TITLE

Review of Draft Pollution Prevention Management Strategies for Polycyclic Aromatic Hydrocarbons in the NY/NJ Harbor by Valle, et al.

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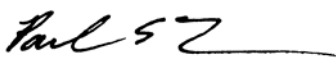Christopher M. Harbourt, Ph.D.

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Review of Draft Pollution Prevention Management Strategies for Polycyclic Aromatic Hydrocarbons in the NY/NJ Harbor by Valle, et al.

Paul S. Miller, PhD and Christopher M. Harbourt, PhD

This review of Valle, et al.'s Draft Pollution Prevention Management Strategies for Polycyclic Aromatic Hydrocarbons in the NY/NJ Harbor (November 20th, 2006) was prepared for the Creosote Council by staff at Waterborne Environmental, Inc. Waterborne conducts studies on the cause and effect of the physical, chemical, and biological processes associated with chemical transport in the environment. Our studies range from field scale experimentation to national scale monitoring programs. We also model complex environmental systems and have a diverse background in statistical and computational methods. For this analysis, we have focused primarily on Section 2.2.2. PAH Production and Use, Chapter 3.0 Environmental Fate and Transport of PAHs, and Appendix B. The format of this document is in outline format referencing pages and paragraphs in Valle et al. following this general overview.

Valle et al. attempt to catalog and estimate all of the sources of PAHs in the environment surrounding the NY/NJ harbor. PAHs are ubiquitously found throughout the environment from both natural and anthropogenic sources. In addition, the area suspected of impacting the harbor is one of the most densely populated areas in the United States (US). When possible or if available, we utilized the original source documents to understand variables used throughout the analysis. While we recognize that the extent of the analysis completed by Valle et al. was a significant effort, there are oversights, generalizations, and unjustified assumptions that seriously affect the comprehensive scientific value in their effort.

Of particular concern is the lack of including error estimates or confidence bounds around assumed or selected values in most sections of the emissions and flux portions of the document. The only section which includes some estimate of error tracking is the section by Totten describing mass balances using actual data. Throughout the text there are numerous examples of rate equations, data fits, spatial averaging, and temporal aggregating (almost always at the yearly average scale) that ignore the variability found in the base underlying data. We have documented some of these instances and have detailed many examples in the following section.

There are numerous instances where observations are spatially and temporally averaged when this over-simplification is unnecessary. We find it difficult to justify the simplification of quantities and rates used in this analysis when better data and methods are available to increase the accuracy of assessments. Finally, it is scientifically responsible to carry some level of statistical confidence through the calculations of flux. The variability in flux parameters, documented from the original source material, warrant more attention from Valle et al.

In addition, there is a serious lack of sound scientific data to adequately assess the various flux components of the harbor system. Considering the vast number of environmental sources of these PAH compounds, including confounding sources from the

exhaust of trucks, trains, ships, airplanes, and automobiles, it is currently an unjustifiable leap to accurately answer base questions, such as "How much?", "From Where?", "To Where?", and "When?". It is our assessment that conclusions could be justified with further collection of highly accurate and precise scientific data collected and targeted to fill assumed gaps in the current assessment of Valle et al. While some of the data used in the analysis are found in quality peer reviewed material, these studies typically measure only one aspect of the system, such as EMAP's sediment sampling data (Adams et al., 1998) or NJADN's atmospheric deposition near the harbor (Gigliotti et al., 2005). This is particularly true of the Contaminant Assessment and Reduction Project's data (http://www.dec.state.ny.us/website/dow/bwam/CARP/index.html) considering also that these data have been listed by the authors as "use with caution" and, in our assessment, are sparse and infrequent. We believe that an accurate understanding of the flux of PAHs into the harbor is not attainable without a pointed monitoring program that documents and quantifies sources of PAH throughout the harbor. Without a more comprehensive source of new data to support weaknesses in the Valle et al. work, it is premature to consider any drastic change in policy or use of PAH containing products.

Section 2.2.2 – PAH Production and Use (p.32)

1. Sections on naphthalene and solvent sources seem to be reasonable but data for naphthalene is scarce. The point sources for naphthalene are quantified from EPA's TRI and are not in doubt.
2. Marine Pilings (p. 33)
    a. Valle et al. concentrated on the analysis of Bestari et al. (1998b) as the primary source of information for PAH losses from marine pilings (5th paragraph, p. 33). Bestari et al. (1998b) provides key information regarding the analysis given by Valle, et al such as,
        i. Pilings used in the analysis were Douglas Fir – other authors list significant variability in the quantity of creosote/PAHs that can be injected into different types of wood (such as Beech Wood and Oak in Kohler, et al (2000)).
        ii. A loss of 50 µg/cm2/day was listed over the 84-day period with PAH waterborne concentrations near background levels by the end of the study. The conclusion was that marine pilings did not adversely affect marine environments.
        iii. The study was conducted over 84 days with peak desorption from pilings occurring at day 7 - thereafter following a pseudo-first order decay rate function. The authors indicate that long term presence of marine pilings has minimal risks to aquatic environments.
        iv. No adsorption to sediment or correlation with distance from pilings was found. Measurable PAH concentrations were also not different from control background conditions.
        v. Release of PAH in this study was for *fresh water* conditions. Results by Ingram et al. (1982) referenced indicated salt water loss rates that are **half** the rates found in Bestari et al. (1998b).

3. Marine Piling PAH Release Rates (1st complete paragraph, page 34)
    a. Valle et al. used a different initial creosote composition (railroad ties - Kohler et al., 2000) from the citation; however, the companion citation lists the composition of the liquid creosote used in production of the pilings (Bestari et al. 1998a)
    b. 9 different creosote formulations were discussed in the work of Kohler et al. (2000). Valle et al. used only 1 in their analysis.
    c. Calculations of loss rates from creosote treated pilings are significantly affected by not using the piling composition, which could be derived from Bestari et al. (1998a), but was not.
    d. Although Bestari et al. (1998b) shows loss values for different PAH compounds, the authors show significant standard deviations in their samples, and, although not mentioned in the text, some of the differences in outer versus inner layer losses and differences between unused pilings and 68-day pilings may not be statistically significant. These loss rates are based on mean values that were not statistically reported.
    e. Rate calculations found in Table 2.18 are scaled to reflect losses in the outer 1 mm of the pilings. Without scaling, these results estimated 68-day loss rates of 34% instead of 14%, which were rescaled; however, the effect of this scaling on the modeled loss over a 30-year pile life was not discussed or verified for accuracy.
        i. It would be a better approach to actually model the correct 68-day loss rate, which would alter k values in the table and may significantly affect 30-year loss rates.
    f. The exposed surface of a piling (or utility pole) also should be considered in the analysis. Presumably, only a portion of the pole will be exposed to the water column since portions of the column will be anchored into the bed material and a portion will remain above the high tide level. Additional considerations include wave action effects on water surface levels and the height of exposed piling above the water surface.
    g. Depending on where marine pilings are found in the watershed or in the harbor, the salinity, temperature, flow rates, and boundary layer flow would significantly affect PAH loss from pilings - none of these factors were considered in the analysis by Valle et al.
4. Releases to Water (1st paragraph, p. 35)
    a. Valle et al. discuss approximate releases to water by marine pilings in the NY/NJ harbor using census data for marinas which represents only businesses with a payroll as defined by the US census focusing on pleasure craft – not waterfront homes or other uses.
    b. Spatially, this data set is not adequate for developing estimates of linear feet of creosote pilings in the harbor or watershed.
    c. Assuming that all marine pilings made in the US are used in the US for marinas is a poor assumption, since there are many other uses for pilings including personal docks, property bulkheads, and bridges, among others.

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Also, an unknown number of marine pilings may be exported outside of the US.

    i. Extrapolating this to the harbor and harbor watershed without even a cursory spatial analysis may be in significant error.

    ii. Also, not considering water salinity and the complex water flow in the estuary is contributing to the error in estimates of PAH concentrations in water (Brooks, 1993).

5. Estimating Losses from Railway Ties (bottom of page, p. 35)

    a. Valle et al. estimate releases from railway ties to the atmosphere and in rainwater. Kohler et al. (2000) details losses from railway ties of different ages in Switzerland.

        i. Valle et al. used Kohler et al.'s analysis to calculate first-order mass losses over the service life of the ties. However, there is no indication that this model accurately represents losses from the ties in question. When evaluating the data in Table 2 in Kohler et al., significant variability exists throughout the range of time periods for 0.5, 1, 6, and 32-year old ties – including a zero loss rate using their method for phenanthrene after 32 years. Losses were noted in younger ties for phenanthrene; however, this points to the fact that there is significant variability in the input data used to develop the rate constants for the 30-year estimates. No statistical fitting diagnostics are mentioned at all – even though a standard deviation or 95% confidence limit should be calculated at the minimum. Further estimation of these amounts would then need to be made taking this variability into account. As a result, there is no confidence in these results particularly when considering the total mass loss.

        ii. Valle et al.'s regression technique to estimate mass loss for chemicals not found in Kohler et al. is questionable. They estimated rate losses of these compounds using a correlated/regression procedure for the octanol-water partitioning coefficient, K_{ow}. This technique needs considerable elaboration. Why use K_{ow} as a regression parameter instead of volatility – the major pathway for loss of PAHs from railway ties. The fact that the correlation coefficient may be better for K_{ow} than another parameter has little meaning. In addition, selecting values of loss rate parameters is not appropriate for larger size molecules.

        iii. Finally, error of regression models, particularly those calculated in log scale, needs to be understood and factored into any analysis. This has not been reported or considered in Valle et al.

    b. Kohler et al. (2000) indicate that beech railway ties of 32 years in service age have lost about 5 kg of creosote and about 0.5 kg of PAHs in the form of 2- and 3-ring PAHs such as naphthalene, acenaphthylene, acenaphthene, anthracene, flourene, and phenanthrene during this time.

    c. Kohler et al. (2000) also indicate that *at most* 1 kg of PAHs is the upper limit of loss over 32 years.

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      i. After summing all of the values for 30-year release in Table 2.20 (p. 36), the total is 1.184 kg (18.4% greater than the maximum possible release). Kohler et al. (2000) clearly stipulates that this is not possible for the creosote composition used in their study and hence that used in Valle et al. The Kohler et al. measured value was 0.5 kg for 32 years for total 16-EPA PAH compounds. Why is the value used in Valle et al. 236.8% <u>greater</u>? Considering these issues, the calculated loss rate has very little meaning without some measure of variability and compounded statistical error.

6. Leaching in water from railroad ties (p. 37)

    a. Valle et al. stipulates that this is an extremely conservative assessment, which is true. The magnitudes reported seem to be exaggerated. The assumption of instantaneous equilibrium is completely invalid. Rain is falling on the wood tie surface, which is nearly impervious and hard, and the ties present an overall small fraction of total surface area to raindrop action. Raindrop impact energy could remove PAH mass by physically detaching and ejecting small sized particles of creosote/PAHs, but instantaneous equilibrium is an extreme assumption. Brooks (2004) reported movement of PAH onto the rail ballast in a microcosm study with maximum concentrations measured at the surface within 5 cm of the tie at the surface; however, no ballast sample or collected sample exceeded background concentrations with depth at the end of the study (18 months). Some slight increases were noted with depth but this might have been due to additional photolysis on the surface of the ballast. There was no indication that PAHs would leach beyond the surface of soils in any great concentration, particularly from ties after their first year of service.

7. Releases to atmosphere (p. 38)

    a. Due to issues in calculating the emissions from railroad ties as mentioned previously, estimates in Table 2.22 (p. 38) are most likely skewed or, at the very least, are not listed with any confidence interval.

    b. Is the number of utility poles spatially calculated for the watershed or area of influence?

8. Utility poles (p. 38)

    a. Although we do not disagree that the release rates of creosote preserved utility poles may be similar in magnitude to the release rates of railroad ties (which is also questionable), the calculated number of poles is debatable. Valle et al. use a national rate for pole placement of 28.5 poles/distribution mile, which is the average value for the nation from their source; however, spatial data is available for the areas in question from the source, UDI through Platts at http://www.platts.com/Maps%20&%20Spatial%20Software/. This data set must be purchased, but represents a possible refinement given the extensive buried electric power system in this largely industrial area. This would replace a tabular data set from UDI used in the analysis of Valle et al., indicating 2.6 million poles.

Section 2.2.2.3 Coal Tar Sealant (p. 42)

1. Valle et al. contacted the American Coal and Coke Chemicals Institute regarding sales of coal tar sealants. The assumptions of sealant sold in the watershed and in New York City are difficult to validate; however, they do seem appropriate if the numbers were derived to include air photo assessments of where these products may be used. It is not clear if this was the case. The application rates for coal tar are reasonable for high-grade sealants, but other values of application rate have also been noted, such as 1 gallon per 60 ft^2 and 1 gal per 80 ft^2. Given the parameter variability, any calculations of this mass load should include statistical error bounds.

2. Mahler et al.'s (2005) study is one of the few studies on parking lot PAH content in storm water runoff from different sealants and, for this reason, needs to be considered. However, there are serious issues regarding the experimental design of this study. In the supplemental information for the article, a set of pictures of the study is included. They are represented here as Figure 1.
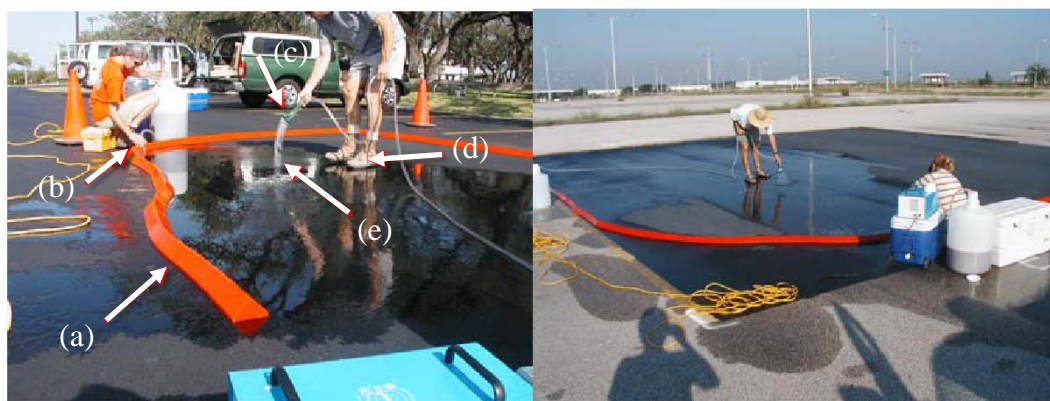
Figure 1. Collecting samples from a sealed parking lot (left) and a sealed test plot (right) – from supplemental information from Mahler et al. (2005).

There are five major problems with Mahler et al.'s (2005) design. Water was not contained in the experiment area with water leaking under the beams (arrow a), and, although estimated, it would be impossible to measure. Water used in the study was distilled, not rain water. Although distilled water was a better selection than tap water, we question the decision to not use actual rainfall. Collection of the runoff water is not described in the paper but is described in another document (Van Metre et al., 2006). Sample collection was done under vacuum at the outlet, which would seem to pick up sediment and particles that may not actually be flowing in response to the flow rate (arrow b). This would directly skew results PAH compounds that may be attached to that sediment. Water was not applied evenly nor at any accurate height to the plot, since it was applied by hand (arrow c). Calibration of sprayers and rainfall simulators in our experience is required to realistically reproduce rainfall –

this approach has no documented precision or accuracy. Highlighted by arrow d is the fact that study personnel are walking in the study area and, even if permissible, should be wearing clean contamination prevention equipment like latex booties! Finally, raindrop velocity is not even close to terminal velocity nor does it represent any kind of quantifiable storm depth or duration (arrow e). Quality controls for our field studies would not permit a study like this, and we therefore question these results.

3. Since sealant only has a useful service life of 3-5 years, it quickly degrades due to environmental conditions and road/lot usage. Valle et al. assume a constant loss of PAHs from the surface; however, Mahler et al. (2005) do not show a constant loss rate with time over the study duration. They found a decrease in total PAH lost over time. Changes in ratios of MWs (molecular weights) for LMW (low molecular weight) and HMW (high molecular weight) compounds also change in time due to the volatilization of LMW PAHs – hence losses of certain forms of PAH may be significantly changing over time. It is not reasonable to assume that the rates are constant. This would affect overall losses from this product over time.

4. Disregarding the fact that the rates do not change over time and the poor study design, the yields from parking lots in Mahler et al. (2005) are also variable including the fact that no statistically significant difference was found between coal-tar and asphalt pavement (p. 5563 1st column). Valle et al. disregards this and uses 946 ug/m^2 for coal tar and 416 ug/m^2 for asphalt. Variability must be included to understand the differences in mass loads from this source.

5. PAH transport loads and concentrations developed from this work could be seriously in error (such as Table 2.26 p. 45).

Section 3.0 Fate and Transport of PAHs from Sources to Harbor

1. This section begins with general discourse on pathways and partitioning compartments of PAHs in the Harbor (Valle et al., p. 108)

2. Fate and transport pathways for atmospheric emissions (p. 109)
   a. Calculating the fractions of PAHs transported from atmospheric sources involves a large number of assumptions regarding a large number of variables and processes. The best solution for estimating contributions from these sources is to actually measure PAH concentrations throughout the harbor from both dry and wet deposition and gas absorption flux into surface water. Considering the harbor is such a critical space, a thorough environmental monitoring plan would be worthwhile.
   b. The assumptions regarding atmospheric emissions starting on page 109 seem acceptable if the only route available is simple estimation instead of actual harbor measurements. Some harbor measurements are included in later sections, which will be considered when those are discussed.

3. Section 3.1.2.1 Advection of Atmospheric PAHs (p. 110)

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      a. Climatological data are reported in hourly values with wind speeds and directions; however, Valle et al. just use available data to calculate an estimate of average annual wind speed and average daily direction. This assumption may be far too simple of an abstraction of ongoing processes. Statistically and computationally, these wind speed records available at a time interval of 1 hour could be included to better estimate airflow in the harbor.

      b. Variations in settling velocities should also be included in estimating the transport of particulates since, by Valle et al.'s own indication (p. 111, top of page), settling velocities can vary in the literature by 250% - why not include this as part of the estimation process?

      c. Valle et al. assume that gaseous forms of PAHs within the harbor are merely replaced by PAHs moving out of the region (bottom p. 111) due to the wind so that the concentration of gaseous PAHs are constant; however, Gigliotti et al. (2005) clearly shows concentration differences across New Jersey so that concentration dilution may likely occur affecting gas absorption rates when the wind blows from inland toward the harbor in addition to when winds are predominantly blowing in from the ocean.

      d. Time discretization to a time step of one hour would further aid in the estimation of gaseous PAH concentrations in the harbor.

4. Section 3.1.2.2 Hydroxide reactions with gaseous PAHs (p. 112)

      a. Valle et al. estimate losses of gaseous PAHs from the atmosphere due to photooxidation reactions with hydroxide radicals. Discretization is an issue with this calculation in that concentration of hydroxide radicals changes throughout the year. Average values for reaction rates are used, even though Simcik et al. (1997) list considerable standard deviations for all of the listed parameters used in Valle et al. Without including these statistical confidence levels in all of the parameters, the values in Table 3.2 (p. 112) also have no confidence. By the authors' admission, "these numbers may be low estimates especially for summer months…" (p. 112 bottom paragraph).

5. Section 3.1.2.3 Gas-particle partitioning of PAH emissions (p. 113)

      a. Valle et al. through personal communication with Lisa Totten provide data on gas/particle partitioning for three sites as part of the NJADN project; however, the data for Sandy Hook near the mouth of the harbor was not included. These data are critical for partitioning phases and considering processes of wind blowing onshore.

6. Section 3.1.2.4 Gas absorption into surface water (p. 113)

      a. Henry's law and gas absorption should be calculated on at least a daily basis considering wind speed and temperature. Valle et al. use the measured data in Gigliotti et al. (2005) for flux estimation, but they do not incorporate the fact that differences in flux rates can be ±65% (Gigliotti et al. 2005).

7. Section 3.1.2.5 Wet and dry particle deposition to land (p. 115)

      a. Again, selected parameters have widely variable values when comparing values across the spectrum of literature. No attempt by Valle et al. is made to understand the effects of this variation on calculations.

8. Section 3.1.3 Fate and Transport Pathways for Land Emissions (p. 116)

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    a. PAH transport of deposited PAH washing off impervious surfaces through the storm sewer system of New York and New Jersey including unknown flows from Combined Sewer Overflows (CSOs) is not understood. The assumptions that follow include 90% transmission of PAHs from all impervious surfaces and the amount of storm flow attributable to CSOs (1/2 of 28% or 14%) are unjustified.

    b. Since the CSOs are clustered near the harbor, understanding the hydraulics of this area is critical to understanding not only flow in the harbor, but also PAH transport and mass loadings to the harbor. This is particularly important for storm sewer systems that are directly draining to the harbor.

    c. Additional details such as oil spills on impervious surfaces and runoff from superfund/ contaminated industrial sites is also not considered.

    d. Finally, new NLCD data (Circa 2001) is available for the study area http://www.mrlc.gov/scripts/mapserv.exe?map=d%3A%5CInetpub%5Cwwwroot%5Clccp%5Cmrlc2k%5Czones%5Czones.map. This data set should be used for all land emissions calculations due to the significant difference in urban growth and changes in land use from the 1992 NLCD, which was used. The 2001 NLCD data are much more representative of land use conditions and comparable in time with the other data sets used in the analysis of Valle et al. The use of this data set would increase the spatial accuracy of emissions predictions.

9. Section 3.1.4 Fate and Transport Pathways for Releases to Water (p. 119)

    a. Valle et al. include a section on some of the theoretical mechanics of hydraulics and dynamics of particle settling and transport in river systems beginning on page 119. It is an extremely complex process especially with the NY/NJ harbor and the intermixing of salt and fresh water, salt water wedge effect, and the movement of the "line" of salt water intrusion. Simple assumptions regarding transport distances are not acceptable for mass load estimations of sediment transport to and from the harbor. This is due to the fact that significant mass loads of transported sediment always occur with the greatest stream flows under the most turbulent of conditions. Assumed values of particle sizes and settling velocities also have little meaning during these periods of high flow. Finally, assuming a transport distance of 20 miles and including water inputs from the first and second counties upriver from the head of tide (p. 121 – bottom) is unjustifiable. The hydrodynamics of the harbor, such as Hydroqual, Inc.'s model of the harbor, need to be included in this analysis if sedimentation rates are truly to be calculated accurately.

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Section 3.2 Summary of Mass Balance (p. 123)

1. Valle et al. present the mass balance work totaling all of the estimates that they have made in Chapter 2 for sources of PAHs to the NY/NJ Harbor. On page 123 (last paragraph) they stipulate that "Most inputs and losses to the Harbor could be calculated within about a factor of 2." <u>There is no justification for this statement in the documentation of the study that we have found</u>. Every method evaluated in this review specifically has had no confidence level associated with a chosen parameter value. Two exceptions to this that they note are oil spills and aerobic degradation of PAHs in the harbor. Oils spills, not counting those on land entering the harbor through direct flow from storm drains or from other sources during wash off, are mentioned as possibly being the largest source of low molecular weight PAH compounds (bottom p. 123).

2. High MW PAHs are listed as being supplied on average approximately 50% by storm flow into the harbor. Sediment and transported particulate concentrations entering into the harbor are poorly understood. The contribution of storm flow volumes and PAH concentrations with storm water to the harbor is also poorly understood. If this represents 50% of all of the high MW PAHs entering the harbor, these quantities should be known with much greater accuracy and precision.

3. Unknown rates of atmospheric deposition, occurrence of oil spills, and very little substantial data for LMW PAHs in the harbor readily call into question findings as to the sources of these inputs to the harbor.

4. A comparison between the estimates of mass flux into the harbor by Totten listed in Appendix B and the results of the source estimates from the main body of text by Valle et al. was undertaken. It seems that any implied agreement between these values is due simply to averaging so many of the dynamics out of the process. In this case, all that is left are the base assumptions without a tie to the reality of a highly variable and dynamic system. It is not possible to imply anything else without actually redoing the calculations.

Appendix B: Mass Balances on Selected Polycyclic Aromatic Hydrocarbons in the New York/New Jersey Harbor Estuary

1. Lisa A. Totten's work includes estimates of mass loads of PAHs based on collected data from CARP (the Contaminant Assessment and Reduction Project), NJADN (the New Jersey Atmospheric Deposition Network), and EPA R-EMAP sampling of the harbor sediment from a 1998 report. An additional report documenting the state of NY/NJ harbor sediment 5 years later from R-EMAP and EPA is also now available (Adams and Benyi, 2003) indicating that mean sediment concentrations in the harbor are lower than those calculated in 1993/4, but, due to the high variance of the 1993/4

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data, concentrations were not significantly different. At the very least, PAH concentrations have not increased in the harbor.

2. Data from CARP, as noted by Totten, have been classified as "use with caution" and have not been published by peer review. This is due to problems in the analytical methods used in estimating the PAHs (contamination by organic resin XAD-2 – Totten p. 5)) and also in possible sample contamination problems. This is extremely problematic when mass loads are being developed using these data as the only source of information. Additionally, the time periods of collection of this data are not used in the mass balance calculation. This is critical when estimating flow based mass transport. As with all sections of this document, very dynamic processes are reduced to annual averages and used to calculate a generalized number. Additionally, other data problems exist when trying to match diverse information collected for other purposes, such as measurements for different molecular structures and measurements of different phases of compounds.

3. Additional data (Totten p. 6) are used by Totten that are unverifiable due to the fact that people contributed this data via personal communication.

4. Flow rates into the bay from tributaries are estimated either as an annual average or a yearly estimate. These arbitrarily selected flows represent a significant source of water flux into the harbor and need more attention. Additional flow values are noted from Hydroqual, Inc. but are aggregated to yearly values. Also, Hydroqual should have been consulted for any sediment transport analysis and associated hydraulics instead of assuming spatial and yearly averages.

5. Deposition concentrations from the NJADN were averaged over the bay (Totten p. 6) even though a spatial interpolation scheme was probably more accurate. Even though only a few sites exist for the calculation of this spatial field, it is better than just averaging the values across the harbor.

6. The extreme variability due to estimating loads from storm event flow is shown in the range of PAH concentration samples at the bottom of page 7 in Totten. Values of five samples from sewer outfalls were from 597 to 598,000 ng/L – three orders of magnitude different in value. The sampling for this section of the document is inadequate placing these mass fluxes into question. PAH concentrations were also not found to be correlated to flow rates; however, this is most likely due to the paucity of data. Totten discusses some of this inadequacy on page 8.

7. The lack of oil spill data is of concern due to the influence of this flux on the masses of LMW PAHs in the harbor. This also does not include the cleaning of tanks, ships, and other industrial equipment that might occur regardless of being reported. Clearly fine spatial sampling of possibly problematic areas is necessary to understand where high concentrations of PAH might be concentrated.

8. Sections on Tidal Exchange (p. 10 Totten), Volatilization (p. 11 Totten), and Aerobic Degradation (p.11 Totten) include so many assumptions that these reported quantities are suspect. Spatial aggregation and yearly estimates of temperature and wind speed are problematic to understanding the real contributions of these fluxes. Additional data are also provided by personal communication for tidal exchange that is difficult to verify.

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9. Sedimentation (p. 13 Totten) rates are very difficult to calculate without the use the hydrodynamic model of Hydroqual. Simply assuming values representing conditions over the entire harbor is not realistic. Sedimentation can occur in very small areas dropping large amounts of particles concentrating adsorbed materials in very specific areas. The tools and models exist to generate a more accurate picture of reality.

References:

Adams, D. A. and S. Benyi. 2003. Sediment quality of the NY/NJ harbor system: A 5-year revisit. United States Environmental Protection Agency, Document #902-R-03-002.

Adams, D.A., J. S. O'Connor, and S. B. Weisberg. 1998. Sediment quality of the NY/NJ harbor system. United States Environmental Protection Agency, Document #902-R-98-001.

Bestari, J. K. T., R. D. Robinson, K. R. Solomon, T. S. Steele, K. E. Day, and P. K. Sibley. 1998a. Distribution and composition of polycyclic aromatic hydrocarbons within experimental microcosms treated with liquid creosote. *Environmental Toxicology and Chemistry*, 17(12):2359-2368.

Bestari, J. K. T., R. D. Robinson, K. R. Solomon, T. S. Steele, K. E. Day, and P. K. Sibley. 1998b. Distribution and composition of polycyclic aromatic hydrocarbons within experimental microcosms treated with creosote impregnated Douglas Fir pilings. *Environmental Toxicology and Chemistry*, 17(12):2369-2377.

Brooks, K. M. 1993. Literature review and assessment of the environmental risks associated with the use of treated wood products in aquatic environments – I ed. Aquatic Environmental Sciences, K.M. Brooks, Principal, 601 Main Street, Suite 401; Vancouver, WA, 98660: Western Wood Preservers Institute.

Brooks, K.M. 2004. Polycyclic aromatic hydrocarbon migration from creosote-treated railway ties into ballast and adjacent wetlands. United States Department of Agriculture: Forest Products Laboratory, Document number, FPL-RP-617.

Gigliotti, C. I., L. A. Totten, J. H. Offenberg, J. Dachs, J. R. Reinfelder, E. D. Nelson, T. R. Glenn, and S. J. Eisenreich. 2005. Atmospheric concentrations and deposition of polycyclic aromatic hydrocarbons to the Mid-Atlantic east coast region. *Environmental Science & Technology*¸ 39(15):5550-5559.

Ingram Jr., L.L., et al. 1982. Migration of creosote and its components from treated piling sections in a marine environment. *Journal of the American Wood-Preservers' Association*, pp 1-8.

WATERBORNE
ENVIRONMENTAL, INC.

Kohler, M., T. Kunniger, P. Schmid, E. Gujer, R. Crockett, and M. Wolfensberger. 2000. Inventory and emission factors of creosote, polycyclic hydrocarbons (PAH), and phenols from railroad ties treated with creosote. *Environmental Science & Technology¸* 34(22):4766-4772.

Mahler, B. J., P. C. Van Metre, T. J. Bashara, J. T. Wilson, and D. A. Johns. 2005. Parking lot sealcoat: An unrecognized source of urban polycyclic aromatic hydrocarbons. *Environmental Science & Technology*, 39(15):5560-5566.

Simcik, M. F., H. Zhang, S. J. Eisenreich, and T. P. Franz. 1997. Urban contamination of Chicago/coastal Lake Michigan by PCBs and PAHs during AEOLOS. *Environmental Science & Technology¸* 31(7):2141-2147.

Valle, S., L. Shor, M. Panero, and L. Totten. 2006. Pollution Prevention and Management Strategies for Polycyclic Aromatic Hydrocarbons in the New York/New Jersey Harbor (Working Draft). For the Harbor Consortium and the "Industrial Ecology, Pollution Prevention, and the NY/NJ Harbor Project of the New York Academy of Sciences", November 20, 2006.

Van Metre, P. C., B. J. Mahler, M. Scoggins, P.A. Hamilton. 2006. Parking lot sealcoat: A major source of polycyclic aromatic hydrocarbons (PAHs) in urban and suburban environments. United States Geological Survey fact sheet #2005-3147, January, 2006.