management programs to address the problems identified in these assessments; and (3) create a grant program that allows EPA to fund state programs for nonpoint source assessment and control. Furthermore, the state assessment reports are required to identify waters impaired or threatened by nonpoint source pollution, to identify the categories, subcategories, or individual sources contributing to the nonpoint source pollution problem, and to recommend the best management practices or measures

to be used to control each category or subcategory of source (Clean Water Act, Section 319(a)(b)(h)and(i)). Certainly the atmospheric deposition of toxics falls under this definition.

The EPA released a guidance document for conducting Total Maximum Daily Loads (TMDLs) to control polychlorinated biphenyl (PCB) impairment of surface waters (EPA, 2011). A TMDL should include estimates of nonpoint source loadings (e.g., atmospheric deposition, contaminated sediment, runoff from contaminated sites, groundwater). The EPA encourages states to consider the following in developing such estimates:

- As with point sources, maps showing the location of key sources or source areas are encouraged.
- Loading estimates should account for air deposition and nonpoint sources other than those nonpoint sources containing loadings from air deposition (e.g., runoff from waste sites, legacy sources). States may wish to use runoff models to estimate PCB loadings to the waterbody from the watershed.
- While not necessary for developing the load allocation (LA), parsing out the contributions to the air deposition loading may be helpful in developing an implementation plan. Parsing out contributions to the air deposition loading is contingent upon decisions regarding the appropriate level of analysis; if contribution from air is small, environmental outcomes or benefits may not be commensurate with the amount of effort spent on this analysis.
- Where possible, the TMDL should include estimates of the contributions from air deposition to permitted stormwater sources and account for such loadings in the point source load estimate, rather than the nonpoint source load estimate. Contributions from nonpermitted stormwater sources may be included in the nonpoint source load estimate.

#### **4. Toxic Chemicals of Interest**

Toxic chemicals of primary interest for atmospheric deposition in Washington were selected based on one or more of the following criteria: (1) listed in Ecology's Persistent, Bioaccumulative and Toxic list, (2) have established water quality criteria, (3) permitted under a stormwater municipal Phase 1 permit and/or NPDES permit, and (4) listed in Washington under the 303(d) list for impaired waters. This selection process yielded 52 chemicals of interest, not including individual congeners ([Table 2](#)), within the chemical groups: organochlorine pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), dioxin and furans, phthalates, and metals. The selection process did not consider the physical properties of the chemicals, which will influence the behavior of the chemicals in the atmosphere and following deposition. The properties of the selected chemicals are described in the remainder of this section.

Many of the chemical groups contain congeners, which have the same basic chemical structure to one another but differ slightly in mass. PCB congeners vary in mass with the degree of chlorination and total 209 different congeners. There are a number of congener groups which are defined by the degree of chlorination, ranging from monochlorobiphenyls (1 Cl atom) to decachlorobiphenyls (10 Cl atoms), and referred to as *homolog* groups. PBDEs are similar in that there are 209 congeners; however, because

there are 3 main formulations of PBDEs, the number of unique congeners in the environment is much less than PCBs. Monitoring and modeling studies often focus on a representative number of congeners or suite of congeners with greater toxicity. It is common that a small suite of congeners can comprise a significant proportion of the total contaminant mass. For example, the San Francisco Estuary Institute monitors 40 PCB congeners that comprise 75-82% of the total PCB mass (SFRWQCB, 2008). In addition, modeling studies often focus on the movement of a single congener (or homolog group) in order to constrain the physical properties and add precision to the model.

The behavior of toxics in the atmosphere is governed by the physical structure of the compounds, and can be described by the octanol-air partitioning coefficient ( $K_{OA}$ ) which is also related to the gas-particle partitioning coefficient and calculated based on the octanol-water coefficient ( $K_{OW}$ ) (Bidleman, 1988; Lohmann et al., 2000). The vast majority of the chemicals identified in this study are not predominantly found in a single medium and can be considered multimedia—they partition into more than one medium (Figure 1). The fugacity ratio of a chemical describes its propensity to migrate among media. At the same environmental concentration, a chemical with a high fugacity ratio is more likely to migrate than one with a low fugacity ratio. Figure 2 describes the fugacity ratios for the chemicals of interest. In general, phthalates, diazinon, and chloroform have ratios around 1. This means they migrate readily between environmental media. In the case of PCBs, it is evident that the propensity to migrate decreases with increasing chlorination. This means the heavier homolog groups are more likely to remain bound to a medium (Figure 2). Similar properties are observed among the PAHs and PBDEs, where the lighter compounds have a greater tendency to migrate.

The atmospheric flux ( $\text{ng m}^{-2} \text{day}^{-1}$ ) of the vast majority of the chemicals listed in [Table 2](#) has been quantified in various phases (wet, dry and gaseous) and in a number of different locations. What is clear from the literature is that there is a great deal of spatial and temporal variability in the measurement and calculation of atmospheric fluxes. It is therefore inappropriate to rely on atmospheric fluxes discussed in the literature to calculate the contribution of atmospheric deposition in regions of Washington. The commonly used mass balance approach for apportioning contaminant loads ( $\text{g year}^{-1}$ ) to a receiving environment, requires site- or region-specific data collection.

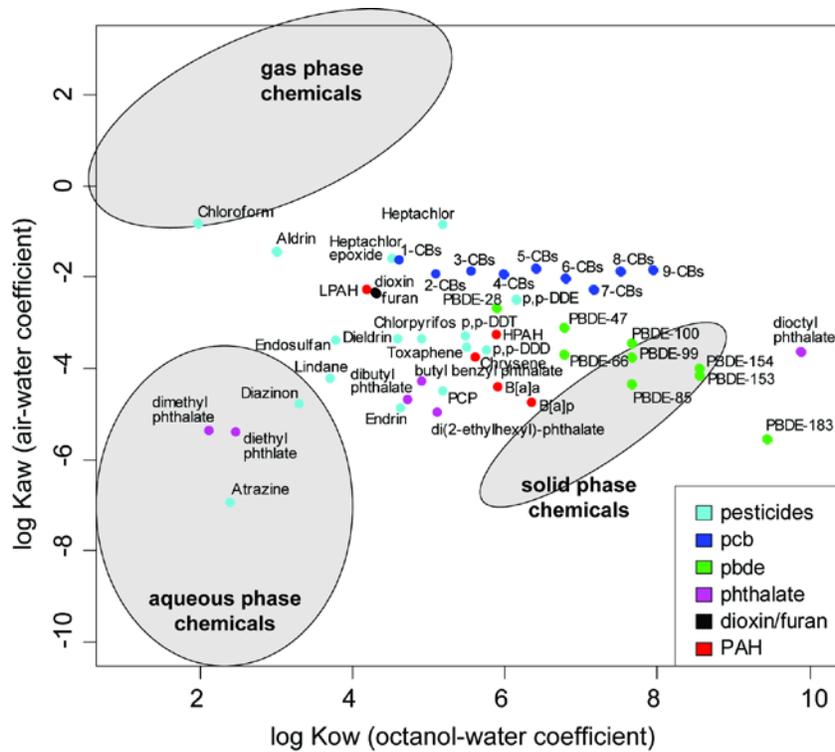


Figure 1: Plot of log Kaw (air-water partition coefficient) and log Kow (octanol-water partition coefficient) for the toxic chemicals of concern. Shaded regions represent ranges of partition coefficients.

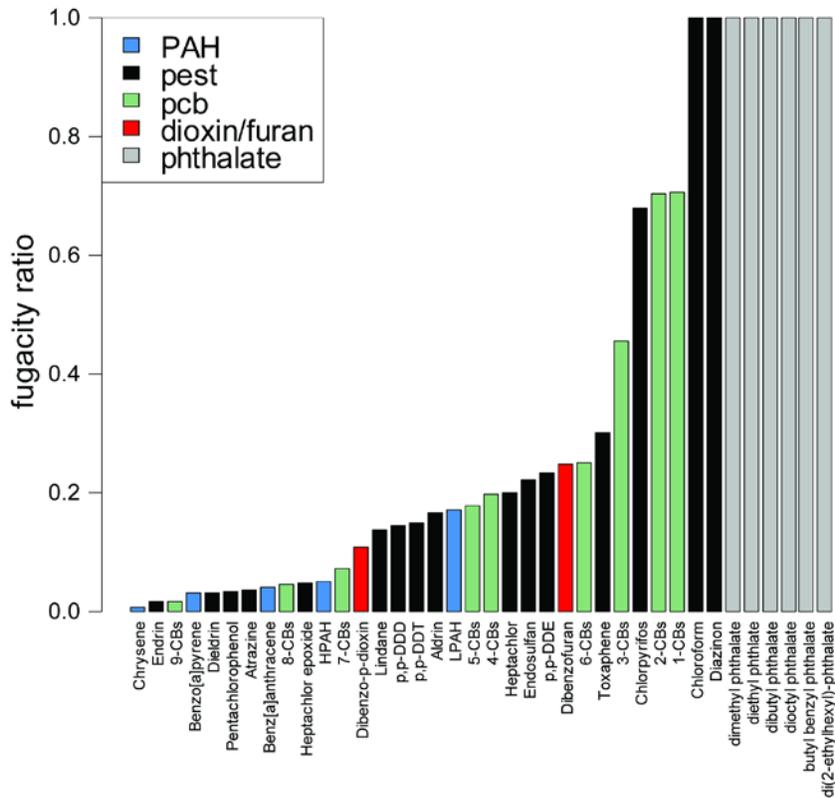


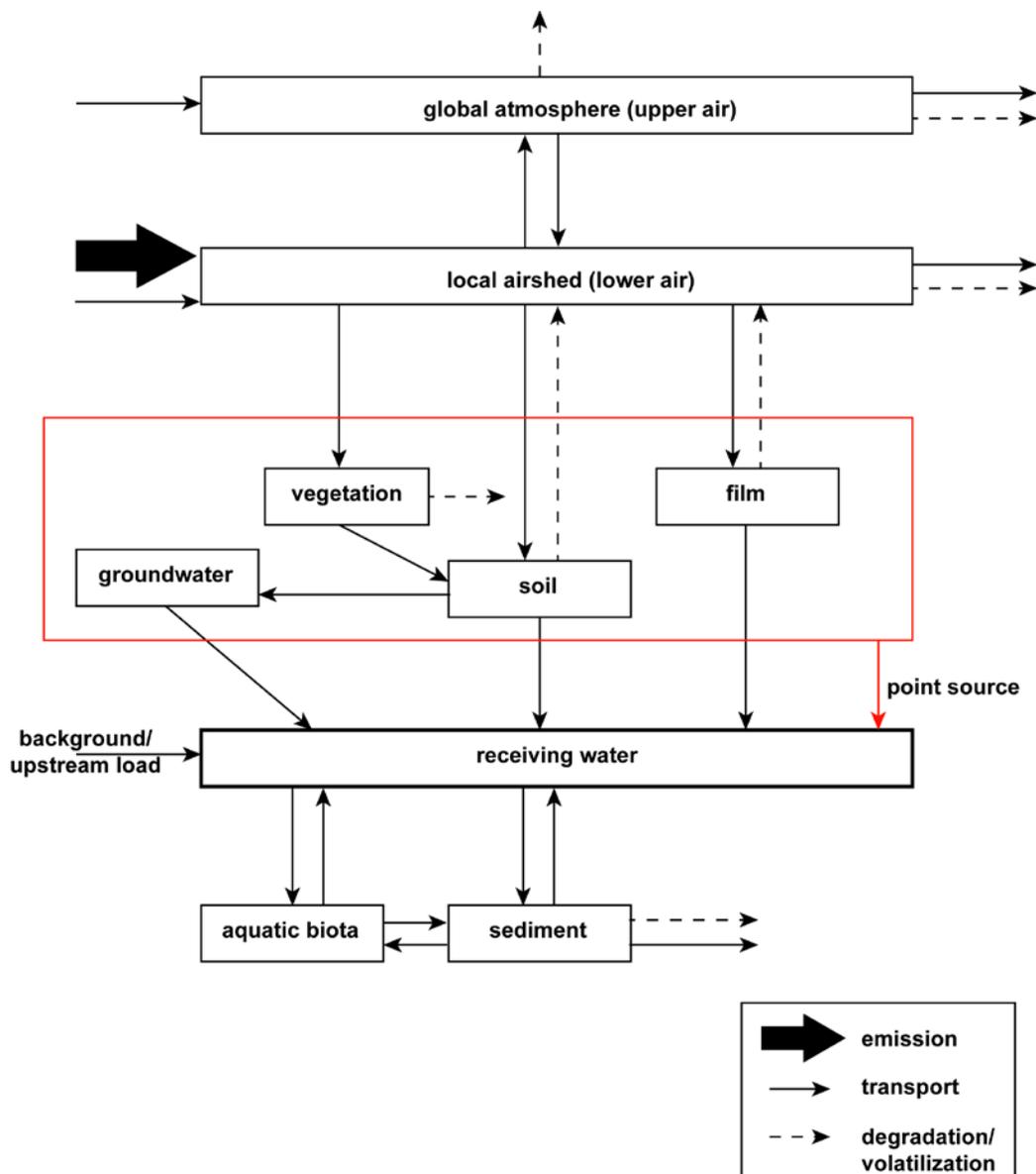
Figure 2: Fugacity ratio of the chemicals of concern.

## 5. Local Scale

Atmospheric deposition at the local scale pertains mainly to urban environments (Figure 3). There are 2 aspects of atmospheric deposition at the local scale:

1. Atmospheric deposition that impacts the receiving waters upstream of an NPDES discharge
2. Atmospheric deposition directly to a site that is then collected in site runoff and discharged within the permitted discharge.

The atmospheric load deposited to a site has been the focus in sampling and modeling programs in urban areas (Diamond et al., 2010; Colton et al., 2013). This review will also focus on the deposition of toxics to an urban site. Quantifying the load attributable to atmospheric deposition and inputs to receiving waters upstream would require a more regional assessment (discussed further in subsequent sections). The upstream load in receiving waters from a specific site can be accounted for through in-stream monitoring (Figure 3).



**Figure 3: Conceptual model of atmospheric deposition of toxics at the local scale. Red box delineates the main receptors at the local scale.**

Conceptually, the movement of toxics from the atmosphere to an urban site is influenced largely by the local airshed that comprises mainly local emissions and inputs from the upper air (Figure 3). A number of studies have shown that even for legacy contaminants like PCBs the current urban environment can act as an ongoing source as older building materials degrade (Diamond et al., 2010; Totten et al., 2006a). In addition, the organic film layer on impervious surfaces in urban environments is an active compartment for the buildup and partitioning of toxics (Diamond et al., 2000). Toxics in gaseous phase can partition into this layer, particulate phase can accumulate on this layer and liquid phase can wash off and adhere to the film (Melymuk et al., 2012). The wash-off or *first-flush* of the organic film during a storm event often has higher concentrations of toxics than the storm event mean concentrations (Lee et al., 2002; Pitt et al., 2004). The load from atmosphere to film to stormwater has been modeled to be  $\sim 1 \text{ g day}^{-1}$

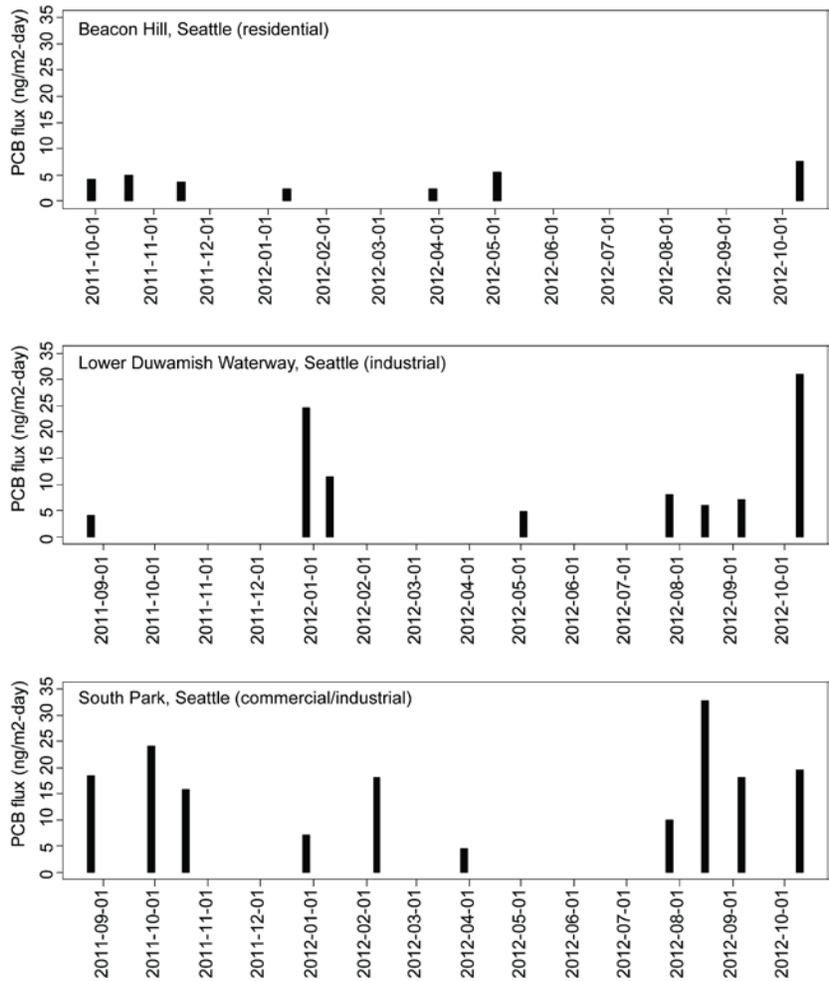
total PCBs (Melymuk et al., 2012). The transfer of toxics from the local airshed to organic films is estimated to be the largest flux in the urban environment (Diamond et al., 2010).

The Mercury Deposition Network (MDN) has 2 operational sites in Washington: WA18 – Seattle and WA03 – Makah National Fish Hatchery. Ecology used to support the WA03 site. Collection of total mercury (Hg) wet deposition at the Seattle site began in March 1996 and has continued on a weekly frequency. For the Seattle record of Hg deposition, the trend in Hg concentration over the period of sampling decreased in the late 1990s and has remained fairly stable since that time ([Figure A-1](#)). When the Hg concentration data are adjusted for precipitation totals and expressed as deposition ( $\text{ng m}^{-2}$ ), the trend has been stable throughout the period of monitoring ([Figure A-2](#)). Likewise, the Makah station shows little trend in concentration or deposition over the period of monitoring (~ 8 years) ([Figure A-3 and A-4](#)). There is a great deal of temporal variability within the data, and this has not changed over the last ~20 years. Seasonally, Hg concentrations are higher in the summer, but there is no significant seasonal trend for Hg deposition. Mercury is generally not a parameter that is detected in municipal stormwater, with the exception of localized hotspots (Hobbs et al., 2015). The impact of mercury on the environment relates more to indirect deposition and food web accumulation at the regional or river basin scale. One of the questions pertinent to Hg deposition is: what proportion of the load is attributable to anthropogenic sources, and then what fraction of that is local compared to extra-regional or out-of-state?

Comparing the 2 MDN sites over a similar time period, where the Makah site represents “out-of-state” contributions, the median concentration at the Makah site is approximately 40% that of the Seattle site ([Table 3](#)). However, the median atmospheric load of Hg at the Makah site is fairly comparable to the Seattle site, suggesting that the Hg load in Seattle is comparable to that being brought in from out-of-state. Conversely, a novel study that aimed at apportioning global and local Hg sources recently suggested that approximately 80% of the Hg deposition in Seattle is of local origin (Lamborg et al., 2013). In the Lamborg et al. (2013) study, the authors indexed the flux of Hg to the flux of the radioisotope  $^{210}\text{Pb}$  which is solely of atmospheric origin. They compared it to a background site in Alaska where there are no local sources. In a modeling and lake sediment core study in Whatcom County, Washington, Paulson and Norton (2008) concluded that Hg sources to the lakes were largely regional or out-of-state, as opposed to nearby local sources (a chlor-alkali plant). Other studies have found that local anthropogenic sources account for approximately 40-87% of the Hg load, which includes existing point sources ([Table 4](#); Leidos and NewFields, 2013). Clearly, further analysis and summary of Hg deposition data needs to be completed to apportion the natural, local anthropogenic, and out-of-state anthropogenic sources.

With the exception of the MDN sites in Seattle and at the Makah National Fish Hatchery, little empirical data exists for the atmospheric deposition of toxics at the local scale in Washington. The most reliable data set comes from work in the Seattle region and Puget Sound (Brandenberger et al., 2010; Colton et al., 2013). Here, Colton et al. (2013) sampled multiple locations within the Green-Duwamish River Basin and have for years collected monthly to bi-monthly bulk deposition samples for PCBs, metals, dioxins and furans, and PAHs. In PCB fluxes to 3 of the sites from residential and commercial/industrial land uses, there is significant variability among the sites ([Figure 4](#)). Indeed, there is a statistically significant

difference between the residential site and commercial/industrial sites ( $p=0.03$ , Beacon Hill – South Park and  $p=0.001$ , Beacon Hill - Duwamish). What is also evident from the data is that there is significant variability over the sample period. For example, the Lower Duwamish site ranges from 4 to 31  $\text{ng m}^{-2} \text{day}^{-1}$ . Given the temporal variability, determining the net deposition to a site and then applying it to an individual stormwater event is unrealistic. It would appear that either bulk deposition and stormwater samples are twinned for comparison or an annual load for both atmospheric deposition and stormwater



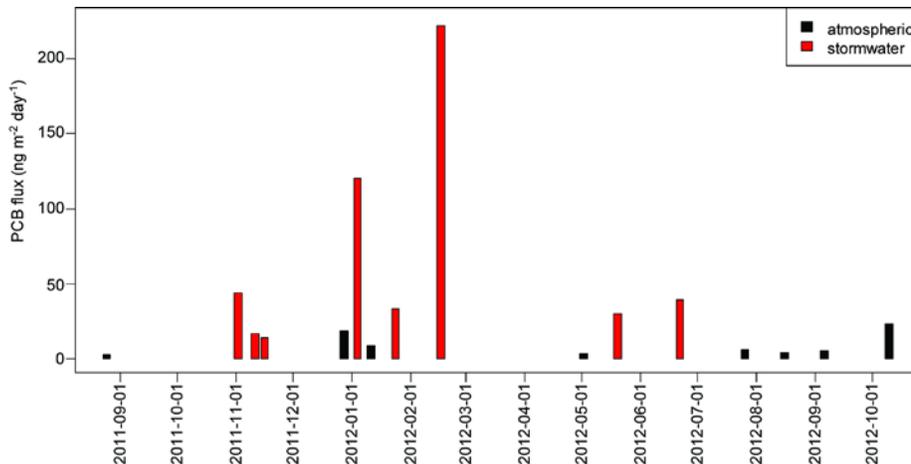
**Figure 4: Comparison of PCB flux data in Seattle from Colton et al., 2013**

should be calculated in order to estimate the % contribution from the atmosphere.

Comparing the Duwamish site to recent stormwater water data from the Port of Seattle (Hobbs et al., 2015) shows possible atmospheric deposition contributions during individual storm events (Figure 5). As a back-of-the-envelope calculation, 2 of the sample events for stormwater and bulk deposition occur within a week or two of each other. Assuming that 75% of the PCB mass in atmospheric deposition ends up in runoff (EPA, 2001), it is estimated that 7 and 12% of the stormwater PCB load could be of atmospheric origin. Comparing the median loads across all sample events from atmospheric deposition and stormwater gives an estimate of

15% attributable to atmospheric origin. Ultimately, this exercise is only useful to highlight that there is a measurable contribution from the atmosphere, which is relevant to a measured stormwater load.

In a report with similar objectives to this paper, Leidos and NewFields (2013) explored the current data gaps to quantify the role of atmospheric deposition to the loading of toxics in the Lower Duwamish Waterway (LDW). The findings from this study were (quoted directly p.54):



**Figure 5: Comparison of atmospheric flux of PCBs and PCB load in stormwater from nearby sites.**

- Atmospheric emissions are a major contaminant source for many of the COPCs. For example, the PAH CAP states that over 70 percent of PAH releases are air emissions. The primary pathway for phthalates to enter the environment is through volatilization from plastics.

- Because the area of the LDW is small compared to the surrounding watershed, the contribution of atmospheric deposition to the river surface is minimal compared to upstream and lateral sources.

- However, the atmospheric contribution due to indirect deposition could be significant, with estimates in this report ranging from just 6 percent of lateral loads to over 100 percent, depending on the assumptions used.
- More work is needed to determine the full extent of indirect deposition, but clearly the atmosphere can be a major pathway for contamination to the LDW.
- Local sources represent a significant portion of contaminant loadings to the LDW from atmospheric deposition for arsenic (77 percent local), cPAHs (84 percent local), and PCBs (95 percent local). Local source control efforts for these chemicals may help to reduce lateral loadings to the LDW.
- Regional sources represent a significant portion of contaminant loadings to the LDW from atmospheric deposition for dioxins/furans (80 percent regional) and mercury (49 percent regional/background). Local source control efforts will have more limited effects in reducing lateral loadings for these chemicals.

Overall, the Leidos and NewFields (2013) study quantified emissions, pulled literature values for back-of-the-envelope calculations, and made efforts to constrain the uncertainty in both analytical and calculated results. But the authors conclude that data are lacking to state with any certainty the relative influence of both indirect and direct deposition of toxics.

A similar study approach was used by Era-Miller (2011) in an internal Ecology memo. Here she surveyed the literature, used fluxes of toxics to estimate an upper and lower rate of input from atmospheric sources and modeled the possible proportions of stormwater contaminants in discharges from the City of Spokane. Estimates ranged from 20% to >100% for PCBs and PBDEs. It's fair to say from studies where literature values are used in back-of-the-envelope calculations that it is not possible to get a realistic estimate of % contribution from atmospheric deposition.

In the urban environment, fugitive dust is an important contributor of metals and other toxics. Metals in particular (e.g., copper from brake pad dust) can be transported in particulate form to waterways (Paulson et al., 2012). There is significant attenuation and retention of particulates on grassy strips on the edge of roads and other vegetation. Often there are temporary repositories in the urban environment for particulates, until storms transport some of the toxics into stormwater systems and urban waterways. One of the main findings from the Paulson et al. (2012) study on the fate and attenuation of copper, PCBs and PBDEs, was that understanding the releases, partitioning, and transport in urban streams is basin-specific.

In summary, the atmospheric fluxes of toxics in the densely urbanized areas of the Puget Sound region appear to be higher than surrounding areas (Colton et al., 2013, Brandenberger et al., 2010) and are likely to be source regions for more rural or remote areas (Cleverly et al., 2007). This is a similar finding to other longer term and more comprehensive studies (Totten et al., 2006b; Persoon et al., 2010; Rodenburg and Meng, 2013). It would likely be the case in other urban areas throughout Washington. The degree to which atmospheric deposition influences the discharge or runoff from an urban site will vary with location, season, and land use. It appears that a measurable portion of the discharge from urban sites can be attributed to direct atmospheric deposition to the site.

#### ***Case Study: PCBs in the City of Toronto***

Miriam Diamond's research group at the University of Toronto has been working for some time to quantify the relative influence of atmospheric deposition of toxics to an urban landscape. They have employed both modeling (Csiszar et al., 2013) and empirical studies (Melymuk et al., 2014) with varying degrees of complexity. Loads and fluxes have been quantified within compartments of the urban landscape and contributions of the urban environment to the adjacent Lake Ontario (Diamond et al., 2010; Melymuk et al., 2014). The annual sampling program consisted of continuous polyurethane foam (PUF) air samplers, monthly, integrated precipitation samples, stream composite samples at representative points in the hydrograph, and composite effluent samples from wastewater treatment plants.

The role of atmospheric deposition was generally found to be significant. A possible exception was the inputs of PBDEs from Toronto to Lake Ontario (<5%), where tributaries and wastewater treatment plants (WWTPs) were more important (~ 40% each). Using the conceptual model defined earlier in this report, the rates of transfer in  $\text{g day}^{-1}$  have been modeled from atmosphere to urban site to receiving water (Figure 6; Diamond et al., 2010).

In the adapted mass balance of PCBs in Figure 6, many transfers are not quantified (e.g. aquatic biota and upstream contaminant loads). However, what is evident is that the vast majority of local emissions are transferred to the upper air and transported. Further work by this group has shown that the transfer of PCBs from the Toronto airshed over Lake Ontario and eventual deposition to the lake accounts for 66% of the total PCB load from the City of Toronto to the lake (Melymuk et al., 2014). The greatest transfer from the local airshed to the urban environment is estimated to be to the films on impervious surfaces.

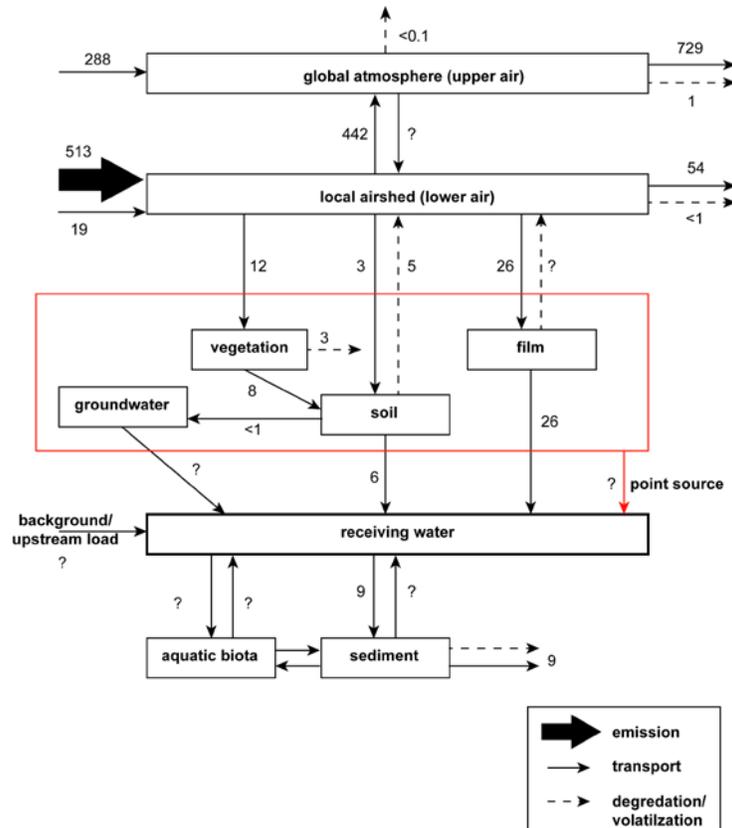
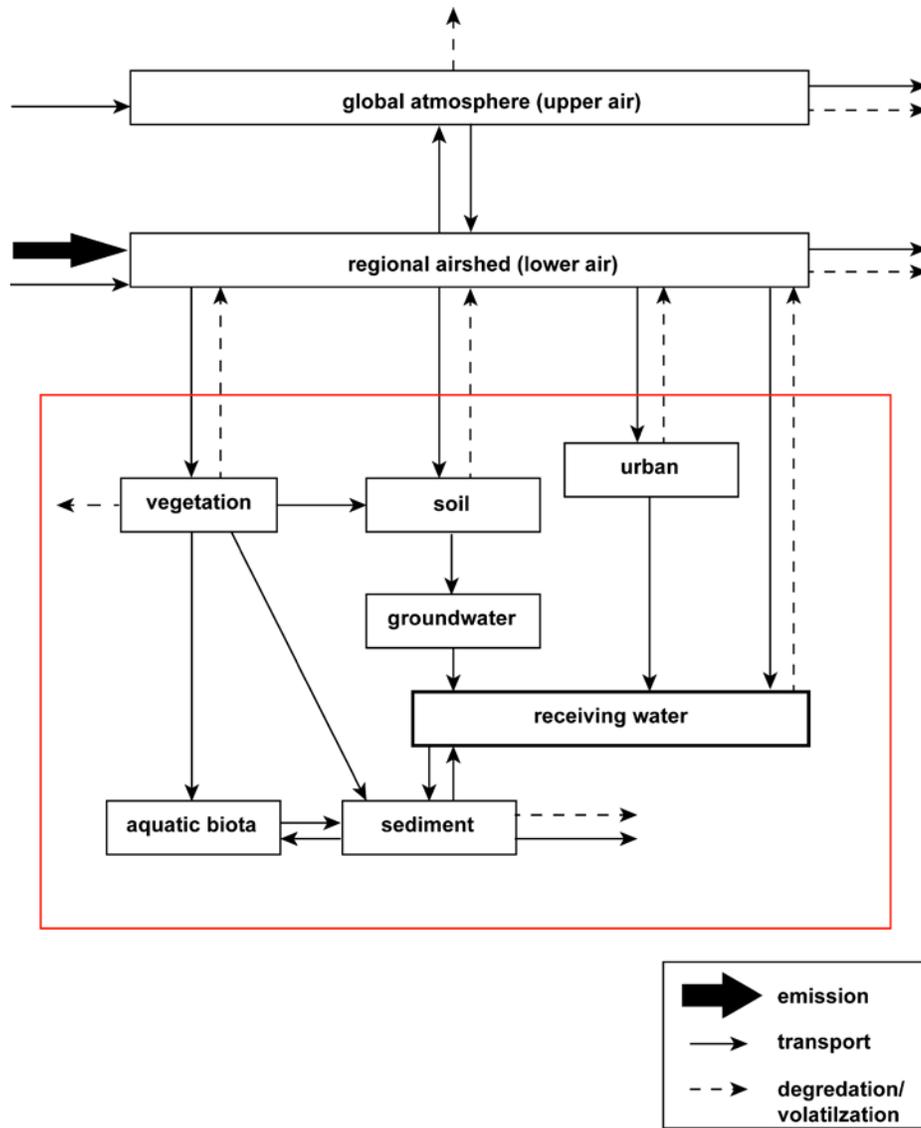


Figure 6: PCB fluxes (g day<sup>-1</sup>) in the City of Toronto (adapted from Diamond et al., 2010). Red box delineates the main receptors at the local scale.

## 6. Regional Scale

Atmospheric deposition at the regional (watershed) scale pertains to indirect deposition in the watershed and transfer to receiving waters, and direct deposition to the receiving waters (Figure 7 conceptual). It is fairly safe to say that previous studies have really only considered direct atmospheric deposition to waterbodies and only those waterbodies with a large surface area (i.e., estuaries, bays, and large lakes). In some of the available studies that explicitly considered the inputs to surface waters, the % contribution from direct atmospheric deposition has a considerable range for all toxics (Table 1). An interesting observation from the work of Brandenberger et al. (2010) was that the atmospheric flux of PCBs in Puget Sound was roughly similar to that in the Strait of Georgia to the north (3.5 kg year<sup>-1</sup>), suggesting a regional flux could be estimated. However, this value seems unrealistic, since an estimated 0.11 kg year<sup>-1</sup> is deposited directly to Lake Washington, which would include regional and local sources (DeGasperi, 2013).



**Figure 7: Conceptual model of atmospheric deposition of toxics at the regional scale. Red box delineates the main receptors at the regional scale.**

The Puget Sound work was based on the collections of bulk (wet and dry) deposition; there has been no work in Washington to partition the atmospheric deposition of toxics on a regional scale into wet, dry, and gaseous phases. The unpublished work of Osterberg and Pelletier (2015) on the Puget Sound Toxics Model (an update of the earlier work of Pelletier and Mohamedali, 2009) highlights some of the caveats in scaling up local measurements of atmospheric deposition to regional scales. Referring to direct atmospheric inputs, the authors state:

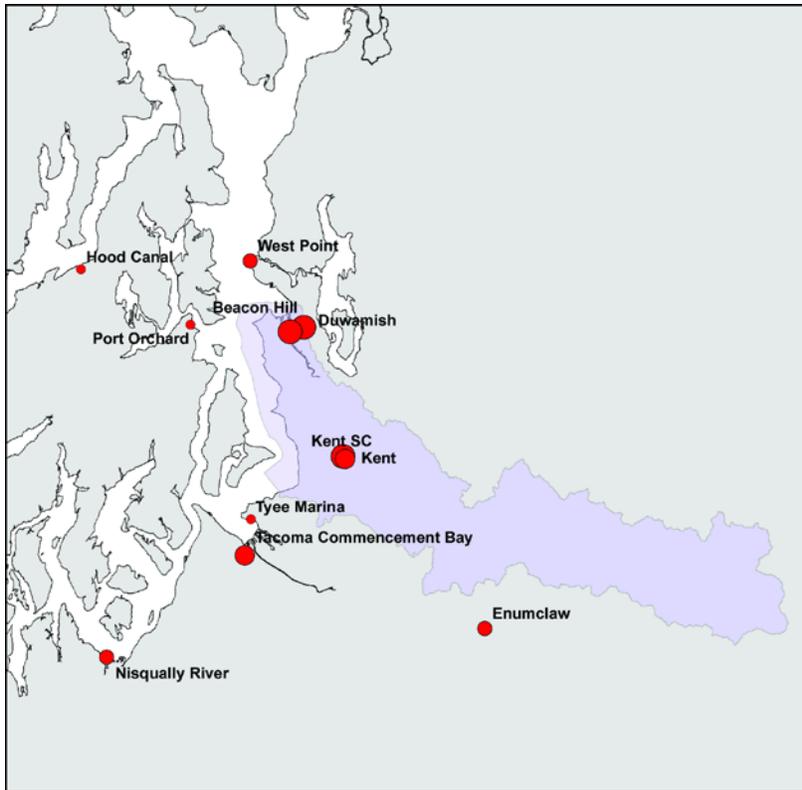
- Loads are minimum or near-minimum estimates.
- Loads for total LPAHs have an additional downward bias due to substitution of zero for non-detects (instead of 1/2 the maximum Detection Limit) and the absence of naphthalene data.
- Low spike recoveries for PCBs and PBDEs in field extraction QA tests suggest that loads may be underestimated compared to the true values (recoveries of 18-45% and 44-82%, respectively).

- Large uncertainties are inherent in extrapolating across a large area while using fluxes measured at a small network of sites. It is likely that strong localized signals (e.g., around high-density urban areas) were under-represented in regional loading estimates.

In large waterbodies the volatilization of toxics can be a significant loss term in a mass balance. For example, in San Francisco Bay the volatilization of PCBs to the atmosphere is greater than the direct atmospheric flux and therefore the Bay is considered a net source of PCBs to the atmosphere (Davis et al., 2007). Similarly, in Lake Superior the lower atmosphere and lake water are considered near equilibrium and the major loss pathway of PCBs from the lake is through volatilization (Hornbuckle et al., 1994). The volatilization of toxics from rivers has not been considered. Losses of PCBs through volatilization from Puget Sound have been modeled but not measured. Osterberg and Pelletier's 2015 study suggests that volatilization from Puget Sound as a loss term is negligible (<5% for most toxics).

The only work to explicitly consider indirect atmospheric inputs of toxics took place in the Delaware River Basin (Totten et al., 2006b). Here, the authors used an empirical relationship for PCBs from headwater watersheds that would receive only atmospheric deposition and compared the river concentrations and load to the measured atmospheric flux. It was concluded that the watershed pass-through efficiency was on the order of 1%. This means 1% of the PCB mass that falls on the watershed is transferred to the receiving water (river). Pass-through rates of 5-20% have been suggested by others (EPA, 2001). Vegetation and land use type are the main factors influencing watershed pass-through rates. Dry particle and gaseous deposition rates depend heavily on the type of terrestrial ecosystem (Horstmann and McLachlan, 1998). Furthermore, the type of terrestrial ecosystem is a reflection of the soil conditions that will also influence the retention of toxics in the watershed (Liu et al., 2014). Forest fires can influence the transfer of toxics bound in the soils and vegetation of the watershed (Primbs et al., 2008). The release of PCBs and other toxics during fires may be particularly relevant to Eastern Washington, where forest fires occur annually.

There have been no studies in Washington that estimate the combined indirect and direct contribution of atmospheric toxics to a waterbody. Combining the work of Colton et al. (2013) and Brandenberger et al. (2010) gives a rough idea of the spatial distribution of PCB fluxes across Puget Sound (Figure 8). Inconsistencies between the studies in the summing of total PCB concentrations make combining data sets tenuous. However, it is clear that the more densely populated urban centers are local sources for higher fluxes of PCBs. This is also true for copper fluxes (Figure 9). Focusing in on the Green-Duwamish River basin (WRIA 9), we can do a back-of-the envelope calculation for the PCB mass contributed across land uses from the measured atmospheric fluxes of Colton et al. (2013; [Table 5](#)). If we use the watershed pass-through rates from the EPA (2001) and compare the cumulative indirect load to a median, instantaneous load recently calculated by the USGS and sampled from the same year (Conn and Black, 2014), approximately 27% of the Duwamish River PCB load is attributable to indirect deposition of PCBs over multiple land uses across the basin ([Table 5](#)). Similar to previous estimates at the local scale in the Duwamish, this exercise is only useful to show there is a measurable contribution from the atmosphere.



**Figure 8: Map of Puget Sound detailing relative measured PCB fluxes. The Green-Duwamish watershed (WRIA9) is highlighted.**

Under the Clean Water Act, Total Maximum Daily Loads (TMDL) must be established for impaired waterbodies. Indeed, it is this regulatory action that has triggered much of the current research and modeling of direct and indirect atmospheric inputs of toxics to surface waters. Under the TMDL framework, diffuse (or indirect) inputs—including atmospheric deposition—must be considered (EPA, 2011). However, very few of the accepted toxic TMDLs truly quantify atmospheric deposition and thoroughly address the % contribution. The only TMDL in Washington to consider atmospheric deposition was the recent PCB study for Lake Washington by King County

(DeGasperi et al., 2013). Here the authors determined that 16% of the PCB load and 30% of the PBDE load was attributable to direct atmospheric deposition to the lake surface (Table 1). Indirect deposition was not explicitly modeled or parsed out of the load from the tributaries entering the lake, which would incorporate the indirect portion of atmospheric deposition and additional point and non-point sources. Adapting the conceptual model to describe the transfer of PCB loads within the Lake Washington watershed demonstrates that a number of the loads are unknown and incorporated into other terms (Figure 10). For example, the inputs from rivers incorporate indirect atmospheric deposition.

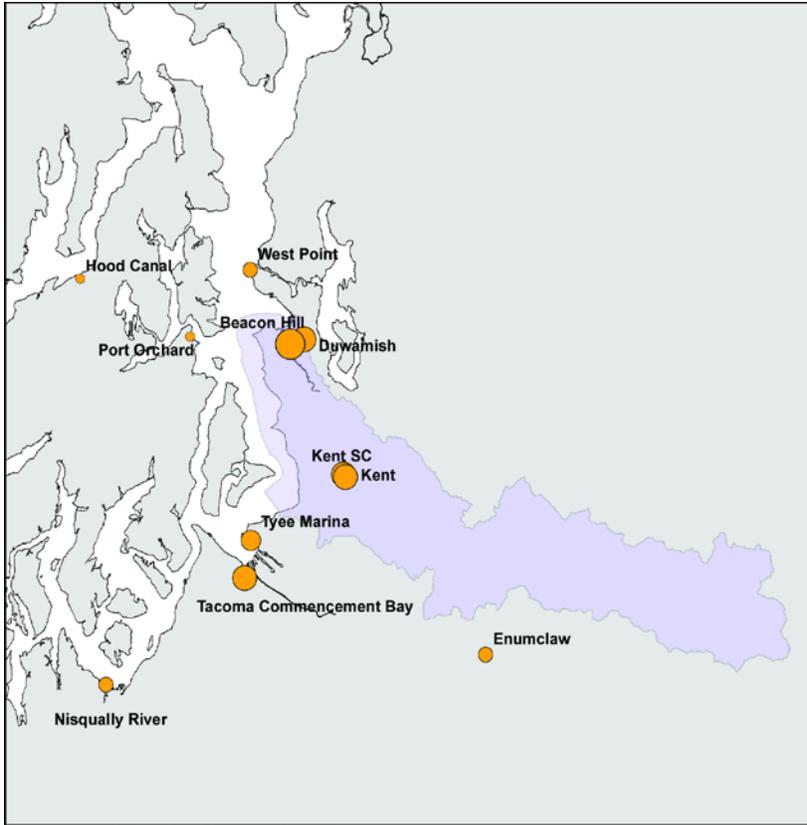


Figure 9: Map of Puget Sound detailing relative measured copper fluxes. The Green-Duwamish watershed (WRIA9) is highlighted.

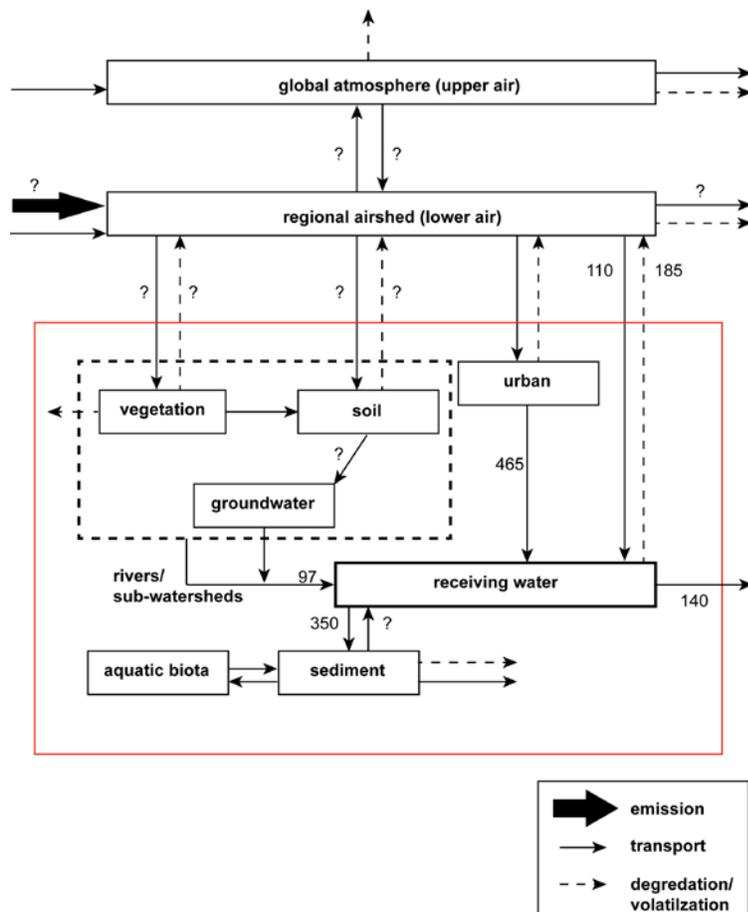


Figure 10: PCB fluxes ( $\text{g year}^{-1}$ ) in the Lake Washington watershed (adapted from DeGasperi, 2013). Red box delineates the main receptors at the regional scale.

Below are concluding remarks about the atmospheric deposition of toxics at the regional scale in Washington:

- The regional evaluation of atmospheric fluxes of toxics seems achievable, based on the work of Colton et al. (2013) and Brandenberger et al. (2010) in Puget Sound.
- The direct deposition of toxics to waterbodies with large surface areas has been measured and modeled in numerous previous studies showing that a waterbody can be a sink or source for contaminants like PCBs.
- Atmospheric deposition to Puget Sound and Lake Washington is a relevant input in the mass balance of toxics.
- No work has been completed to evaluate indirect deposition to watersheds and transport of toxics to waterbodies.
- Determining the relative contribution of atmospheric deposition to loads of toxics in surface waters is a watershed-specific exercise.

### Case Study: Delaware River Basin Council (DRBC) TMDL

The DRBC has been working on the reduction of PCBs to the Delaware River for the last ~20 years. Through the implementation of a detailed TMDL, they have an understanding of the myriad of PCB sources to the basin (DRBC, 2003). The gathering of empirical atmospheric deposition data was undertaken by Lisa Rodenburg (formerly Lisa Totten) at Rutgers University over ~ 10 years of monitoring. Wet, dry, and gaseous fluxes were measured in multiple locations throughout the basin (Totten et al., 2006b). This data provided the basis for the direct atmospheric deposition terms (inputs and losses) for the PCB fate and transport model (Suk and Fikslin, 2011). Because the monitoring program also established sample sites in headwater regions of the basin, the indirect atmospheric deposition could be assessed. It was concluded that this PCB flux or load from the watershed was negligible (Totten et al., 2006b) and therefore not included in the model or the revised TMDL. Ultimately, the final mass balance presented in the TMDL depicts the Delaware River as net source of PCBs to the atmosphere (Figure 11).

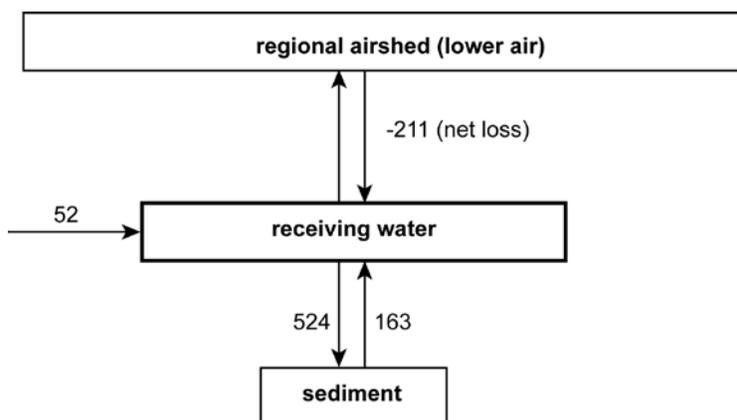
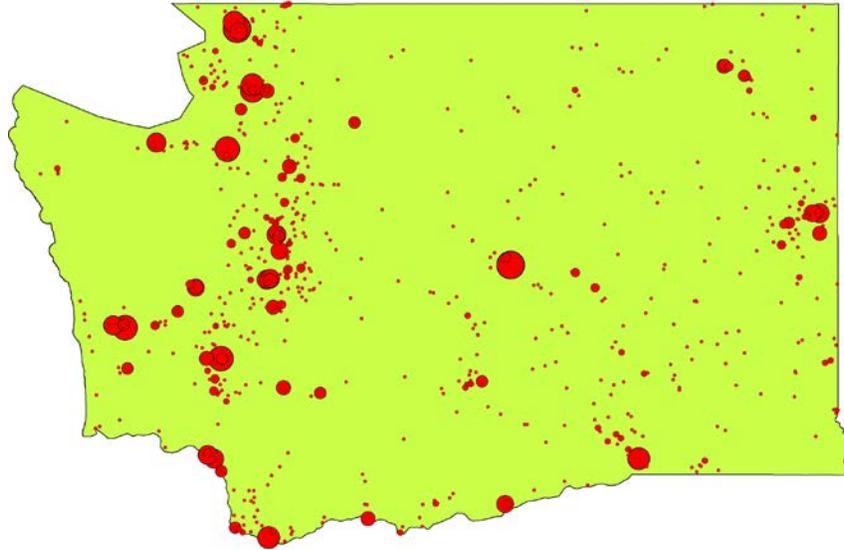


Figure 11: Mass balance of PCBs ( $\text{g day}^{-1}$ ) in the Delaware River basin (adapted from DRBC, 2003).

## 7. Statewide Scale

The wind and air mass movement across Washington is generally from west to east, with increased wind velocity up the Columbia River Valley (Figure B-1). In fall and winter, wind direction is more from the northwest, while in the summer it's from the southwest. This suggests that western urban centers could act as potential source of toxics for eastern Washington waterbodies. The reported particulate emissions (PM<sub>10</sub>; particulate matter <10  $\mu\text{m}$ ) for the state reveal that greater particulate emissions occur in western Washington, with some large contributions in the Wenatchee and Spokane region (Figure 12). No statewide emissions data is available for the toxics of interest in this study.

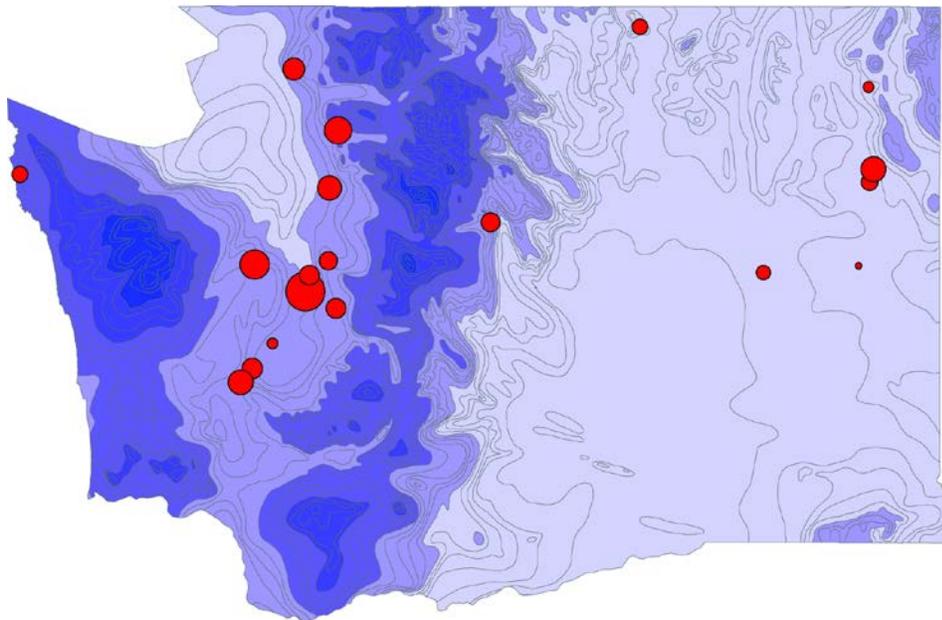


**Figure 12: Particulate matter (< 10µm) emissions in Washington. Data accessed through the EPA (<http://www.epa.gov/air/emissions/where.htm>)**

Similar to the regional TMDL studies, much of the work on statewide assessments of atmospheric deposition of toxics has been triggered by the TMDL process, although it is hard to identify many examples where a comprehensive assessment has taken place. The state of Minnesota compiled an ambitious statewide TMDL for Hg (MNPCA, 2007). Studying mercury is useful to a statewide approach because of the likelihood that a significant proportion of the Hg being deposited originated from out-of-state. Indeed, in many cases defining this load is one of the focal points of the study (Table 4). The Minnesota Hg TMDL is almost entirely based on empirical observations. Using measured emissions, lake sediment cores, and measured Hg deposition, the TMDL determined that 30% of the Hg was natural and 70% of the Hg was anthropogenic. Of the 70% anthropogenic Hg, 40% is local and 30% is out-of-state. A similar approach could be used in Washington with further data collection. The statewide deposition of Hg is something that deserves further attention, as there continues to be a statewide advisory on fish consumption for Hg (WADOH, 2015).

The assessment of atmospheric deposition of toxics statewide has received no explicit study in Washington. However, a number of studies that have examined how toxics are accumulating in undisturbed lake biota and sediments highlight some of the spatial patterns in Washington (Furl and Meredith, 2011; Johnson et al., 2010). The assumption here is that the undisturbed lakes/watersheds are receiving all toxic inputs from the atmosphere. Mercury accumulation in sediments of undisturbed lakes should be related to the atmospheric flux of Hg(II) to the lake surface and watershed. By calculating the enrichment factor for each lake (modern flux : background flux) from radioisotope-dated sediment cores, we can see the broad pattern of Hg enrichment across the state (Figure 13). The pattern suggests that greater deposition of Hg has occurred in western Washington, where a significant portion of the atmospheric Hg is possibly of local origin (Lamborg et al., 2013). Simply averaging the enrichment factors for eastern and western Washington (3.25 and 7.09, respectively) shows how there has been greater deposition of Hg in modern times (the last 20 years). The background flux of Hg from these

sediment cores (pre-1900s) could be used to determine the percent “natural” (not human-caused) contribution to Washington once the modern atmospheric fluxes are understood with more certainty. A similar approach was used in Minnesota during the compilation of the statewide TMDL for Hg (MNPCA, 2007). Given the differences in enrichment from eastern and western Washington, two estimates of natural contributions should be calculated. The concept of a “natural” background could also be used for the other inorganic toxics (e.g., copper and zinc).



**Figure 13: Map of relative mercury enrichment from lake sediment cores. Contoured on annual precipitation totals, where dark shading corresponds to higher totals.**

PCBs in tissue of fish from undisturbed lakes can also give an indication of the atmospheric deposition across the state (Figure 14; Johnson et al., 2010). Here, it appears there are significant PCB inputs to lakes in western Washington and on the eastern slope of the Cascades. This suggests that PCBs from western Washington fall out over the Cascades in precipitation (likely snowfall) and enter these lake ecosystems. This phenomenon, known as cold-trapping, has been observed in other mountainous regions (Grimalt et al., 2001; Daly et al., 2007; Gallego et al., 2007; Wania and Westgate, 2008). It has also been suggested that trapping or filtering of atmospheric toxics by forested landscapes and storage in forest soils can have a greater influence, leading to higher concentrations, than direct fallout (Liu et al., 2014). The PCB concentrations in fish tissue from the Johnson et al. (2010) study are occasionally much greater than the concentrations used by Washington to list waters as impaired under CWA Section 303(d). This finding suggests that understanding the spatial distribution of the atmospheric deposition of PCBs in Washington is worthwhile.

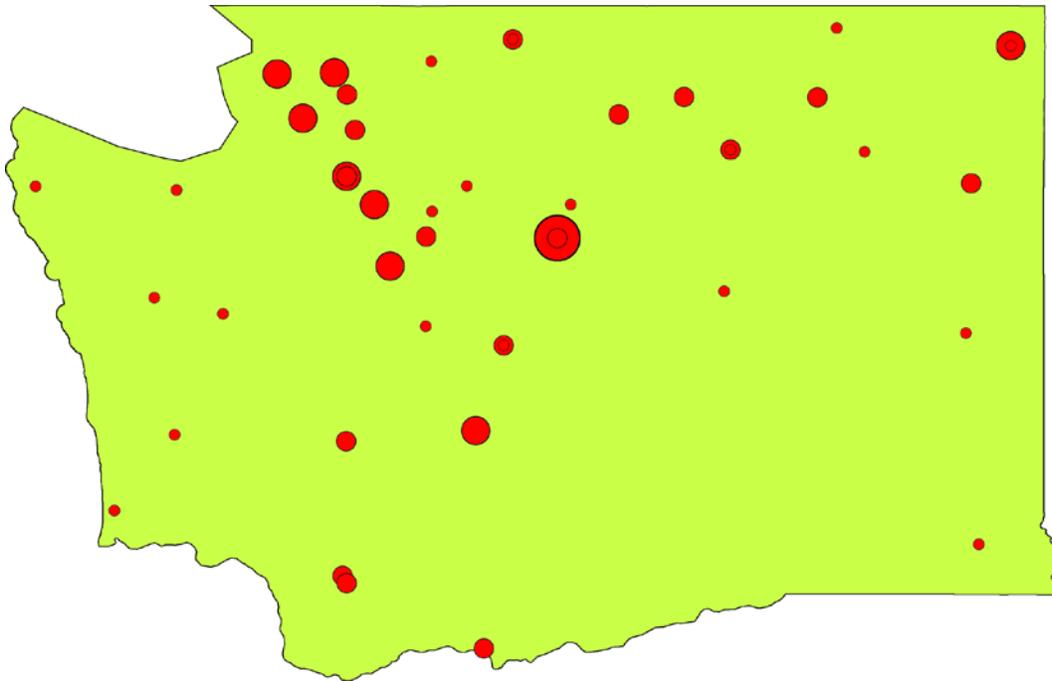


Figure 14: Relative concentrations of penta-chlorobiphenyls (PCBs) in fish tissues from undisturbed lakes.

## 8. Uncertainties and Variability

### *Measured and Estimated Uncertainty*

The study of atmospheric deposition of toxics is difficult because of the uncertainty that surrounds the measurement of such low concentrations and the temporal and spatial variability of those measurements. Some of the Washington regional studies on atmospheric deposition of toxics used many samples that would not meet data quality objectives for precision in the field ([Table 6](#)). In many cases, the field replicates were outside an acceptable threshold of > 50% relative percent difference. Furthermore, the recovery of spikes in field blank samples were outside an acceptable range of 50-130%; in many samples there was a bias low which suggests that atmospheric fluxes were underestimated during these sample events (acknowledged in Brandenberger et al., 2010). Some of the sample variability described in [Table 6](#) may be a function of the collection method. It is possible that collecting bulk deposition samples (wet and dry) could be more susceptible to uncertainties because of the variability of particulate matter in the sample. The interference of particulate on passive gas-phase samplers is well known (Melymuk et al., 2014).

In the scoping exercise by Leidos and NewFields (2013) for the LDW, where loads for indirect deposition were calculated based on measured fluxes (Colton et al., 2013), the ranges of % contribution to “lateral” loads from the landscape were ~10% to >100%. Similar to attempts by Era-Miller (2011) to estimate indirect loads, the uncertainty is too large to make these estimates useable. Much of this uncertainty is attributable to the variability in sample location and time (season). Atmospheric fluxes of toxics will vary greatly from location to location and over short timescales (weeks) to long timescales (inter-annual).

The level of acceptable uncertainty and variability in the data will depend on the study question. For example, constraining a regional background annual flux for PCBs would require a broad sample network, collecting enough samples to understand inter-annual variability. Understanding the contribution of wet and dry precipitation to a stormwater discharge would require localized sampling at a daily or weekly frequency.

### ***Reducing Uncertainty and Variability***

In order to reduce the uncertainty in measurements, there needs to be a rigorous field and laboratory QC program. The National Atmospheric Deposition Network (NADP) and the Integrated Atmospheric Deposition Network (IADN) are two long-term (>20 years) atmospheric deposition programs which involve a network of sample stations and laboratories. These networks have guidance documents and reports that would aid in establishing a suitable QA/QC program ([Table 7](#)). In a recent evaluation of the IADN QA program, Wu et al. (2009) found a high level of compliance in an inter-laboratory comparison.

Co-locating wet and dry samplers with meteorological stations may be an effective means to reduce sample variability (EPA, 2001). However, sampling dry deposition introduces some uncertainty because of the assumption of dry deposition velocities that is necessary to calculate fluxes. This dilemma highlights the importance of determining what quality of data is necessary to answer the study question. If possible, reducing the period of time that the sampler collects can reduce the possibility for cross-contamination. For example, the Mercury Deposition Network (MDN) collects samples daily following the start of precipitation to reduce the chances of any particular sub-sample being contaminated or otherwise altered. Daily samples are composited into a weekly sample for analysis.

It is estimated that ~ 25% of the project budget should be devoted to QA/QC.

## **9. Modeling Approaches**

Atmospheric deposition has been incorporated into model frameworks using a module to estimate fluxes from emissions (e.g., Csiszar et al., 2013) and as a measured boundary (input) condition to another fate and transport or watershed model (e.g., Davis, 2004). Models of air deposition are also used to track and predict plume dispersion and emissions from point sources; these models are not considered here. The goal of this scoping exercise is to develop an approach that could be used in Washington to determine the contribution of atmospheric deposition to surface waters. Based on a review of the literature and conversations with external modeling groups (pers. comm. J. Yearsley, M. Diamond, D. Muir, and L. Rodenberg), it would be most appropriate to consider defining atmospheric deposition fluxes through measurements and not models. However, at the local (urban) scale, an emission or multimedia model that estimates the atmospheric flux from emissions, and is validated through measurements, may be particularly useful in source reduction. Modeling of Hg emissions and comparing to lake sediment archives of Hg was explored by Paulson and Norton (2008) in Whatcom County, Washington.

In these broadly described uses of models to incorporate the atmospheric deposition of toxics, there are no models currently used at Ecology that do this. One exception is a simple fate and transport model that considers atmospheric deposition as a boundary condition (e.g., Pelletier and Mohamedali, 2009).

### ***Local Scale***

Modeling the deposition of toxics at the local (urban) scale has focused on the role of wash-off from impervious surfaces and the contributions to stormwater. The work of Diamond and others in Toronto was to establish a multimedia model (MUM-Fate) that described the fate and transport of a measured emission in an urban landscape (Diamond et al., 2010; Csiszar et al., 2013). Supplemental studies also provided empirical data on the contaminant concentrations and burdens within the model compartments (e.g., organic films on impervious surfaces) (Diamond et al., 2010; Melymuk et al., 2014). The empirical data included an understanding of the gas-particle transfer, from data obtained using passive air samplers to measure the gas phase. A more complex version of the MUM-Fate model was developed: the Spatially Orientated (SO)-MUM, which is the MUM model coupled with a boundary layer forecast and air pollution transport model (Csiszar et al., 2013). In the end the SO-MUM model did not outperform the simpler MUM-FATE model in predicting the flux of toxics from air to land to water. Using a model that incorporates local emissions and relates this to deposition and stormwater discharge would help identify opportunities for source reduction.

In the urban landscape, engineers have been modeling the transport of particulates and runoff from impervious surfaces for some time (Metcalf and Eddy, 1971). A widely used model is the EPA's Storm Water Management Model (SWMM), which is a dynamic rainfall-runoff model for the simulation of the runoff quantity and quality in an urban environment (Rossman, 2010). It has the ability to model pollutant build-up and wash-off, but considers atmospheric deposition as a boundary condition. SWMM is similar to other stormwater models; it is a relatively small desktop model and could be adapted to incorporate more fate and transport terms.

Lastly, a model used in the Seattle region on a number of different land-uses is the Distributed Hydrology Soil Vegetation Model (DHSVM) (Wigmosta et al., 1994). Recently, this model has been adapted for stream temperature and water quality (Sun et al., 2014). It is a large model that requires significant computing power; it would need further adapting for toxics studies. Atmospheric deposition is considered a boundary condition. This model could incorporate multiple discharges and sites that may impact a single urban stream.

Ecology currently does not have any in-house models that could be used to estimate the contribution of atmospheric deposition in an urban stormwater catchment.

### ***Regional Scale***

One of the main data gaps in all studies of atmospheric deposition of toxics is quantifying the indirect load passing through a watershed. To do this, a hydrodynamic model of the watershed would need to be adapted to model fate and transport of toxics. Again, it would seem that atmospheric fluxes of toxics should be measured and considered a boundary condition. There are any number of watershed,

hydrodynamic models of varying degrees of complexity and varying empirical requirements ([Table 8](#)). The models range from statistical to more deterministic. Given the uncertainty that the application of any model to atmospheric deposition, preference should be given to a more deterministic approach where model compartments can be constrained as much as possible.

Another approach to assessing indirect deposition would be to follow the work of Totten et al. (2006b) where an empirical relationship was derived for a small watershed that was known to receive only atmospheric deposition. By measuring the total atmospheric flux of the contaminant of concern across the basin and then measuring the concentration and load in the stream, the watershed yield could be derived. This would also allow for the calculation of pass-through efficiency in different terrestrial ecosystems within Washington, which could then be applied to approximate indirect loads in other watersheds.

Modeling the direct wet deposition to a waterbody is simply achieved by knowing the atmospheric flux and multiplying by the surface area of the waterbody. Incorporating the diffusion of the gas phase across the water boundary requires using knowledge of the concentration in gas phase, wind velocity, lake water temperature and the chemical characteristics of the contaminants. The diffusion of the gas-phase into a waterbody is only relevant when dissolved air concentrations are high enough relative to water concentrations (Totten et al., 2001). This is unusual and not expected in Washington waterbodies.

Ecology has a fate and transport model for toxics that incorporates direct atmospheric deposition (Pelletier and Mohamedali, 2009) and an in-stream model for water quality and temperature that would need to be adapted for the fate and transport of toxics (Pelletier et al., 2006). Ecology currently has no watershed hydrodynamic model.

### ***Statewide***

A model framework currently exists for meteorological conditions and an air quality module for emissions of particulates and ozone (University of Washington and Washington State University<sup>1</sup>). Currently the role of these models is primarily to detect and predict poor air quality in urban areas due to fire (woodstove and wildfire) and ozone. It may be possible to interface some of the statewide models with measured atmospheric deposition data. The Western Regional Air Partnership—a voluntary group of local, state, federal, and tribal agencies— provides technical analyses and databases to assist states in understanding mercury and particulate deposition.

Ecology does not have the capacity to model the transport and deposition of contaminants statewide. Collaborations would be necessary to begin to model statewide atmospheric deposition. However, an empirical (monitoring) approach to evaluating the spatial distribution of toxics would be more informative and reliable.

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<sup>1</sup> UW runs the Weather Research and Forecasting (WRF) Model and WSU runs the WRF model with the Community Multiscale Air Quality (CMAQ) module.

## 10. Assessment of Atmospheric Deposition

### ***Advisory Panel***

A technical advisory panel would be recommended for any large project or program on atmospheric deposition of toxics. Many people were consulted during the research of this paper and are a resource for further discussion. They include:

Measurement: Derek Muir, Environment Canada  
Richard Grace, AXYS Analytical  
Jenée Colton, King County  
Lisa Rodenburg, Rutgers University  
Dan Jaffe, University of Washington – Bothell (not consulted)

Modeling: Greg Pelletier, EAP Ecology  
Ranil Dhammapala, AQP Ecology  
John Yearsley, EPA and UW Computational Hydrology Group  
Miriam Diamond, University of Toronto

Site Selection: Dale Norton, EAP Ecology  
Holly Davies, W2R, Ecology  
Rachel McCrea, WQP Ecology

In addition, a larger atmospheric deposition program would require the appointment of a QA/QC officer.

### ***Study Questions***

The main question behind any future study of atmospheric deposition is: *How important is atmospheric deposition of toxics to surface water in Washington, compared to other toxics sources?*

At the local scale, potential questions are:

- What is the proportion of toxics in stormwater runoff attributable to atmospheric deposition?
- How does the atmospheric flux of toxics vary seasonally?
- What are the major sources of toxics to the site?

At the regional scale potential questions are:

- What proportion of the load of toxic contaminants in a river or lake is attributable to atmospheric deposition?
- How does the atmospheric flux of toxics vary seasonally and annually?
- What are the major sources of toxics to the region?

At the statewide scale potential questions are:

- What proportion of atmospheric deposition is local and what proportion is out-of-state? In the case of mercury, what additional proportion is natural?
- What are the major sources of toxics to the state?

- What is the spatial and seasonal distribution of atmospheric deposition of toxics?

### ***Sampling Program***

It should be clear from the primary question behind any future study of atmospheric deposition that an accurate answer will depend on reliably quantifying the entire mass balance for the study scale of interest. Therefore, any future study should consider the prior work accomplished and assess whether the study of atmospheric deposition could dovetail with existing data. It would be advisable to develop any follow-up projects on a pilot basis, where the data would be directly applicable to an existing issue or project.

As described by the EPA (2001) the types of data pertinent to a study of atmospheric deposition include:

- wet deposition rates
- dry deposition rates
- ambient air quality data and deposition velocities (to calculate the dry deposition rate)
- meteorological data (rainfall amount daily or weekly, wind speed, wind direction)
- good inventories of sources that emit pollutants of concern locally, regionally, and perhaps nationally (an ideal inventory should include all sources, emission heights, speciation of emissions, rates of emissions, the exit velocity, and the stack gas temperature)
- sophisticated meteorological data sets (to input into transport models)
- watershed transport ratios or models
- loading rates from sources other than atmospheric sources
- emissions chemical “fingerprints”
- ecological data showing impacts of atmospheric deposition

### *Local scale project ideas:*

King County and the greater Seattle area is really the only area in Washington with previous data on atmospheric deposition of toxics. There is the interest and background to support further detailed study at the local scale. In particular, the Lower Duwamish Waterway, where a scoping study on atmospheric deposition has also been carried out (Leidos and NewFields, 2013), has a working group with King County, Ecology, and others who could advise on selecting site and developing a local scale project (pers. comm., R. McCrea).

Selecting a small, previously studied stormwater catchment would allow for intensive study of atmospheric inputs, runoff composition and efficiency, end-of-pipe composition, and receiving water composition (including upstream load). Steps would include:

- Begin with using a simple multimedia model to describe the flux of toxics throughout the landscape (e.g. Diamond et al., 2010).
- Should the simple model not appear robust enough or ineffective, select a more complex model that could be used in other stormwater catchments (e.g., Sun et al., 2014).
- Pull back-trajectories of prevailing wind to the site, to help with possible source identification.

- Consider quantifying fluxes of toxics in all phases.
- If bulk samplers are used for wet and dry deposition, collocate multiple samplers (minimum 3) for replication.
- Collect samples on a bi-weekly or monthly basis over the course of a year or more.
- Characterize the relative influence of atmospheric deposition on an annual basis.

*Regional Scale Project ideas:*

Select a watershed with a fairly well-defined TMDL mass balance and simple boundary, preferably with undisturbed upper sub-watersheds (e.g. Spokane or Upper Yakima). The goal should be to characterize atmospheric deposition across different land uses within the watershed; therefore, the sampling locations should represent different land uses. Consider using a master-satellite approach to sites, where one master site is measured more frequently and the satellite locations are used to increase the spatial coverage. Use the undisturbed sub-watersheds to estimate pass-through rates and characterize “background” deposition to the watershed (e.g., Totten et al., 2006b). This will allow the local urban influence to be parsed out.

An additional approach may be to collaborate with the Intensively Monitored Watersheds program or the Continuous Freshwater Monitoring program in a well-studied, undisturbed watershed. The focus of this would be to understand in greater detail the fluxes of toxics and pass-through in a forested landscape. Sampling would be more detailed than the previous suggestion and include ecosystem compartments such as: throughfall precipitation, runoff, vegetation, soils, shallow subsurface flow, groundwater, and stream/river chemistry.

*Statewide Scale Project ideas:*

At the state scale, there would be fewer chemicals of concern. Metals (except mercury) are not conducive to long-range transport. In general, those persistent semi-volatile compounds with lighter congeners or compounds are highly susceptible to long-range transport and would be of concern statewide.

Monitoring atmospheric deposition of toxics at a statewide scale will require collaborating and relying on existing sampling networks. The assessment could focus on both spatial and temporal aspects. Spatially, a synoptic survey using passive samplers would describe the gas phase concentrations of toxics (for example, a transect across the state through watersheds of interest from previous or ongoing studies). Ecology also monitors PM<sub>2.5</sub> and PM<sub>10</sub> at a number of locations. The filters from these active sampling events are archived and may be available for further chemical analysis (pers. comm., R. Dhammapala). Lastly, the Snotel network of snowpack monitoring sites operated by the USDA could be sampled near peak snowpack for a complete wet deposition flux of toxics to Washington mountains. Advantages of using the Snotel sites are that they are accessible, have historical meteorological data, and would have ancillary data on accumulation and soil moisture in some cases.

In order to assess the temporal aspect of statewide deposition, the master-satellite approach should be used, where the master site is part of an ongoing network such as the Mercury Deposition Network.

There are 2 sites in Washington, including the coastal Makah National Fish Hatchery (supported in part by Ecology) and Seattle. Adding an additional site in eastern Washington would capture the long-term variability in a very different biogeoclimatic zone.

## **11. Recommendations**

This paper describes a scoping exercise that evaluated the potential influence atmospheric deposition of toxics has on water quality in the state of Washington. While it was possible to summarize the available data sets and do some back-of-the-envelope calculations, the estimates presented in this paper really only serve to highlight that there is a measurable atmospheric contribution of toxics worth quantifying with more certainty. This is particularly true for urban environments, for which most of the current data exist. The following are prioritized recommendations for follow-up actions to this paper:

1. Focus on a short list of toxics to sample in a pilot field study.
2. Coordinate the choice of toxics and study locations with WQP priorities.
3. Any future work should involve the compilation of an advisory group to scope projects.
4. Pilot project at the local scale: collaborations and interest exist for a pilot study at the local scale in the Lower Duwamish River watershed (WRIA 9). Select a previously studied stormwater catchment. Consider the use of a simple multimedia model to validate during the study, which could then be employed in other urban catchments.
5. Pilot project at the regional or watershed scale: consider a pilot study on the regional atmospheric deposition of toxics in a watershed such as the Spokane River or Green-Duwamish River, where there is interest from existing projects. The watershed should have undisturbed sub-watersheds that could aid in defining a purely atmospheric contribution. Consider working towards the use of a hydrodynamic model that could be used in future TMDLs or source assessments for toxics.
6. Discuss whether a hydrodynamic model, where atmospheric contributions can be measured and defined as a boundary condition, would be worthwhile developing for Washington. It would be applicable to TMDLs and urban streams.
7. Quantify the modern (last ~ 10 years) mercury and lead loading in Seattle and estimate what the natural background contributions would be from the sediment core data Ecology has previously collected. The estimate of natural background contributions is relevant to all geographic scales.
8. The deposition of mercury and PCBs statewide would seem to be directly applicable to water quality issues. There is a statewide freshwater fish advisory for mercury and current PCB concentrations in tissue of fish in lakes receiving only atmospheric inputs are above the concentrations used by Washington to list waters as impaired under CWA Section 303(d). An assessment of these parameters statewide would be worthwhile.

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Lisa Rodenburg, Rutgers University  
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## Tables

**Table 1: Summary of % contributions from atmospheric deposition of toxics to select surface waters in the U.S.**

region	scale	parameter	% atmospheric	model	level of empirical data	reference
Lake Michigan	regional	Atrazine	32.4	mass balance	high	MacDonald et al., 2000
Santa Monica Bay	regional	chromium	40	mass balance	high	Stolzenbach et al., 2001
Puget Sound	regional	Copper	2-27	mass balance	high	Osterberg and Pelletier, unpublished data
Santa Monica Bay	regional	Copper	15	mass balance	high	Stolzenbach et al., 2001
San Francisco Bay	regional	dioxin	58	mass balance	high	Allen and Yee, 2012
Santa Monica Bay	regional	lead	99	mass balance	high	Stolzenbach et al., 2001
Santa Monica Bay	regional	nickel	8	mass balance	high	Stolzenbach et al., 2001
Lake Ontario (nr. Toronto)	regional	PAH	10	mass balance	high	Melymuk et al., 2014
Puget Sound	regional	PAH	3-50	mass balance	high	Osterberg and Pelletier, unpublished data
Lake Ontario (nr. Toronto)	regional	PBDE	<5	mass balance	high	Melymuk et al., 2014
Puget Sound	regional	PBDE	9-85	mass balance	high	Osterberg and Pelletier, unpublished data
Lake Washington	regional	PBDE	30	mass balance	moderate	DeGasperi, 2013
Puget Sound	regional	PCB	2-52	mass balance	high	Brandenberger et al. 2012; Osterberg and Pelletier, unpublished
Lake Superior	regional	PCB	51%	mass balance	high	MacDonald et al., 2000
Lake Ontario (nr. Toronto)	regional	PCB	66	mass balance	high	Melymuk et al., 2014
San Francisco Bay	regional	PCB	0^	mass balance	high	San Francisco Bay Regional Water Quality Control Board, 2008
Delaware River Basin	regional	PCB	7.7	mass balance and modified EPA's WASP model	high	DRBC, 2003 (Table 2.17)
Toronto	local	PCB		multimedia (MUM-Fate)	high	Diamond
Lake Washington	regional	PCB	16	mass balance	moderate	DeGasperi, 2013
Hudson River	regional	PCB	~3%	mass balance	moderate	Totten et al., 2004
Lake Superior	regional	Toxaphene	31.1	mass balance	high	MacDonald et al., 2000

region	scale	parameter	% atmospheric	model	level of empirical data	reference
Puget Sound	regional	Zinc	3-46	mass balance	high	Osterberg and Pelletier, unpublished data
Santa Monica Bay	regional	zinc	34	mass balance	high	Stolzenbach et al., 2001

^ San Francisco Bay is an atmospheric source of PCBs

**Table 2: Toxic chemicals of concern relevant to atmospheric deposition**

parameter	Kow	Koa	Kaw	fugacity ratio	group
Aldrin	3.01	4.44	-1.43	0.17	pest
Atrazine	2.40	9.33	-6.93	0.03	pest
Lindane	3.71	7.93	-4.22	0.14	pest
Chloroform	1.97	2.78	-0.81	1.00	pest
Chlorpyrifos	4.90	8.90	-3.36	0.68	pest
Dichlorodiphenyltrichloroethane (p,p-DDT)	5.47	10.40	-3.28	0.15	pest
Dichlorodiphenyldichloroethane (p,p-DDD)	5.75	9.60	-3.59	0.14	pest
Dichlorodiphenyldichloroethylene (p,p-DDE)	6.14	9.30	-2.49	0.23	pest
Diazinon	3.30	9.10	-4.79	1.00	pest
Dieldrin	4.60	7.94	-3.34	0.03	pest
Endosulfan	3.78	7.15	-3.37	0.22	pest
Endrin	4.63	9.50	-4.87	0.02	pest
Heptachlor	5.19	6.04	-0.85	0.20	pest
Heptachlor epoxide	4.51	6.09	-1.58	0.05	pest
Pentachlorophenol	5.18	9.68	-4.50	0.03	pest
Toxaphene	5.50	9.02	-3.52	0.30	pest
1-CBs	4.61	6.22	-1.61	0.71	pcb
2-CBs	5.09	7.07	-1.93	0.70	pcb
3-CBs	5.55	7.58	-1.86	0.45	pcb
4-CBs	5.98	8.12	-1.93	0.20	pcb
5-CBs	6.40	8.90	-1.81	0.18	pcb
6-CBs	6.80	9.46	-2.00	0.25	pcb
7-CBs	7.17	9.86	-2.28	0.07	pcb
8-CBs	7.52	9.90	-1.87	0.05	pcb
9-CBs	7.93	11.00	-1.82	0.02	pcb
PBDE-28	5.88	8.56	-2.68	unk	pbde
PBDE-47	6.77	9.87	-3.10	unk	pbde
PBDE-66	6.77	10.47	-3.70	unk	pbde
PBDE-85	7.66	12.01	-4.35	unk	pbde
PBDE-99	7.66	11.43	-3.77	unk	pbde
PBDE-100	7.66	11.10	-3.44	unk	pbde
PBDE-153	8.55	12.70	-4.15	unk	pbde
PBDE-154	8.55	12.55	-4.00	unk	pbde
PBDE-183	9.44	14.98	-5.54	unk	pbde
dimethyl phthalate	2.12	7.47	-5.35	1.00	phthalate
diethyl phthalate	2.47	7.86	-5.39	1.00	phthalate
dibutyl phthalate	4.72	9.42	-4.70	1.00	phthalate
dioctyl phthalate	9.87	13.51	-3.64	1.00	phthalate

parameter	Kow	Koa	Kaw	fugacity ratio	group
butyl benzyl phthalate	4.91	9.20	-4.29	1.00	phthalate
di(2-ethylhexyl)-phthalate	5.11	10.07	-4.96	1.00	phthalate
Dibenzo-p-dioxin	4.30	6.63	-2.33	0.11	dioxin/furan
Dibenzofuran	4.31	6.68	-2.37	0.25	dioxin/furan
LPAH	4.19	6.70	-2.28	0.17	PAH
HPAH	5.88	10.29	-3.24	0.05	PAH
Benz[a]anthracene	5.91	9.50	-4.39	0.04	PAH
Chrysene	5.61	10.40	-3.74	0.01	PAH
Benzo[a]pyrene	6.35	10.80	-4.73	0.03	PAH
Lead	NA	NA	NA	NA	metals
Copper	NA	NA	NA	NA	metals
Arsenic	NA	NA	NA	NA	metals
Mercury	NA	NA	NA	NA	metals
Zinc	NA	NA	NA	NA	metals

**Table 3: Summary of Mercury Deposition Network data from Washington's two active stations**

site	minimum	25th percentile	median	mean	75th percentile	maximum
<b>Concentration (ng L<sup>-1</sup>)</b>						
Seattle	1.4	4.61	8.02	11.93	12.84	94.58
Makah	0.24	2.1	3.14	4.89	5.295	85.3
<b>Load (ng m<sup>-2</sup>)</b>						
Seattle	0.72	55.58	106.7	175.8	224.1	2652
Makah	0.31	48.04	102.4	171.6	202.4	4117

**Table 4: Summary of atmospheric mercury contributions in water quality studies**

region	scale	% local/ regional	% out-of- state	% natural	model	level of empirical data	reference
NE USA	multiple states	87	13	NA	Regional Modeling System for Aerosols and Deposition (REMSAD)	moderate	NE States, 2007
MN	statewide	40	30	30	empirical	high	MNPCA, 2007
Willamette Basin, OR	regional	47.7	unk	unk	multimedia	moderate	Hope, 2008
Lake Whatcom	regional	41	59*	unk	empirical; dispersion modeling	low	Poulson, 2004

NA=not assessed

\* amount attributed to "tributaries", could also include local sources

**Table 5: Estimates of indirect atmospheric deposition of PCBs in the Green-Duwamish Watershed.**

Land use	pass-through rate	atmospheric PCB flux (ng m <sup>-2</sup> -day) <sup>a</sup>	land use area (km <sup>2</sup> ) <sup>a</sup>	indirect load (g day <sup>-1</sup> )	
forested	5%	0.71	786	0.028	
commercial/industrial	75%	7.51	75	0.422	
residential	50%	4.26	223	0.475	
agricultural	25%	0.71	13	0.002	
transportation	75%	7.51	86	0.484	
				cumulative indirect load	1.412
				median instantaneous load <sup>b</sup>	5.136
				% indirect deposition	27%

<sup>a</sup> Colton et al., 2013

<sup>b</sup> Conn and Black, 2014

**Table 6: Field and lab quality control data from previous atmospheric studies**

contaminant	contaminant group	field replicate RPD (%)	blank recovery (%)	study
arsenic	metals	9-29	98.5	Colton et al. 2013
cadmium	metals	27-44	103.5	Colton et al. 2013
chromium	metals	5-21	98.5	Colton et al. 2013
copper	metals	2-29	105	Colton et al. 2013
lead	metals	0-31	105	Colton et al. 2013
mercury	metals	11-140	93.2	Colton et al. 2013
nickel	metals	2-30	104	Colton et al. 2013
silver	metals	140-158	107	Colton et al. 2013
vanadium	metals	2-27	100	Colton et al. 2013
zinc	metals	3-26	109.5	Colton et al. 2013
benzo(a)anthracene	HPAH	0-7	80.8	Colton et al. 2013
benzo(a)pyrene	HPAH	3-14	2.2	Colton et al. 2013
benzo(b,j,k)fluoranthene	HPAH	0.3-7	94	Colton et al. 2013
benzo(g,h,i)perylene	HPAH	1-4	91.8	Colton et al. 2013
chrysene	HPAH	4-6	95.8	Colton et al. 2013
dibenzo(a,h)anthracene	HPAH	2-41	97.6	Colton et al. 2013
fluoranthene	HPAH	2-26	97.3	Colton et al. 2013
indeno(1,2,3-Cd)pyrene	HPAH	0.5-12	98.2	Colton et al. 2013
pyrene	HPAH	2-25	92.7	Colton et al. 2013
acenaphthene	LPAH	3-23	53.8	Colton et al. 2013
acenaphthylene	LPAH	10-37	18.6	Colton et al. 2013
anthracene	LPAH	1-79	15.1	Colton et al. 2013
fluorene	LPAH	11-30	85.3	Colton et al. 2013
naphthalene	LPAH		64.8	Colton et al. 2013
phenanthrene	LPAH	4-15	69	Colton et al. 2013
total PCBs	PCB	12-68	85	Colton et al. 2013
dioxin/furan	dioxin/furan	1.3-35	102	Colton et al. 2013
total PCBs	PCB	12-41	18-43	Brandenberger et al. 2010
total PCBs	PCB	NA	45-159	Crecelius et al. 1991
naphthalene	LPAH	NA	10-40	Crecelius et al. 1991
acenaphthene	LPAH	NA	30-70	Crecelius et al. 1991
perylene	HPAH	NA	60-120	Crecelius et al. 1991
PAHs	PAHs	5-36	NA	Brandenberger et al. 2010
PBDEs	PBDEs	0-103	NA	Brandenberger et al. 2010
metals	metals	22-55	NA	Brandenberger et al. 2010
mercury	metals	2-98	NA	Brandenberger et al. 2010

contaminant	contaminant group	field replicate RPD (%)	blank recovery (%)	study
methylmercury	metals	8-142	NA	Brandenberger et al. 2010
arsenic	metals	5	98	Brandenberger et al. 2010
cadmium	metals	9	98	Brandenberger et al. 2010
chromium	metals	37	99	Brandenberger et al. 2010
copper	metals	2	100	Brandenberger et al. 2010
lead	metals	1	100	Brandenberger et al. 2010
nickel	metals	4	98	Brandenberger et al. 2010
zinc	metals	2	100	Brandenberger et al. 2010

**Table 7: Quality control measures used by the Integrated Atmospheric Deposition Network**

Parameter	analytical accuracy expressed as % recovery for matrix spikes	analytical precision expressed as relative % difference (RPD)	overall precision expressed as relative % difference	limit of detection
<b>Air Organics</b>	<b>50-130%</b>	<b>&lt;50%</b>	<b>&lt;100%</b>	<b>0.003 ng m-3</b>
PCBs	50-130%	<50%	<100%	0.003 ng m-3
Pesticides	50-130%	<50%	<100%	0.003 ng m-3
PAHs	50-130%	<50%	<100%	0.003 ng m-3
<b>Precipitation Organics</b>	<b>50-130%</b>	<b>&lt;50%</b>	<b>&lt;100%</b>	<b>NA</b>
PCBs	50-130%	<50%	<100%	0.005 ng L-1
Pesticides	50-130%	<50%	<100%	0.1 ng L-1
PAHs	50-130%	<50%	<100%	0.1 ng L-1

**Table 8: Comparison of watershed models**

	SWAT	WAMRF	HSPF	LSPC	DHSVM
Link	<a href="#">SWAT-TAMU</a>	<a href="#">WARMF-EPA</a>	<a href="#">HSPF-Aqua Terra</a>	<a href="#">LSPC-EPA</a>	<a href="#">DHSVM</a>
GIS support	BASINS - integrated	BASINS - manual	BASINS - integrated	Stand-alone	?
Watershed scale	small to large	Medium	Small to Medium	Medium to Large	Large
Atmospheric deposition	Boundary condition	Boundary condition	Boundary condition	Boundary condition	Boundary condition
GW	included	included	included	included	Included
Timestep	Daily	Daily	1-hr	1-hr	1-hr
Surface Runoff	SCS curve number / Green & Ampt	Catchments w canopy, ET, surface runoff (Mannings n), GW infiltration	Pervious and impervious land segments; complex hydrology surface and subsurface	same as HSPF	Overland flow; shallow subsurface flow; infiltration interception
Instream flow	Manning's n, modified Rational	mass balance w Mannings n	mass balance routing w rating tables	same as HSPF	Manning
Instream processes	Transport / deposition / phytoplankton algae only / simplified nutrient cycles	Transport / deposition / 3 spp. phytoplankton + periphyton / limited nutrient cycles	transport / deposition / CBOD / phytoplankton & periphyton / complex nutrient dynamics	same as HSPF	Transport / deposition / simplified nutrient cycles/ no algal uptake
TMDL support	built-in BMPs	decision-support	manual	dynamic	Erosion and sediment transport module
BMP integration	Ag practices; Veg filter strips; grassy swales	Buffer, fertilization, ag bmps, fencing, septics, land use change	manual %red by LU	%reduction by LU	?
Overall complexity	Moderate	Moderate to high	Very high	Very high	High
Documentation	Excellent	Poor	Good	Good	Good
Ownership	Public - TAMU/EPA	Semi-public, framework free, but needs private support	Public - EPA	Public - EPA	Public-UW
Comments	Simple, ag-focused, widely used	Poorly documented. Hangman Ck	Complex. Widely used	HSPF w GUI	Complex

## Appendix A: Mercury Deposition Network (MDN)

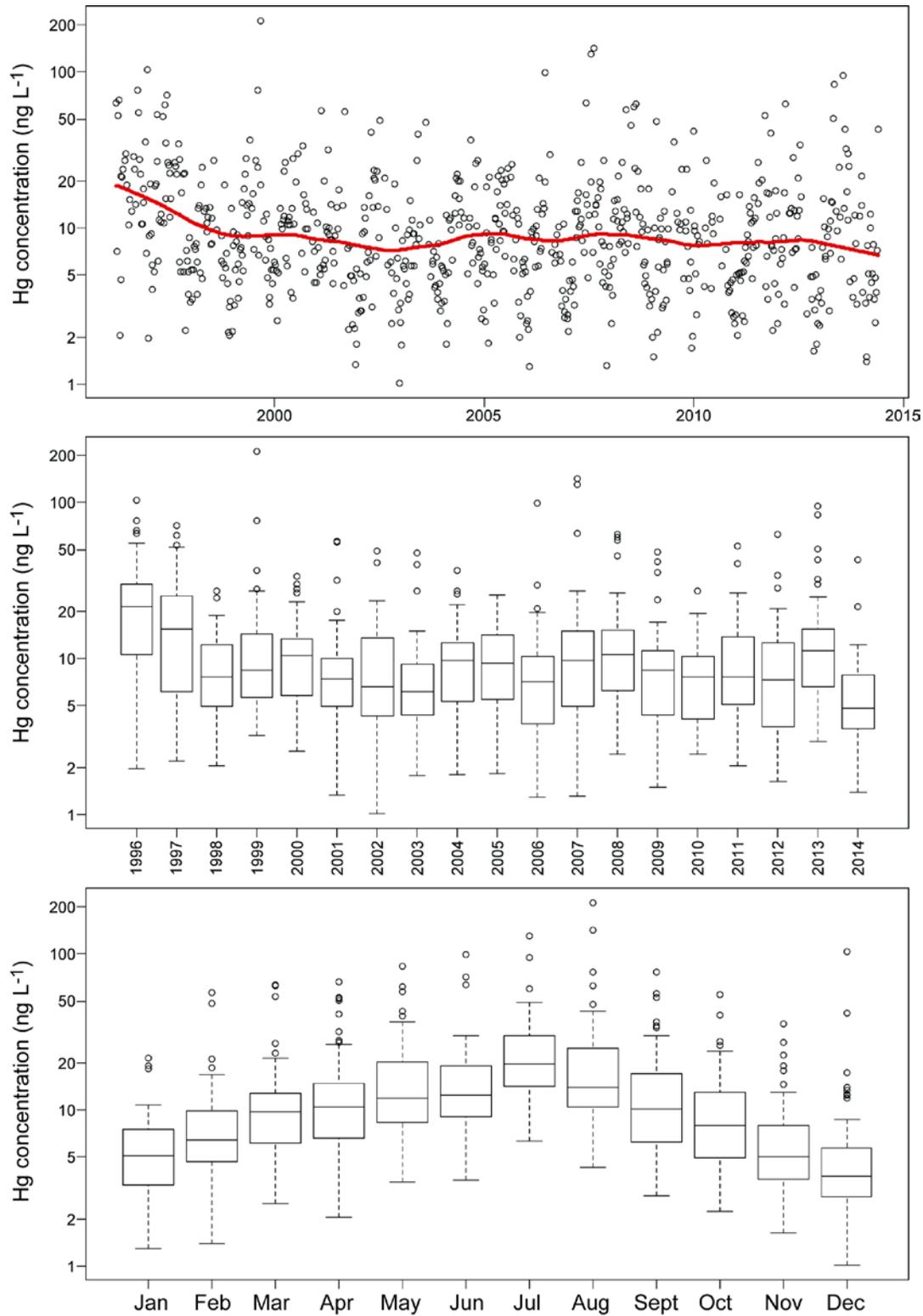


Figure A-1: Mercury (Hg) concentrations in precipitation at Seattle MDN site WA18.

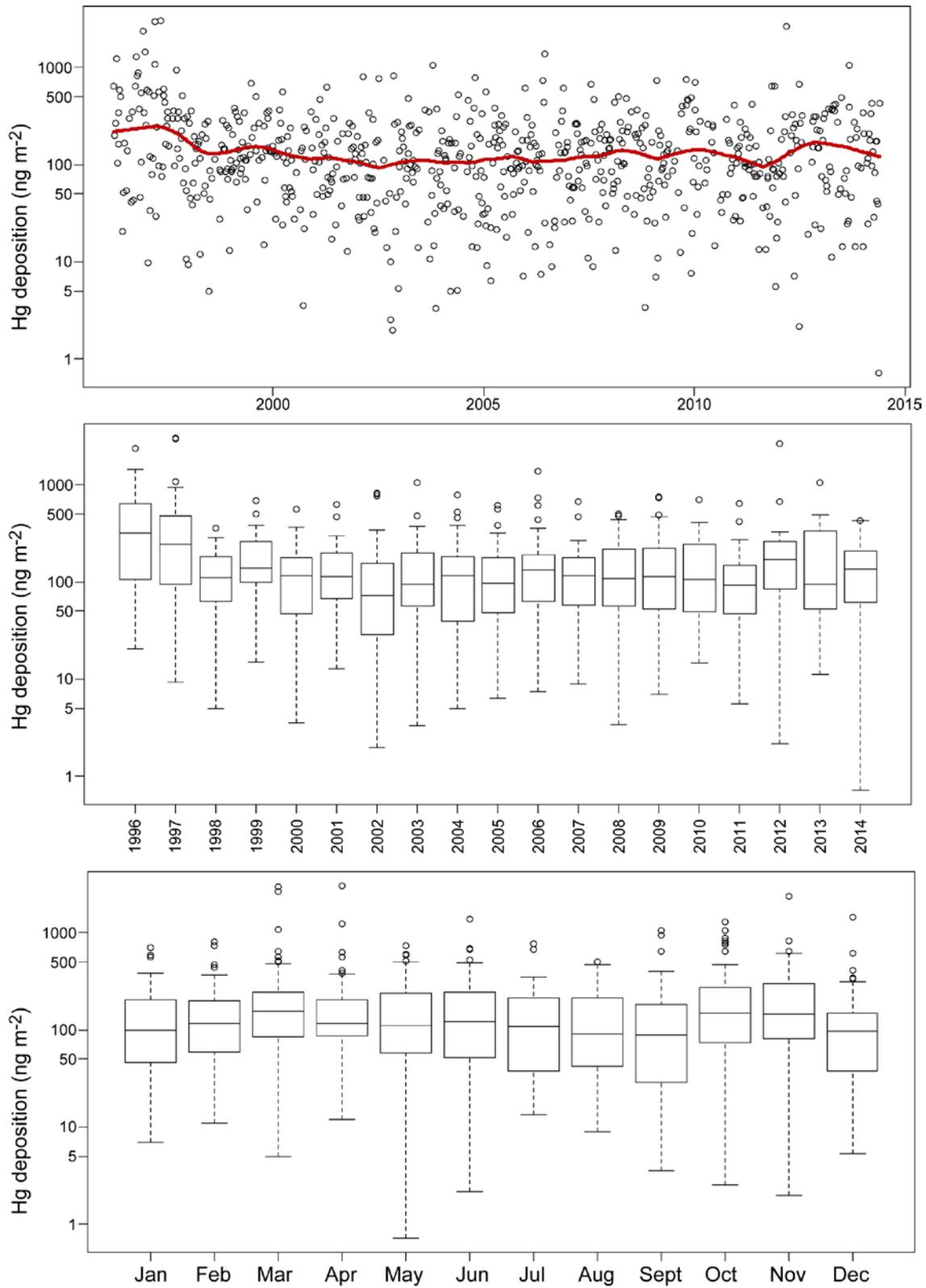


Figure A-2: Mercury (Hg) wet deposition rates at Seattle MDN site WA18.

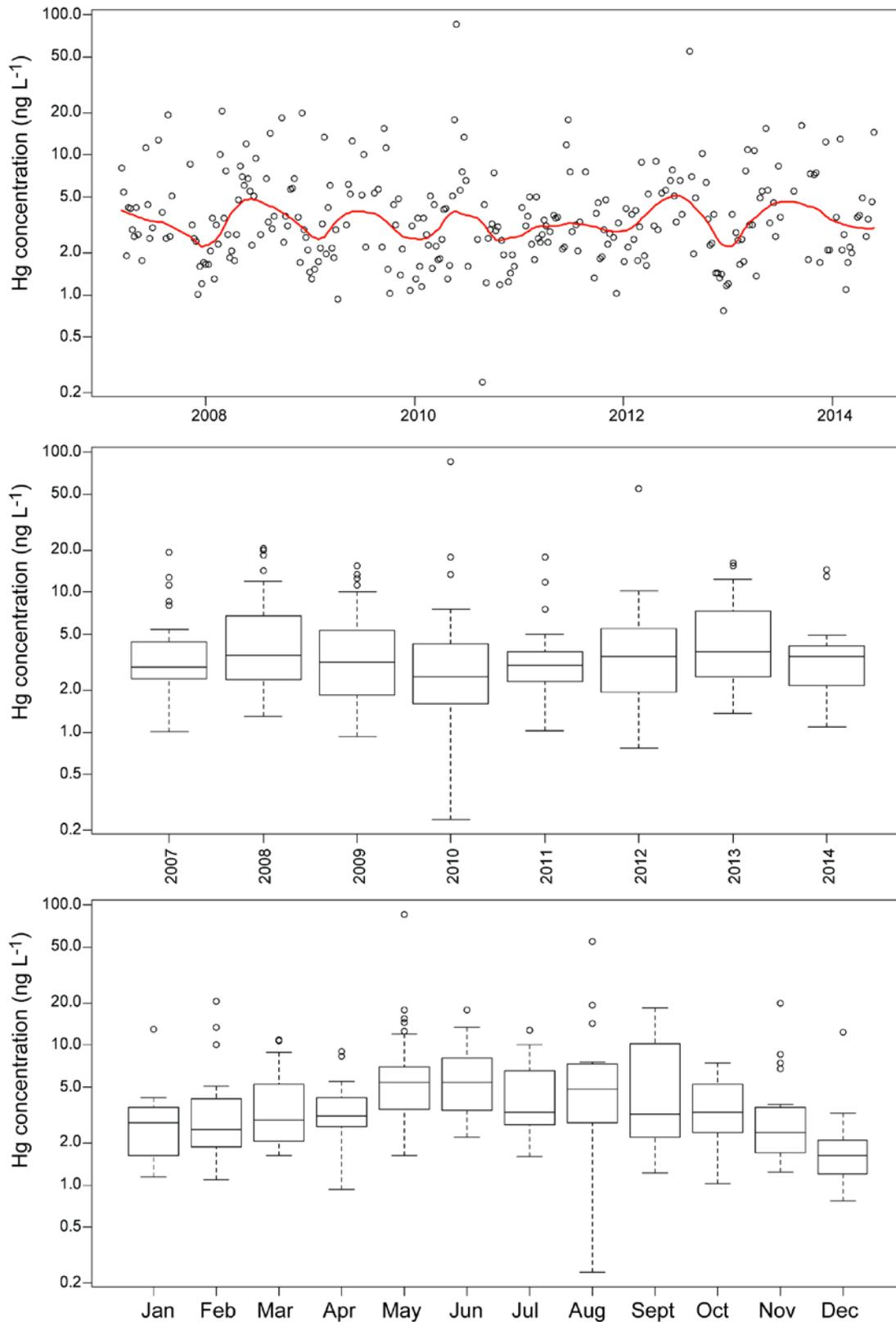


Figure A-3: Mercury (Hg) concentrations in precipitation at Makah MDN site WA03.

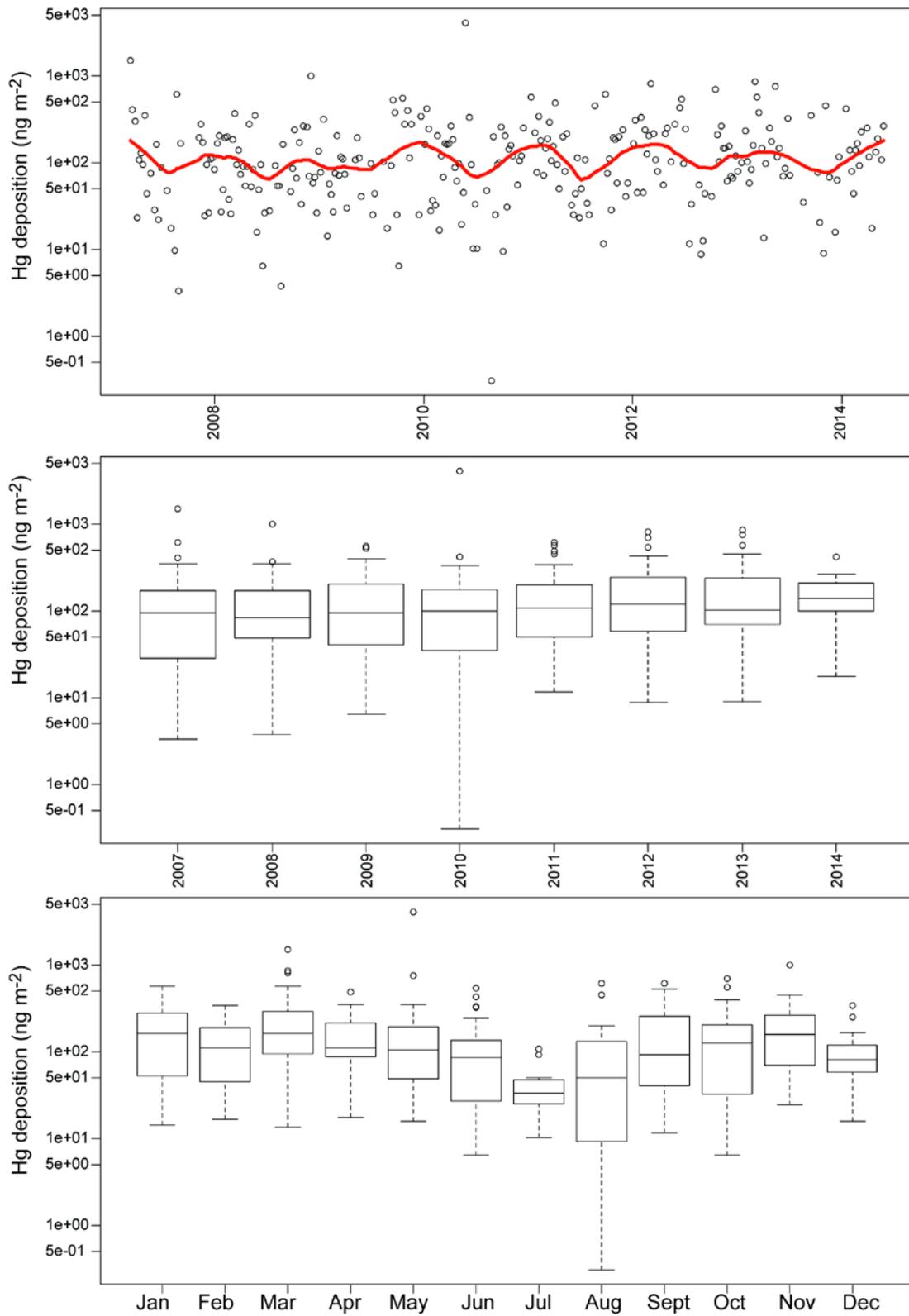


Figure A-4: Mercury (Hg) wet deposition rates at Makah MDN site WA03.

## Appendix B: Wind Patterns in Washington

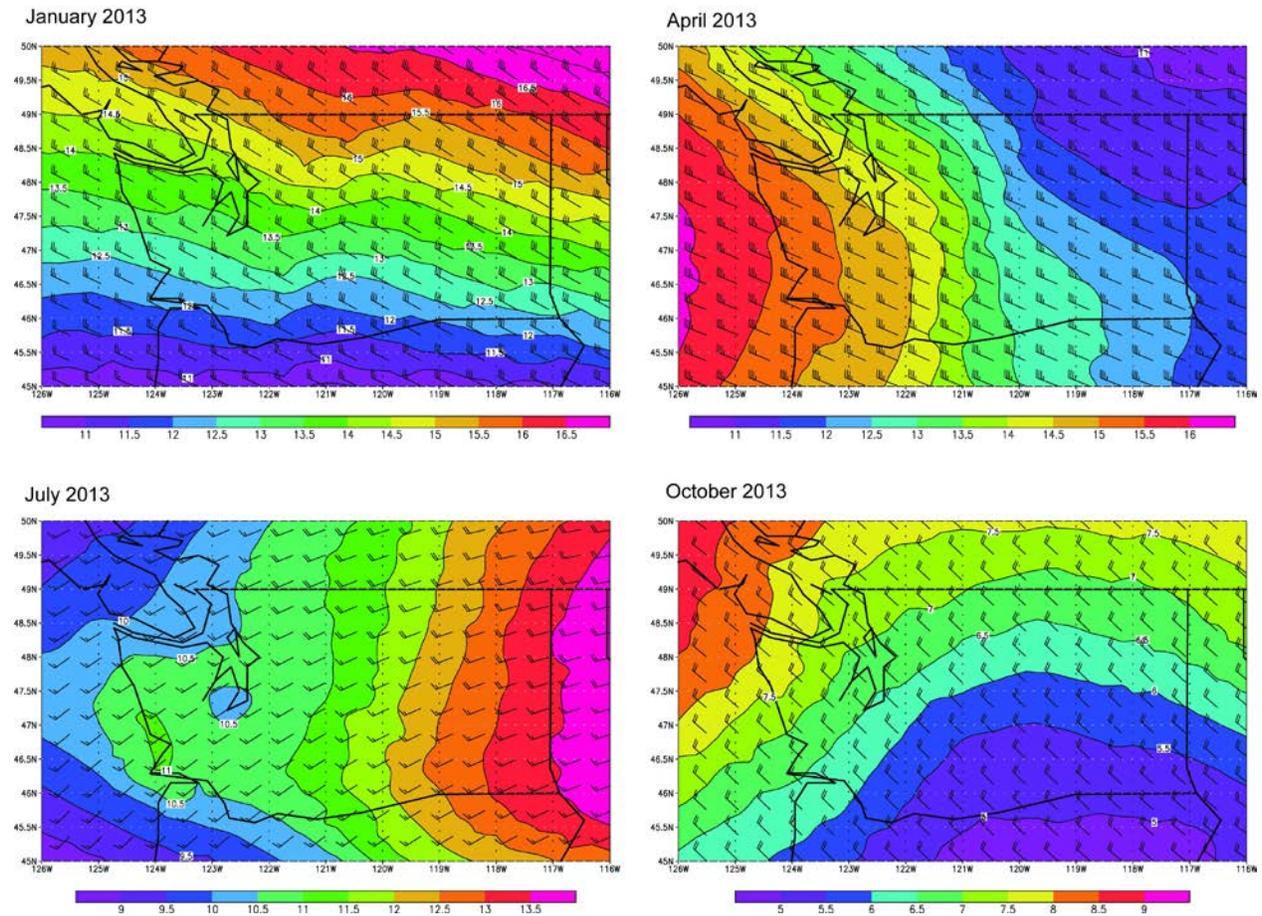


Figure B-1: Predominant wind patterns in Washington. Arrows indicate prevailing direction and contours indicate wind speed. Data graphed from the NOAA North American Regional Reanalysis (<http://www.emc.ncep.noaa.gov/mmb/rrean/>).