A Chemical Contaminant Mass Balance Framework for Chesapeake Bay

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EXECUTIVE SUMMARY

Introduction

Chemical contaminants in the water and sediment of Chesapeake Bay can affect ecosystem functions as well as pose a direct threat to human health via drinking water and the consumption of aquatic organisms (e.g., fish and shellfish). The recently-published Chesapeake Bay Basinwide Toxics Reduction Strategy Reevaluation Report (Chesapeake Bay Program, 1994d) described the results of a multi-year effort to evaluate the nature, extent, and magnitude of the Bay's chemical contaminant problems. While this study continued the Bay Program's effort to account for the sources of chemical contaminants, a more exacting examination of *both* the sources and sinks is needed.

One way to place this information into a coherent framework is with the development of a chemical contaminant mass balance. A mass balance approach requires that the quantities of chemical contaminants entering the Bay, less the amount stored, transformed, or degraded within the system, must equal the amount leaving the Bay system. The objective of this report is to develop a chemical contaminant mass balance framework for Chesapeake Bay. Once fully developed this framework will point out initial steps, definitions, data needs, capabilities, and problems that are involved in the development of a mass balance, and would place the various monitoring, research, and modeling studies into a holistic picture helping to focus future studies and management actions on specific cleanup actions.

A mass balance model is defined here as an equation that describes a process where matter entering a system, minus matter leaving the system, equals matter stored, transformed, or degraded within the system. In this regard, a mass balance model establishes a process for identifying and consistently evaluating all ways that chemical contaminants can enter and exit a waterbody such as Chesapeake Bay. The construction of a mass balance needs to account for the various fluxes or movements between the different interfaces within the Bay, including the air-water, Bay-ocean, and sediment-water interfaces. Both sources to the Bay and sinks from the Bay would be combined with internal process information to provide an indication of the relative magnitude of the Bay's various inputs and outputs and overall fate of chemical contaminants.

Therefore, a thorough understanding of the physical, geochemical, and biological processes within Chesapeake Bay is needed in order to fully develop a realistic mass balance. Also, understanding how similar classes of chemicals cycle through the Bay is needed to help make predictions concerning the fate of specific chemicals that may be too costly to investigate individually.

Inputs to Chesapeake Bay

The calculation of input fluxes to Chesapeake Bay is a complex task. Problems inherent in these types of calculations include: 1) a general lack of data, 2) comparability of chemical measurements and forms for each source category, and 3) incomplete reporting of the various sources. In many cases, the reporting programs in which data were collected were not set up with the objective of calculating a load or flux, but rather for assessing the potential biological effects via comparison with numerical water quality standards. Despite these limitations, initial load estimates need to be established to assess the relative magnitude of point and non-point inputs and where data needs are greatest to improve future load estimates.

The loads from the various sources to the tidal Bay are compared in Table A-1. The ranges presented for atmospheric deposition, river transport, urban runoff, and shoreline erosion were not calculated similarly, and may be based upon as little as two estimates. Unfortunately, organic contaminant data for the various sources are lacking, as there is not a coherent program to measure these parameters, except for the atmospheric and river monitoring studies.

For copper, zinc, and chromium, river transport fluxes are substantially higher than other sources. The second largest source of trace metals to the tidal Bay appears to be urban runoff. However, the range of estimates for urban runoff is large, and should be an area of future study to help constrain these values. Shoreline erosion, along with river transport, appear to be important sources of chromium and zinc. Generally, there is a lack of adequate data for the quantification of the inputs of most organic contaminants. The river transport flux for total polychlorinated biphenyls (PCBs) is approximately ten times greater than atmospheric deposition. Unfortunately, there are no data for the other possible sources of these chemicals to the Bay. Urban runoff is the dominant source of the polycyclic aromatic hydrocarbons (PAHs), chrysene and benzo[a]pyrene, to the Bay.

Table A-1. Summary of contaminant loads to the entire tidal waters of Chesapeake Bay.

Chemical	Atmospheric Deposition	Urban Runoff	River Transport	Shoreline Erosion	Point Sources
Metals					
Cadmium	1.3 - 1.6	0.95 - 5.3	37 - 71	1.0 - 1.9	0.62
Chromium	2.2 - 4.2	5.4 - 30	200 - 270	83 - 90	19
Copper	11 - 15	15 - 84	270 - 450	28 - 29	37
Lead	9.5 - 15	190 - 360	310 - 410	27 - 28	5.3
Zinc	31 - 52	84 - 460	130 - 220	96 - 120	160
Organics					
Benzo[a]pyrene	0.054 - 0.13	0.094	0.19 - 0.36	ND	0.044
Chrysene	0.093 - 0.19	0.24	ND	ND	0.007
Total PCBs	0.030 - 0.039	ND	0.37 - 0.38	ND	ND

Loads are in metric tons per yr. ND - No Data.

These data illustrate the current status of the loading information available as part of the *Chesapeake Bay Basinwide Toxics Loading and Release Inventory* (Chesapeake Bay Program, 1994a). While there are many assumptions and problems with the current data set, this exercise highlights areas that need further study in order to synthesize a more complete understanding and quantification of the sources of potentially toxic chemicals to Chesapeake Bay. Recommendations for future loadings studies include: 1) for all sources determine a consistent chemical fraction (e.g., total, total recoverable, dissolved), 2) use lower detection limit methods for both dissolved and particulate analyses, 3) include urban stations in the atmospheric deposition network, 4) undertake a comprehensive sampling of major point source dischargers, and 5) initiate site specific studies to better estimate the urban flux of chemical contaminants.

Preliminary Input-Output Mass Balance of the Maryland Portion of the Tidal Bay

To illustrate some of the problems, pitfalls, and usefulness of constructing a simple input-output mass balance, information and data from various sources were collected and compared for the Maryland portion of tidal Chesapeake Bay. Only specific trace metals (e.g., copper, lead, and zinc) were quantified due to a larger existing database for these metals than for organic contaminants.

Yearly burial rates of copper, lead, and zinc to the Maryland portion of the Bay ranged from 220 to 680 metric tons/yr, 360 to 1,200 metric tons/yr, and 1,400 to 4,300 metric tons/yr, respectively. For both copper and lead there is a reasonable agreement between quantified inputs and burial, while for zinc the output via sediment burial is approximately three times as high as the inputs. It is unclear why the burial of zinc is much higher than its input, compared to both copper and lead (i.e., all sources and sinks were estimated similarly). Variations in the concentration of surficial concentration of zinc may require further study. Conversely, there may be many unaccounted or underestimated sources that also need to be assessed or re-assessed. It appears that the total load introduced to this area can be balanced by what is lost or buried in the sediments, and very little is transported to the southern portion of the Bay. However, while the closeness of these fluxes may be real, there are many areas of uncertainty, both for sources and sinks, that prohibit any definitive conclusions at this point. This exercise helps focus future research and monitoring programs in order to lower the uncertainty between inputs and outputs and enable Bay managers to make scientifically-based decisions regarding contaminants in the Bay.

Towards a Mass Balance for Chesapeake Bay

The example input-output mass balance for the northern Bay appears to be consistent in that there is a reasonable agreement between total inputs and the loss of these metals via burial. Unfortunately, due to the lack of data it is impossible to quantify the uncertainty many of these estimates. However, while the amount of uncertainty in this analysis is most likely large, this study does allow a focusing of monitoring efforts on specific sources and geographic areas that would greatly improve and expand a mass balance. Overall, basic monitoring information is needed for almost all sources and sinks identified in this document. While these monitoring data will not provide information as to the effects of chemical contaminants, they do provide the needed information as to where and how much a reduction in a particular source load is needed. Until both sources and sinks are better quantified, future input-output balances will remain uncertain and of limited quantitative use.

For a more complete mass balance model to be useful, its development must be driven by the objectives that *both* managers and scientists decide upon. Also, there are many questions concerning the feasibility of using a mass balance approach to manage or evaluate chemical contaminants in Chesapeake Bay. For example, if a concerted effort is applied to determine the absolute inputs and outputs from significant sources and sinks, will enough specific information exist to help managers of the various sources of contaminants (e.g., point source regulators or urban planners) determine the need for potential additional regulation of these sources? Also, if additional regulatory actions are taken, will living resources that are affected by contaminants respond and show some improvement (e.g., fewer fish advisories)?

As can be seen from the simple input-output model for Maryland, the data needs for any of these tasks are enormous and would therefore be very expensive. However, the development of a simple input-output mass balance could be a first step and would be less expensive while providing useful information to bay managers. The results generated from such a project would also be a part of the initial data requirements for a larger modeling framework if developed. This information is needed to help focus clean-up efforts and the limited dollars to areas and sources that will make the biggest difference in the overall health of Chesapeake Bay.

INTRODUCTION

Chemical contaminants in the water and sediment of Chesapeake Bay can affect ecosystem functions as well as pose a direct threat to human health via drinking water and the consumption of aquatic organisms (e.g., fish and shellfish). The recently-published Chesapeake Bay Basinwide Toxics Reduction Strategy Reevaluation Report (Chesapeake Bay Program, 1994d) described the results of a multi-year effort to evaluate the nature, extent, and magnitude of the Bay's chemical contaminant problems. Also, this report pointed to ways to reduce the impact of contaminants, and to what information is needed to determine future actions. While this study continued the Bay Program's effort to account for the sources of chemical contaminants, a more exacting examination of *both* the sources and sinks is needed. The identification and quantification of the different sources, sinks, and storage of anthropogenic and natural chemicals in Chesapeake Bay is an important step towards understanding their cycling and potential effects in the Bay.

One way to place this information into a coherent framework is with the development of a chemical contaminant mass balance. A mass balance approach requires that the quantities of chemical contaminants entering the Bay, less the amount stored, transformed, or degraded within the system, must equal the amount leaving the Bay system. With a working mass balance budget, various control strategies can be simulated to evaluate long-term changes for each contaminant (see Chesapeake Bay Program, 1994b). Such simulations and predictions can be valuable in the assessment of the effect of chemical contaminants on human and ecosystem health, and can help make expensive monitoring programs within the Bay more cost-effective.

The objective of this report is to develop a chemical contaminant mass balance framework for Chesapeake Bay. This framework will point out initial steps, definitions, data needs, capabilities, and problems that are involved in the development of a mass balance. This framework would place the various monitoring, research, and modeling studies into a holistic picture helping to focus future studies and management decisions on specific cleanup actions.

CONCEPTUAL FRAMEWORK

The mass balance framework for chemical contaminants would involve a fate and transport set of calculations or model(s) for particle-reactive chemicals. If bioaccumulation of contaminants in phytoplankton, zooplankton, and fish is included, then a food-web dynamics model (e.g., Thomann et al. 1989; 1992) would be incorporated into the fate and transport computations. Each type of model is complex, but would yield important information concerning potential impact and cycling of contaminants within the Bay. A conceptual model of the sources, transport, and fate of chemical contaminants within Chesapeake Bay is presented in Figure 1. Depicted in this model are the different sources of contaminants, both point and non-point. A long-term goal of any modeling exercise is to integrate hydrodynamic, water quality (both chemical contaminants and nutrients), and ecosystem function models for a comprehensive understanding of Chesapeake Bay. While this objective is daunting, Kemp and Baker (1994; preliminary results) and Kemp et al. (1995; preliminary results) initiated a model simulation study of relevant ecosystem interactions in the control of chemical speciation, transport, and biological effects of synthetic organic chemicals (e.g., polychlorinated biphenyls). Their goal is to describe the relevant processes controlling bioavailability and accumulation of these chemicals in the Bay. Also, Madden et al. (1994) proposed to use a similar computational framework to study organic contaminant ecosystem interactions within Baltimore Harbor, which has been listed as a Chesapeake Bay Region of Concern (Chesapeake Executive Council, 1994).

In the following section, the different physical and biogeochemical processes that play a role in the cycling of chemical contaminants are introduced. This information is crucial in the understanding and development of a mass balance framework for chemical contaminants in the Bay.

Processes Influencing the Fate of Chemical Contaminants within Chesapeake Bay

Physical Processes

Estuaries, such as Chesapeake Bay, are dynamic systems in which physical processes such as circulation, stratification, mixing, and flushing are affected primarily by temporal changes in river

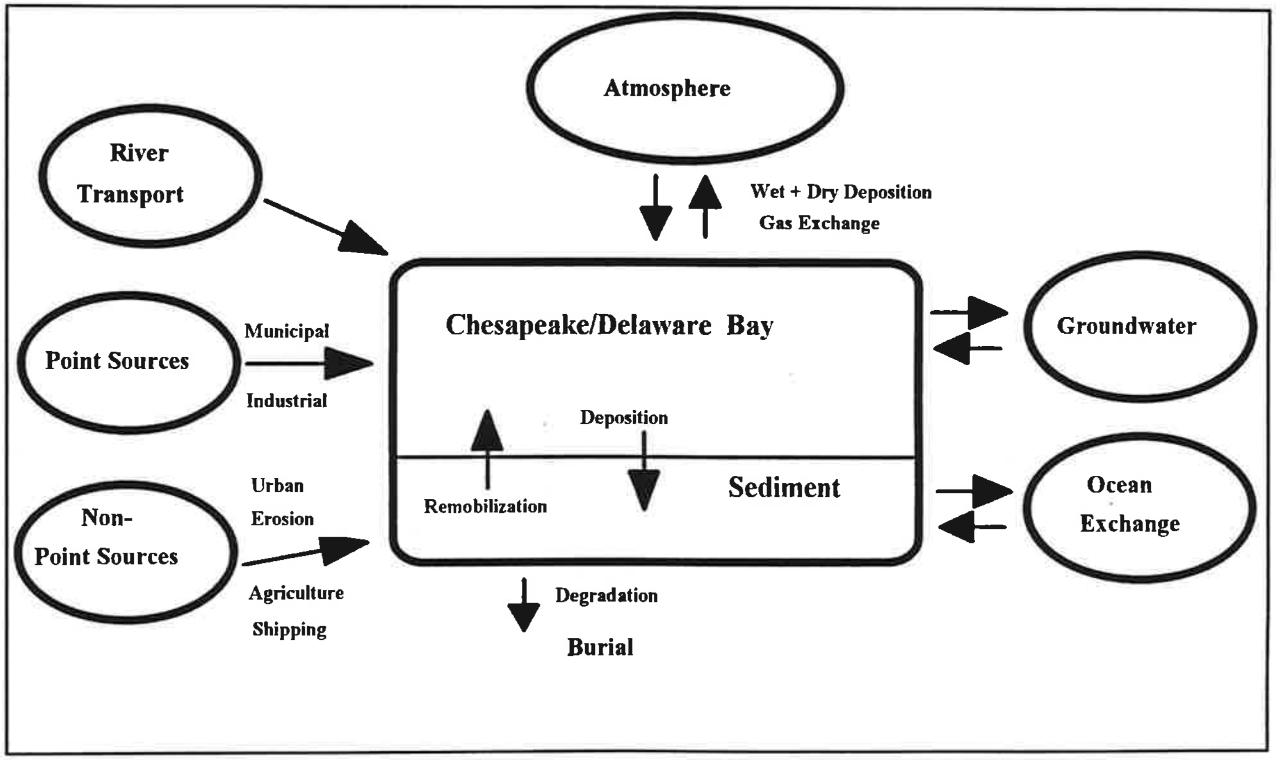


Figure 1. Conceptual model of the different inputs and outputs to tidal Chesapeake Bay.

discharge, tides, and wind patterns. In a partially-stratified estuary (e.g., Chesapeake Bay), these processes have been classified according to the time scale in which they occur (Itsweire and Phillips, 1987). Seasonal physical processes are mainly determined by solar heating and freshwater inflow, and generate a two-layer estuarine circulation (Pritchard, 1952; 1967). The strength of stratification affects the amount of vertical mixing between bottom and surface layers. Short-term processes can be broken down to those that are greater than a tidal period and less than approximately a month, and those that are less than a tidal cycle. These processes include wind forcing, tidal variations, fronts, and plumes. Shorter-term influences include turbulent mixing that also have time scales of less than a tidal cycle. Itsweire and Phillips (1987) stated that seasonal and some short-term mixing processes control the horizontal distribution, transport, and diffusion of water properties, while small-scale mixing processes control vertical distributions and exchange. The specific temporal and spatial scales ultimately will affect the mixing, transport, potential reactions, and residence time of chemical contaminants.

Variations in water currents from tidal action can have an important effect on suspended matter and particle-bound chemical contaminants (Officer, 1981). Short period increases in current velocity can resuspend and transport bottom sediments to other locations, transporting particle-bound material as well. At a site in northern Chesapeake Bay, Sanford et al. (1991) measured near bottom increases of suspended sediments from a background of approximately 15 mg/L to 50 mg/L within an hour of the maximum tidal current. Schubel (1968) and Nichols (1986) reported 4 to 10 time higher suspended sediment concentrations in studies of the northern Bay area. The increase in concentration of suspended sediments and particle-reactive contaminants during tidal as well as storm events (Sanford, 1994; Swift, 1994; preliminary results) would increase the time chemical contaminants spent in the water column (i.e., increase residence time) and thus would have a major role in the cycling and potential biological effects.

The transport and cycling of chemical contaminants are affected by the movement of water and various biogeochemical reactions occurring within the estuary. Processes like river flow, tidal and storm resuspension of bottom sediments, biological uptake and degradation help determine the overall distribution and flux of material through an estuary. Material can be transported in either the dissolved or particulate phases, and many interactions between these phases occur during transport within the Bay. The mixing behavior of chemical contaminants during transport down an estuary can be classified according to their reactivity. Chemicals that are unreactive during transport and generally follow the distribution of non-reactive chemicals (i.e., salt) are termed conservative, while chemicals that are removed or added to the dissolved phase during transport are described as nonconservative (Boyle et al. 1974). Conservative mixing is indicated by a linear distribution between the dissolved concentration of a chemical contaminant and its corresponding salinity, while a curvi-linear relationship generally indicates either a source or sink of material (Boyle et al. 1974; Officer, 1979; Kaul and Froelich, 1984 and others). This graphical and computational method for assessing the mixing behavior and quantity of a dissolved species removed or added is technically not applicable to particulate-bound contaminants as they are also affected by resuspension and settling within the estuarine environment.

Riverwater concentration variability and hydrodynamics play a significant role in the interpretation and modeling of property-salinity plots (Loder and Reichard, 1981; Officer and Lynch, 1981; Cifuentes et al. 1990). An assumption in using property-salinity plots is that the dissolved salt is mixed conservatively and that the endmember concentration, either freshwater or saltwater, remains constant relative to the hydrodynamic residence time within the estuary. This is not always the case, especially for freshwater concentrations. For example, Cifuentes et al. (1990) showed that significant variations in the freshwater concentration of nitrate (at 0‰ salinity) over time can result in an apparent removal (nonconservative behavior) during transport through the Delaware Estuary. When endmember variability was taken into account within the modeling framework, the distribution of nitrate indicated conservative behavior. Therefore, it is necessary that this tool for evaluating the behavior of chemical contaminants during mixing takes into account the potential variability of chemical concentrations of both endmembers.

The importance in understanding how physical processes modify the fate, transport, and effect of chemical contaminants is related to the movement of material and overall residence time a contaminant resides in the waters of the Bay. The longer the residence time, the longer the various reactions have to act on a chemical contaminant. For example, if the freshwater flow into the Bay is large, then a dissolved contaminant in the water would have a short residence time within the system. With a short time period spent within the Bay waters, biogeochemical reactions such as biological uptake/degradation and flocculation/adsorption reactions would have less time to modify the speciation and chemical form of a contaminant. The contaminant would then be flushed out onto the coastal shelf unaltered by estuarine processes. If the freshwater flow into the Bay is small, the residence time of the water increases. Biogeochemical reactions could then alter the chemical form of a contaminant, removing it to the particulate phase with possible subsequent settlement to the bottom, or by making it more or less bioavailable. Therefore it is important to understand the physical dynamics within Chesapeake Bay and their relationship to the time (and spatial) scales of different biogeochemical reactions.

Geochemical Processes

As organic or inorganic particle-reactive chemical contaminants are transported down an estuary, they can undergo several types of geochemical transformations and reactions. Many of these processes can alter the chemical form and speciation of a contaminant, thereby affecting its biological availability and fate. It is important to identify these processes to help determine the type and complexity needed for a mass balance framework. In fact, many of these processes are currently under investigation as part of the National Oceanic and Atmospheric Administration's Chesapeake Bay Environmental Effects Toxics Program (National Oceanic and Atmospheric Administration, 1993; 1994; 1995).

A dominant factor in the cycling of a chemical contaminant is its distribution or partitioning between dissolved and particulate forms. Processes that can influence chemical contaminant phase distribution within the estuarine environment can include: flocculation of colloidal matter, adsorption-desorption, precipitation-dissolution, and complex formation. Many of these processes are modified as a result of salinity, reduction-oxidation equilibria (i.e., redox), and pH changes within the estuarine environment. Also, depending on the physical-chemical properties of each contaminant, these processes will affect the contaminant's speciation, bioavailability, and fate differently. However, many of these processes and changes can be predicted for specific classes of metals or organic contaminants using basic geochemical principles. This helps in the development of a mass balance framework for Bay chemical contaminants.

The partitioning between the dissolved and particulate phases of a contaminant is governed by many of the factors listed above. Most suspended particles in the water column are negatively charged and cationic metals are attracted to their surfaces. Many trace metals (e.g., type A metals like chromium (Cr) and cobalt (Co)) are adsorbed onto clay surfaces through ion-exchange reactions or onto surface hydroxides of iron or manganese (Stumm and Morgan, 1981). Scavenging of metals is generally thought to consist of multiple steps (Jannasch et al. 1988). The first step is the rapid uptake of metals, via exchange with protons of the hydroxyl group of oxides, followed by a much slower step with other binding sites. Once a contaminant is particulate bound it can settle to the bottom to be buried or resuspended. One tool to describe the partitioning between dissolved and particulate forms of a chemical is the distribution, or partition coefficient, defined here as $K_d = C_p/C_w$ (units: L/kg), where C_p is the concentration of a specific contaminant associated with a given mass of particles and C_w is the concentration of the same contaminant in a given mass of water. In theory, this empirical ratio describes the equilibrium partitioning of a contaminant between the dissolved and particulate phases; however these phases are, at best, operationally defined and are dependent on the method of filtration. Operationally, C_w includes material that is both truly dissolved and colloidal material that can pass through a particular filter (e.g., 0.40 µm pore size filter). Also, material that is either sorbed onto the particulate matter during filtration or desorbed from the particles can limit the use of K_d as an accurate measure of the partitioning between chemicals.

The use of K_d is limited by factors other than the filtration step. It is assumed that the ratio between dissolved and particulate phases is at equilibrium (i.e., complete reversibility), and equilibrium should remain constant over a range of environmental conditions. Depending on the particle residence time within the estuary, kinetic effects can be very important in determining the degree to which a chemical is dissolved or associated with the particulate phase. In other words, if a particle is removed quickly from the surface waters to the sediments, it may not have enough time to come into thermodynamic equilibrium with the dissolved fraction. Also, for many metals and organic compounds, the physical-chemical environment within the estuary is very important in determining the degree to which a contaminant may be in the dissolved or particulate phase (i.e., K_d). As a contaminant moves down the estuary it experiences variable conditions of ionic strength, pH, particle concentration, and redox conditions. Each of these conditions can either enhance or hinder sorption reactions and ultimately affect the bioavailability and removal of contaminants from the water column.

Organic contaminants, many of which are hydrophobic, tend to associate or partition with either the organic fraction on particles or with dissolved organic matter (e.g., humic or fulvic material) (Eadie et al. 1990; 1992; Baker et al. 1991; Bergen et al. 1993; Brownwell and Farrington, 1986). As with inorganic contaminants, the distribution coefficient can be used to help describe the fate of organic compounds. The partitioning is related to factors such as the structure, composition, and concentration of both the contaminant and organic matrix on the particle surface. For example, Karickhoff et al. (1979) and others have shown that as the fraction of organic carbon on the particle (f_{oc}) increases, K_d increases. By dividing K_d by f_{oc} the organic carbon distribution coefficient (K_{oc}) is obtained, and this parameter has been shown to be useful in modeling the behavior of hydrophobic organic contaminants (Di Toro et al. 1992).

Currently there are hundreds to thousands of organic compounds that can have some type of environmental impact. For many modeling efforts it useful to have a K_{oc} for each compound. To predict the K_{oc} values, another parameter, the octanol-water partition coefficient (K_{ow}), is needed. The K_{ow} is a laboratory- or empirically-derived parameter that describes the tendency of a compound to partition in either octanol or water, and is a measure of its lipophilicity (i.e., tendency to dissolve in the organic or more non-polar fraction). Generally, the higher the K_{ow}, the more hydrophobic the compound is and the greater the association with organic carbon; hence a higher K_{oc}. A linear relationship has been found between K_{oc} and K_{ow} enabling the prediction of the phase distribution of many compounds (Karickhoff et al. 1979). Therefore, the octanol-water coefficient can be applied to predict the partitioning behavior of organic contaminants in an estuary.

The impact of dissolved organic matter (DOM) on the fate and effect of organic compounds and trace metals is also very important. A general observation is that dissolved organic matter enhances the solubility of many organic contaminants to some degree. However, differences can arise depending on the type of the DOM. Eadie et al. (1990; 1992) showed that specific organic contaminants were not significantly bound to DOM derived from the Great Lakes. Boehm and Quinn (1973) showed a reduction in the solubility of n-alkanes when riverine and estuarine DOM were removed, but no change in solubility with the polycyclic aromatic hydrocarbons (PAHs) phenanthrene and anthracene. However, the binding and solubility is most likely contingent on the structure, composition, and concentration of DOM and the type of contaminant. The solubility of specific aromatic hydrocarbons was significantly influenced by the presence of naturally occurring DOM from terrestrial sources with little or no influence using DOM from oceanic or coastal sources (Whitehouse, 1985). However, the data from Whitehouse (1985) also showed that solubility enhancements were compound specific, with higher molecular weight PAHs (e.g., benzo[*a*]pyrene) more soluble in marine DOM. Variations in the composition between marine and terrestrial DOM could therefore have an important role in these results. Terrestrial humic material are derived from lignin whereas marine humics are derived from phytoplankton. Marine humics are thought to be less aromatic and more aliphatic in composition, with a greater protein and carbohydrates character (Stuermer and Payne, 1976; Harvey et al. 1983). The modification of humic substances as river water mixes with seawater in the estuary would most likely have a large role in the fate of contaminants (Fox, 1983; Sholkovitz, 1976). This is especially true for contaminants that are introduced in the upper tributaries (near urban centers) where the initial mixing of terrestrial, estuarine, and marine humics occurs.

Organic complex formation can also have an important role in the speciation and bioavailability of many trace metals. Many metals like, lead (Pb), copper (Cu), and mercury (Hg) (e.g., type B metals) are biologically active and tend to associate with organic matter (Stumm and Morgan, 1981). Organic-metal complex formation can either increase or decrease the adsorption of metals onto particles. For example, recent studies by Godtfredsen and Stone (1994) showed that copper bound to manganese (III, IV) oxides can be released and complexed by the addition of specific organic compounds and extracted natural organic matter. The extent of complex formation of metals by DOM (e.g., humic and fulvic acids) is dependent on the concentration of DOM and the competition for available sites within the humic matrix between metals and major cations (Reuter and Perdue, 1977). Mantoura et al. (1978) suggested that the stability of organic-metal complexes follow the Irving-Williams order of stabilities of chelates with metal ions. This sequence indicates that Cu and Hg should form the strongest complexes. In this regard, many researchers have shown that organic complexes control the speciation of Cu in estuarine waters. Preliminary studies by Donat (1995; preliminary results) in Chesapeake Bay suggest that over 90% of the dissolved Cu is complexed to dissolved organic matter and that at least two types of organic ligands (i.e., a strong and weak fraction) are present. Similarly, the organic forms of dissolved cadmium (Cd), which is low on the Irving-Williams order, accounted for between 25% and 70% of the total dissolved Cd (Donat, 1995; preliminary results). His results indicate only one major ligand class was involved with Cd complex formation. The importance of organic-metal complex formation is that these complexes can be a dominant form of many metals affecting their geochemistry and biological availability in the estuary.

For many organic contaminants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons, air-water exchange (i.e., evaporation or volatilization) is an important environmental pathway that cannot be ignored in a mass balance of Chesapeake Bay. The exchange of a chemical across the air-water interface results from the transport of a particular chemical to the interface from the bulk phase (either water or air) linked with its transport across a water and air stagnant film (i.e., the stagnant film model; Liss and Slater, 1974). Generally, the less soluble compounds with higher vapor pressure will have a greater tendency to be in the gas phase than compounds that are more soluble (Mackay, 1991). The rate of transfer is related to the compound of interest (i.e., its Henry's Law constant) and a combination of the liquid and gas phase resistance (Liss and Slater, 1994; Mackay, 1991). For compounds that are very insoluble with large Henry's Law constants the mass transfer is primarily related with the liquid film. Environmental conditions such as wind speed and temperature also need to be taken into account in a modeling exercise. Eisenreich (1987) and more recently Achman et al. (1992) showed that volatilization is an important factor controlling the fate of PCBs in the Green Bay (Lake

Michigan). For example, Jeremiason et al. (1994) calculated that volatilization, not sedimentation, was the dominant loss mechanism for PCBs from the waters of Lake Superior. Preliminary work by Dickhut et al. (1994) and Baker et al. (1994) indicates that this process can be very important in the cycling and fate of both PCBs and PAHs in Chesapeake Bay and its tributaries.

While volatilization would have little effect on the fate of most trace metals (e.g., Cu, Cd, or Zn), it can be extremely important for metals or metalloids that have volatile organic forms such as mercury (e.g., CH_3Hg) or selenium (e.g., $(CH_3)_2Se$). This is also true for elemental Hg (Hg^0), where air-water exchange can be an important sink or source for lakes (Fitzgerald et al. 1991; Amyot et al. 1994) and estuaries (Mason et al. 1993).

Biological Processes

Biological activity within an estuary can have a large effect on the chemical speciation, phase distribution, and overall fate of many contaminants, both trace metals and organic compounds. Many trace metals, for example, are required elements for cellular metabolism (Lehninger, 1975). Metals such as iron (Fe), manganese (Mn), zinc (Zn), Cu, and cobalt (Co) are incorporated into specific organic molecules, such as chlorophyll and enzyme co-factors which enter into specific photosynthetic reactions. Cobalt, for example, is the central metal atom in the core of vitamin B_{12} which is a growth factor for many aquatic plants (Raymount, 1980). Many organic compounds (e.g., PCBs, DDTs, atrazine, and certain aromatic hydrocarbons) are anthropogenic and are not needed for plant or animal growth. While many metals can be essential to life, most are toxic at sufficiently high concentrations and for some there is a narrow concentration range between what is required for growth and what is toxic.

Uptake of trace metals into plant or animal tissue can occur via both passive or active mechanisms via solution, food, and sediment sources (Luoma, 1983). Some metals can be taken up and used in cellular growth, biochemically altered to lesser or greater toxic forms (e.g., detoxification via metallothionein; Couillard et al. 1993), or can cause deleterious effects to cellular growth. A major factor that affects the uptake and cellular incorporation of trace metals or metalloids (i.e., bioavailability) is the element's chemical form or speciation (i.e., oxidation state). Factors that can affect the speciation of trace metals include salinity, inorganic and organic complexation, reduction-oxidation potential, and pH. For many metals, it is the free metal ion concentration or activity (Sunda and Guillard, 1976; Morel and Hering, 1993; Riedel and Sanders, 1988; Newman and Jagoe, 1994) and the amount of metal bound within the organic matrix (i.e., cytoplasm) of a cell (Luoma et al. 1992; Reinfelder and Fisher, 1994) that plays a major role in bioavailability and trophic transfer, respectively. Recently, Phinney and Bruland (1994) showed that low molecular weight, lipophilic organic Cu, Cd, and Pb complexes enter diatom cells (e.g., *Thalassiosira* sp.) by diffusion across the plasma membrane. Once inside the cell, the metals in these complexes can become biologically available by binding with internal binding sites via intercellular ligands. This passive mechanism acts in parallel to active transport of free metal ions. Other metals such as mercury (Hg) and tin (Sn) form lipophilic organo-metallic complexes (e.g., methyl-Hg) that can accumulate in the food chain due to their greater lipid solubility (i.e., bioaccumulation).

Biological processes that affect organic contaminants include uptake (both passive and active), trophic transfers, and microbial degradation (Hale and Huggett, 1988). Thousands of anthropogenic organic compounds can be transported to and through the estuary. These include organic contaminants that have low water solubilities and high octanol-water partition coefficients (e.g., log $K_{ow} \geq 3$ compounds such as polychlorinated biphenyls) as well as many compounds with high water solubilities (e.g., triazines). Many of the former compounds partition to the organic fraction of particles and are transported with suspended matter or deposited to the sediments.

Organic contaminants, like polychlorinated biphenyls (PCBs), can be taken up passively by phytoplankton via a two-step mechanism involving an initial surface adsorption phase then transfer through the lipid bilayer (Swackhamer and Skoglund, 1991). At slow growth rates, the log K_{ow} predicted the accumulation of lower molecular weight PCB into the phytoplankton cell, whereas higher molecular weight compounds did not show a consistent relationship. Steric hindrances slowed the transport of larger higher molecular weight compounds across the cell's membrane and could account for the observed results (Stange and Swackhamer, 1994;

Skoglund and Swackhamer, 1994).

Uptake of organic compounds by phytoplankton is an initial step in the bio-transfer of contaminants through the estuarine food web. Up the food chain, these contaminants tend to partition into the lipid fraction of organisms depending on factors such as the concentration of dissolved organic carbon of the water (which affects bioavailability), the lipophilicity of the compound, the size and shape of the compound (i.e., cell membrane effects), and the lipid content of the organism (Knezovich, 1994; Landrum et al. 1985). Many of these compounds can also be degraded via chemical and biological mechanisms. Chemical degradation reaction processes include photochemical degradation, reduction-oxidation (redox) reactions, and hydrolysis. Hydrolysis reactions affect mainly esters, carboxylic acids or amides, while redox reactions include, as an example, the reductive dehalogenation of DDT to DDD via electron transfer from the bacterial oxidation of organic matter and iron reduction (Zoro et al. 1974; Kobayashi and Rittmann, 1982). Photodegradation is a very important abiotic process that can affect the concentration and forms of many organic contaminants. The suspended sediment concentration, amount of humic substances in the water, and the water-solid partitioning are important factors in the photodegradation of many compounds.

Biodegradation is one of the more important processes affecting the fate of petroleum hydrocarbons in the marine environment (Gibson, 1977; Gerlach, 1981; Lee and Ryan, 1983; DeLaune et al. 1990 and others). Degradation rates can vary depending on whether the compound is an aliphatic or aromatic hydrocarbon and its specific structure (i.e., length of chain, number of branches, number of aromatic ring groups) (Gerlach, 1981; Wild and Jones, 1993). DeLaune et al. (1980) showed that specific sediment characteristics (e.g., pH, pE, temperature) were important factors in the activity of hydrocarbon degrading microorganisms. Also, aromatic hydrocarbon biodegradation is enhanced in sediments that have been previously contaminated with hydrocarbons, implying that there is an adapted population of microorganisms that can degrade aromatic hydrocarbons.

Recently, there have been numerous studies on the biological degradation of PCBs and other halogenated organic compounds. DeLaune et al. (1990) reviewed some aspects of biodegradation and stated that most organic contaminants degrade faster under aerobic conditions. However, for compounds like DDT and PCBs, anaerobic reductive dechlorination is an important transformation process. Studies on the anaerobic degradation of PCBs in non-marine systems have shown extensive dehalogenation, mainly on the non-ortho substituted chlorines (Sokol et al. 1994; Rhee et al. 1993; Abramowicz et al. 1993). However, under marine conditions, with abundant sulfate, reductive dechlorination of PCBs was shown not to occur (Alder et al. 1993). It may be that the presence of sulfate could inhibit the dechlorination process, however microbial dechlorination of chlorophenols has been linked to bacterial sulfate reduction in marine systems. Capone et al. (1994; 1995; preliminary results) showed that 2,4 - dichlorophenol was degraded in sediments from the middle portion of the Chesapeake Bay. Alder et al. (1993) showed reductive dechlorination of PCBs in methanogenic sediments (i.e., no sulfate present) from New Bedford Harbor with no degradation under sulfate reducing conditions. However, Ofjord et al. (1994) showed that anaerobic dechlorination of PCBs did occur in both the presence and absence of sulfate, although specific rates were not presented.

The loss of many organic contaminants can be mediated by microbial processes within the water column and more importantly, the sediments. In many cases, the degradation products have less biological activity than the parent compound, but in some cases (e.g., DDT) the daughter compound is more biologically active (i.e., DDE). However, if an accurate accounting of the fate of organic contaminants is needed within the Bay, an understanding of both chemical and biological degradation is needed.

Physical and Biogeochemical Processing of Contaminants within an Estuary

Contaminants can be retained in the system by many processes as well as be degraded to non-toxic or even more toxic chemicals with time. Depending on the reactivity of a particular contaminant (i.e., reaction half life) and the hydrodynamic residence time, a contaminant can also be washed out of the estuary unaltered. Sharp et al. (1984) defined two zones or filters in an estuary that can affect the fate of material. During estuarine transport geochemical and biological reactions can remove material from the water column and these "filters" can be located in different regions of the Bay system. For example, geochemical filtering would occur in the areas of the Bay where suspended particulate concentrations are highest as there would more sites for dissolved-particle reactions and removal. Biological removal and transformations would be located in areas of the Bay where turbidity is lower and greater microbial production (i.e., both phytoplankton and bacteria) occurs due to increased light levels.

Many processes remove contaminants from the water column to the sediments only for a certain time period before they are re-introduced back into the system. Therefore, the distinction between permanent removal and temporary storage should be made. For example, particle-reactive contaminants can be removed from the water column via sedimentation. A portion of the sediment with bound contaminants may be carried upstream due to net upstream transport in the bottom waters. However, many physical processes and geochemical reactions at the sediment-water interface can re-introduce these contaminants back into the water column over various time scales. Sediments and bound contaminants can be resuspended into the benthic boundary layer or higher up in the water column by tidal and storm currents (Sanford et al. 1992; Sanford and Halka, 1994; preliminary results). A portion of the suspended material will re-settle to the bottom while the remainder may be carried upstream due to density-driven estuarine circulation. Diagenetically controlled reactions can also mobilize or release particle-bound contaminants to the pore waters where advection and diffusion processes can exchange these chemicals back into the overlying water (Riedel et al. 1995; Cornwell et al. 1995; preliminary results). In addition, benthic organisms can facilitate the exchange of contaminants between the benthos and overlying water (Schaffner and Dickhut, 1995; preliminary results), for both dissolved and particulate forms. Only after a sufficient amount of time will contaminants be buried permanently within the sediments. Also, during these exchange processes the form and speciation of contaminants can be altered to either to a lesser or greater bioavailable form, thereby changing their overall effect to the Bay's living resources.

For many contaminants, the air-water interface is equally important compared to the sediment-water interface, and plays a major role in the fate and cycling of contaminants. In fact, the surface area of the Bay in contact with the atmosphere is relatively similar to that in contact with the sediments. Given the physical mixing behavior of the Bay, there is most likely a short transit time between chemical contaminants entering the Bay from the atmosphere and removal to the bottom sediments. As discussed previously, atmospheric deposition can be an important source of contaminants to the Bay. Also, the volatilization of many organic compounds from the water to the atmosphere can be an important loss term from the estuary. This exchange of material needs to be quantified in order to determine the net input (or output) of contaminants from Chesapeake Bay.

The construction of a mass balance needs to account for the various fluxes between the different interfaces within the Bay, including the air-water, Bay-ocean, and sediment-water interfaces. Other sources and sinks would be combined with this information to provide an indication of the relative magnitude of the Bay's various inputs and outputs and overall fate of chemical contaminants. Understanding how similar classes of chemicals cycle through the Bay is also needed to help make prediction concerning the fate of specific chemicals that may be too costly to investigate.

Mass Balance Development for Chesapeake Bay

A mass balance model is defined here as an equation that describes a process where matter entering a system, minus matter leaving the system, equals matter stored, transformed, or degraded within the system. In this regard, a mass balance model establishes a process for identifying and consistently evaluating all ways that chemical contaminants can enter and exit a waterbody such as Chesapeake Bay. With a clear understanding of all inputs and outputs of a given pollutant it is then possible to understand the relative importance of the various human-influenced sources. At this point, Bay managers can focus on the source(s) with the largest influence (by mass and bioavailability) to reduce the load (and effects) within a waterbody. Overall, a mass balance can be a predictive tool that allows informal prioritization and allocation of directed and basic research, remedial actions, and regulatory efforts for water quality management.

Modeling Framework

The development of a Bay mass balance for contaminants involves five steps. These steps include: 1) the identification and prioritization of specific mass balance objectives, 2) the identification of the important compartments within the Bay system, 3) the identification and quantification of inputs to the various identified compartments, 4) the identification and quantification of outputs from various compartments, and 5) the rates of transfer between the interfaces of compartments. Inherent in the development of a Bay mass balance is the acquisition of monitoring and research data and information. Therefore, an overriding area for a Bay mass balance is proper data handling and quality assurance/control of individual programs to ensure that data can be compared within and across media (i.e., air, water, sediments, and biota).

A mass balance model for the Bay can be constructed at different levels of complexity depending on the objectives of the study. The complexity of a model would also rely on the amount and quality of data available to run and validate the computations as well as the financial resources available to complete the study. However, a simple preliminary model can be developed, using existing data, to help point out data gaps and provide a rough idea of the relative inputs, outputs, and compartment residence times within the Bay. Objectives of such a mass balance study could include: 1) validation of the loading estimates, 2) calculation of the residence time of contaminants within a compartment, 3) determination of the fate of contaminants, and 4) would allow Bay managers to predict and evaluate the impact of specific management decisions on the levels of chemical contaminants in different compartments. Further development of a Bay mass balance, with additional compartments and interfacial transfers, can be accomplished as objectives are modified and the necessary data requirements are met. A more complex model, however, demands an increase in financial commitment. This involves not only possible computer time to run the model, but monies for the collection of data to feed into the computational framework. Furthermore, the development of a Bay mass balance should not be intended for every possible chemical contaminant measured in one or more of the Bay's different compartments (e.g., sediment, water, and biota). A few chemicals, which are representative of major classes of chemical, should be focused on for initial model development. These chemicals could include select trace metals such as lead (Pb), copper (Cu), and arsenic (As), and organic contaminants like polychlorinated biphenyls (PCBs) or polycyclic aromatic hydrocarbons (PAHs). These elements and groups of compounds span a wide range of physical-chemical properties and biogeochemical reactivity, would help to illustrate some of the processes controlling the fate of contaminants within the Bay. Most importantly, an accurate and reliable base data source needs to be developed that allows inter- and intra- comparisons between concentrations and fluxes with the model.

Compartments of Chemical Contaminants in Chesapeake Bay

The development of an accurate understanding of the various inputs and outputs (i.e., mass balance) to a system first entails the selection of the relevant and important compartments (i.e., boxes) and transfers (i.e., fluxes) of contaminants between compartments. In other words, a simple mass balance model consists of well-mixed boxes connected to their environments by various exchange processes (e.g., advective and diffusive transport, particle settling, biological uptake to name a few). Most often these compartments are determined by the various physical-geochemical interfaces in an estuary such as the air-water, sediment-water, river-Bay-ocean, and land-water boundaries. For the Chesapeake Bay system, examples of the different compartments or boxes include the bottom sediments, Bay water, atmosphere, above the fall-line watershed, and the ocean. In some instances, a compartment may appear to be similar chemically (e.g., water column and bottom sediments), but can be further separated due to physical (e.g., density differences between surface water and deep water) or geochemical variations (e.g., oxic surface sediments versus anoxic bottom sediments) into additional compartments. The selection of compartments should be made to best meet the objectives of the study while still keeping geochemical relevance to the system.

A number of different physical compartments or boxes can be identified for Chesapeake Bay. As a starting point, three main compartments or boxes can be identified: the atmosphere above the water surface, the water column, and the sediments. This simple division can be further

Table 1. Potential compartments for the development of a Bay mass balance.

Major Compartments	Sub-compartments[1]
Atmosphere[2]	
	Surface boundary layer (0 to -30 m)
	Top of troposphere (> -30 m)
Water column[3]	
	Surface water (0 to 10 m)
	Bottom waters (> 10 m)
Sediment[4]	
	Biogeochemical active zone (0 to 10 cm)
	Burial zone (> 10 cm)
Ocean[1]	
	Surface water (0 to 10 m)
	Bottom water (> 10 m)
Groundwater[2]	
	Sub-surface aquifer (0 to 100 m)
	Deeper aquifer (> 100 m)

[1] Sub-compartment depth ranges are for illustrative purposes only. [2] z is negative upwards from the air-water interface. [3] z is positive downward from the air-water interface. [4] z is positive downward from the sediment-water interface.

sub-divided into additional compartments, if necessary (Table 1). These compartments may be sufficient for fate and transport studies and simple residence time calculations, but depending on the specific objectives of the study the number of sub-compartments with each box (e.g., water, sediments, air) can be quite different. For example, if a goal is to understand the bioaccumulation of contaminants in fish or benthic organisms, it is important to further subdivide the water compartment to include dissolved and particulate fractions. Only specific sub-fractions of the dissolved and particulate phases are bioavailable for uptake by organisms and must be taken into account. Dependent on the objectives of the project, the relevant compartments need to be selected, the specificity of the chemical and biological analyses within each compartment will have a direct effect on the cost for the program.

Transport Processes of Chemical Contaminants to Chesapeake Bay

Many important transport vectors or sources can bring chemical contaminants into tidal Bay waters (Figure 1). These inputs of contaminants include: point sources, urban and agricultural runoff (i.e., non-point sources), direct spills, atmospheric deposition, river transport, groundwater flow, and ocean-Bay exchange. While some of these transport mechanisms for certain metals and some organic compounds are part of background geochemical cycles within coastal areas (e.g., atmospheric deposition and river transport), all have been impacted to some degree by the influence of human activities. For example, major ions and trace metals entering the Bay via river transport are derived from atmospheric deposition and the physical and chemical weathering within the watershed of the Bay (Troup and Bricker; 1975; Correll et al. 1981; Katz et al. 1985). These inputs have been occurring since the Bay's geologic formation. Added to this source are point (e.g., municipal and industrial) and nonpoint (e.g., agricultural and urban runoff) sources within the watershed. Also, due to near- and far-field atmospheric transport mechanisms, atmospheric deposition may contain substantial amounts of anthropogenically-derived metals and organic compounds (Baker et al. 1994). At present, it is difficult to determine how much of a particular metal is derived from weathering processes or human activities in river transport or other sources, although attempts have been made (see for example, Helz et al. 1985; Windom et al. 1991). For specific organic chemicals like polychlorinated biphenyls, atrazine, or DDTs, however, all sources are anthropogenic as these chemicals are not produced naturally.

Listed in Table 2 are many of the transport processes of natural and anthropogenic chemicals to Chesapeake Bay waters. Also, listed are many of the different removal mechanisms and biogeochemical reactions that need to be understood. Most of these processes are difficult and costly to quantify. An initial attempt to quantify the transport mechanisms of chemical contaminants to the tidal Bay's waters was made by the Chesapeake Bay Program (1994a). While there were many problems with this study, it does provide an understanding of the complexity of trying to quantify a diverse range of sources with data that were not necessarily collected for source/loading information.

Along with the selection of various compartments and loadings information, the various pathways and processes that can affect the mass transport between or within compartments need to be identified. The various inputs, outputs, and processes that have been shown to occur or could occur in the Bay system are listed in Table 2 and shown in Figure 1. The pathways listed in Table 2 may not always be uni-directional in the movement of contaminants from one compartment to another. For example, tidal exchange may transport material from the ocean to

Table 2. Potential sources, sinks, and processes of chemical contaminants in tidal Chesapeake Bay waters.

Inputs	Outputs	Processes
River transport[1]	Sedimentation[4]	Adsorption-desorption
Atmospheric deposition[2]	Burial[5]	Precipitation
Point Sources (i.e., pipes)[3]	Volatilization	Solubilization
Urban runoff	Biotic degradation	Complexation
Agricultural runoff	Abiotic degradation	Flocculation
Shoreline erosion	Ocean-bay exchange	Volatilization
Boating activities	Sediment-water exchange	Resuspension
Oil spills	Fish Migration	Biotic uptake/transformation
Groundwater	Fish/Shellfish harvest	Biotic/Abiotic degradation
Ocean-bay exchange		
Sediment-water exchange		
Fish Migration		

[1] River transport contains most sources above the fall line.
[2] Both wet and dry deposition.
[3] Municipal and industrial sources.
[4] Non-permanent removal of contaminant from the water column.
[5] "Permanent" removal of contaminant from water column.

the Bay as well as from the Bay to the ocean. The net exchange rate is related to many factors including the concentration difference between compartments and water exchange rate at the ocean-estuary interface.

Another important bi-directional exchange is at the air-sea interface. The flux of organic compounds and trace metals to land and water surfaces can be accomplished by wet (i.e.,water) and dry (i.e., aerosol) deposition (Whitehead and Feth, 1964) as well as gas exchange (Atlas and Giam, 1986; Duce et al. 1991). The return flux of material from the water to the atmosphere can also occur from processes such as bubble ejection of water and particles, and volatilization of gaseous material from the water surface (e.g., Hg and PCBs) (see Baker et al. 1993 for a review). Recent work by Achman et al. (1992) has shown that the volatilization of hydrophobic organic compounds, such as PCBs, is an important removal mechanism from the waters of Green Bay in Lake Michigan. Volatilization of organic material such as PCBs can also occur from land surfaces as well. It is estimated that a substantial portion of the total PCB burden in southern England soils has been lost via volatilization and long range transport (Alcock et al. 1995). The loss and eventual transport of the PCB could then affect more remote areas (U.S. EPA, 1994).

The exchange at the sediment-water interface can be an important process controlling the fate of contaminants in Chesapeake Bay. Deposition of particle-bound contaminants to the sediments may temporally retain many contaminants. Certain trace metals and organic compounds can be remobilized into the porewaters of the sediments creating concentration gradients that allow the flux of dissolved contaminants from the sediments to the overlying water. This process has been shown to be very important in the cycling of nitrogen in Chesapeake Bay (Kemp and Boynton, 1992) and can be equally important in the cycling of contaminants (Riedel et al. 1987; 1995; preliminary results; Cornwell et al. 1995; preliminary results). These processes are generally controlled by the oxidation-reduction state of sediments and have recently been shown to be affected by the presence of benthic organisms (Riedel et al. 1987; 1995; preliminary results; Schaffner and Dickhut, 1995; preliminary results).

Major assumptions in mass balance modeling are that each compartment is well-mixed and all inputs and outputs are accounted for within the modeling framework. Conceptually, the variation in the concentration (C) of a contaminant over time in a well-mixed box of constant volume (V) can be described as:

$$V\, dC/dt = QC_{in} - QC_{out} - R \qquad (1)$$

The terms on the right side of equation (1) include the total input (QC_{in}), output (QC_{out}) and loss or reaction (R) within a box, compartment, or system. In many simple cases, the reactions within a compartment are described as first-order with respect to the concentration (i.e., kC; where k is the first-order rate constant). If there is no change in the storage of a contaminant within each box or compartment and the concentration remains unchanged, then the system is at steady-state. For a first-level preliminary model however, steady-state conditions should be assumed. Steady-state assumptions mean that the concentration and amount within each box or compartment remains the same (i.e., V dc/dt = 0) over the time scale in question and that the sum of all inputs to the tidal Bay ($[\Sigma Q_{in}C_{in}]_i$; where i is the identified sources) are equal to the sum of the loss terms ($[\Sigma Q_{out}C_{out}]_j$; where j are the identified outputs). The use of a steady state system is dependent on the spatial and temporal resolution of the model's output, which is related to the objectives of the study. While steady state assumptions allow easier mathematical formulation and calculations, they may not always be true.

Many assumptions underlie the use of mass balances in describing systems like Chesapeake Bay. Some are related to the scale, both temporal and spatial, chosen for the formulation (see Thomann, 1995). For example, in estuaries large concentration gradients exist within the water and sediment structure for many contaminants. Also, many biogeochemical processes are seasonal in nature due to their temperature dependence (e.g., microbial processes). For example, the flux of specific trace elements from the water column into the biogeochemically active zone of the sediments can be related to the oxygen concentrations within the sediments and overlying water (Riedel et al. 1995; preliminary results), which can vary substantially in the Bay on time scales of hours to months (Cutter et al. 1985; Sanford et al. 1990; Diaz et al. 1992). These types of processes can yield non-steady state conditions related to the time scale that is to be represented by the model.

One aspect of any model formulation that needs to be considered is the scale (i.e., spatial and temporal) required to meet the objectives and goals. The resolution of the model can be on length scales of the entire Bay or specific tributaries over time scales of monthly to decadal changes. Also, the scaling size of the various compartments will affect the model's output and data needs.

As a guide to how the Bay system responds and the relevant time scales that should be used in data acquisition, the recent sediment core work by Owens and Cornwell (1995) and Baker et al. (unpublished data, see Chesapeake Bay Program, 1994d) provides some interesting information. Their work showed substantial decreases in sediment concentrations of various contaminants over the previous 10 to 30 years. The resolution of their data is on the order of 2 to 5 years using ^{210}Pb dating and suggests that loadings data encompassing the last five years is needed for an accurate and relevant mass balance.

Other scaling problems that need to be addressed include the use of a few measurements in a specific area of the Bay which are then applied or scaled up to the entire Bay water surface or watershed. For example, the few benthic flux studies done in the Bay for contaminants are generally located in a few areas (Riedel et al. 1995; preliminary results; Cornwell et al. 1995; preliminary results). The fluxes determined from these studies may not be characteristic of the entire Bay and will bias the overall flux given the different sediment types in the region (Hobbs, 1983; Hennessee et al. 1986; Kerhin et al. 1983; 1988). This problem (i.e., a few measurements applied to the entire Bay) for many flux studies (e.g., benthic, air-sea, water fluxes) will hinder the accuracy of any model. Also, the impact of storm events have only been partially studied for some inputs. Only with a concerted effort (i.e., money) will more measurements be made to help increase a Bay mass balance model's accuracy. However, in the initial modeling framework and data input, the areas of greatest data needs can be pointed out so that the limited resources can be focused properly and scientifically.

Summary

Conceptual mass balance models are excellent tools to assess the dynamic behavior of contaminants in Chesapeake Bay. These models combine system-specific processes with properties of individual chemicals or classes of chemicals under investigation. Once in place they help to predict concentrations resulting from different loading scenarios and can help understand various impacts to living resources (see Chesapeake Bay Program, 1994b). Also, when model results are compared to field data they can provide insights into unrecognized sources or processes.

While mass balance modeling has been successfully applied to nitrogen and phosphorus cycling in the Bay (see Chesapeake Bay Program, 1994b; Boynton et al. 1995), the sources, pathways, and sinks for chemical contaminants are less well understood. A graphic description of a representative model for Chesapeake Bay is presented in Figure 2. This framework includes a food chain compartment to allow estimation of bioaccumulation for various living resources of the Bay. Again, many of the processes, pathways, and transfer rates are not known for the Bay's ecosystem and would hinder the development of this type of mass balance. It is, therefore, necessary to focus the mass balance approach in two directions.

First, a pilot mass balance which includes a food chain component (Figure 2) could be started in a smaller ecosystem of the Bay prior to expansion to the whole Bay. The selection of a specific area would be determined on the amount and availability of high quality data and the need of mangers to have specific questions answered concerning specific pollution control strategies that may be implemented in an area. The integrated model will then be used to predict concentrations in the various media in response to different management control actions. Second, a lower tiered level mass balance (i.e., input-output balance) could be constructed for the whole Bay following the outline described in Figure 1. This type of model would determine the major inputs and outputs of contaminants to and from the Bay. A subset of the processes listed in Table 2 could be quantified using best available data; and if the resources are available, projects could be initiated to help fill in specific gaps.

The models shown in Figures 1 and 2 serve as an outline of the compartments and processes

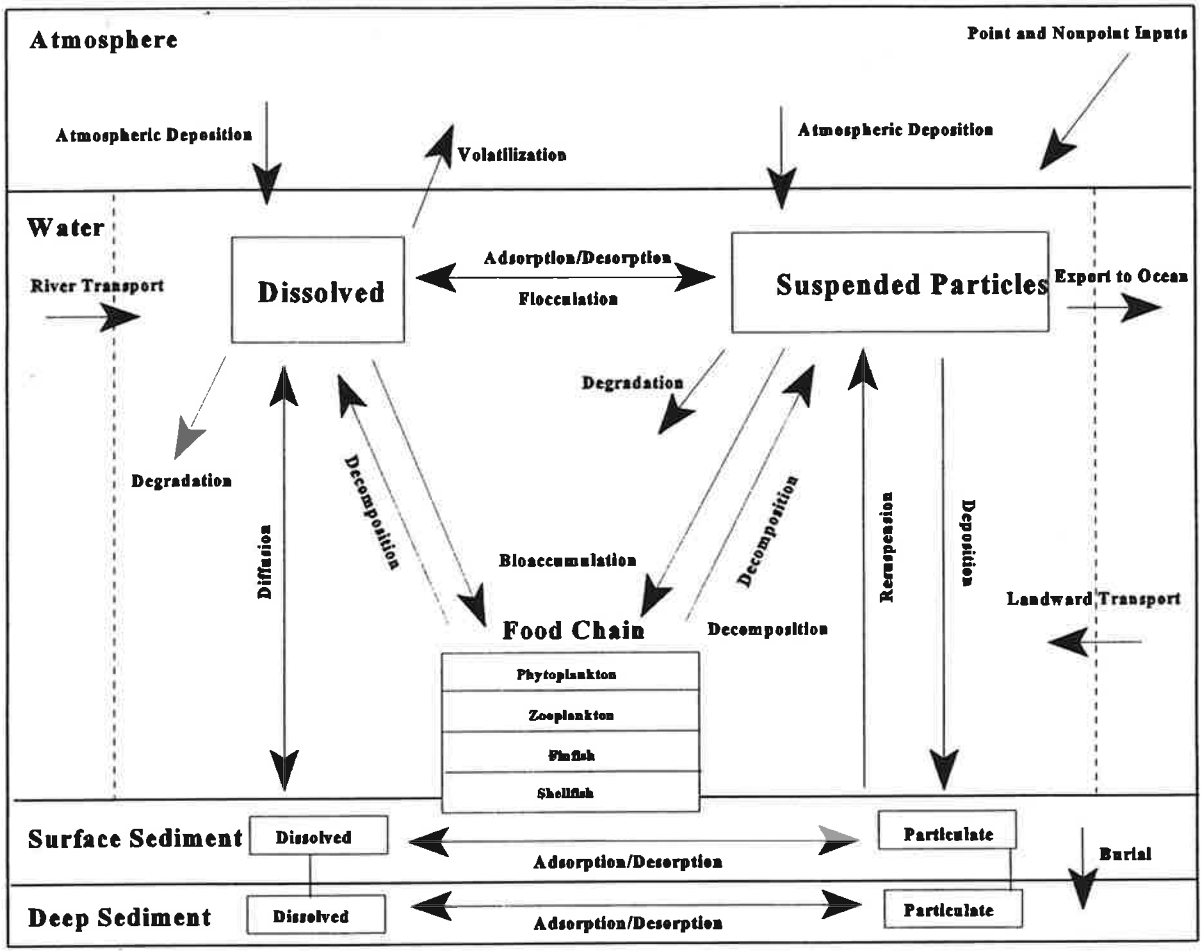


Figure 2. Graphic description of a mass balance showing major processes and pathways for Chesapeake Bay

that should be included in a contaminant mass balance for Chesapeake Bay. This particular model is not inclusive of all possible processes and serves only as a starting point. One of the important aspects of this framework is the accurate quantification of the sources of contaminants to the tidal Bay. Inherent in this exercise is an understanding of the limitations and uncertainties in the quantification of the various sources. The recently published *Chesapeake Bay Basinwide Toxics Loading and Release Inventory* (Chesapeake Bay Program, 1994a) is the second comprehensive attempt in determining the loadings to the Bay. It is substantially more accurate and inclusive then previous loading estimates (Chesapeake Bay Program, 1982). As a first-order approach, a mass balance helps to serve as a check on the accuracy of the identified inputs and outputs used in the mass balance. The model can then help to point out areas in need of better and more data or additional compartments and sources that need to be included within the framework. In other words, the construction of a simplified mass balance helps to put loadings information into a realistic perspective, and provides a focus for future research projects (Chesapeake Bay Program, 1994a).

LOADING ESTIMATES TO TIDAL CHESAPEAKE BAY: A SUMMARY

The calculation of input fluxes to Chesapeake Bay is a complex task. Problems inherent in these types of calculations include: 1) a general lack of data, 2) comparability of chemical measurements and forms for each source category, and 3) incomplete reporting of the various sources. In many cases, the reporting programs in which data were collected were not set up with the objective of calculating a load or flux, but rather for assessing the potential biological effects via comparison with numerical water quality standards. Despite these limitations, initial load estimates need to be established to assess the relative magnitude of point and non-point inputs and where data needs are greatest to improve future load estimates.

Inputs that were quantified include point sources (municipal and industrial), non-point sources (shoreline erosion and urban runoff), river transport, and atmospheric deposition. Sources of contaminants from spills and coastal ocean-bay exchange were not quantified, although they should not be overlooked in future budgets. All estimates include only those below the fall-line

(BFL) from Maryland, Virginia, and the District of Columbia. Also, these estimates are considered edge-of-field loads in that they do not consider fate and transport processes that would modify the actual input of a contaminant to a specific point within the tidal Bay. Data for these loading calculations were obtained from the *Chesapeake Bay Toxics Loading and Release Inventory* which included information from the Chesapeake Bay Fall-line Monitoring Program, Chesapeake Bay Atmospheric Deposition Program, and various published and unpublished reports (Chesapeake Bay Program, 1994a,c).

Comparison of the Various Fluxes to the Bay

The loads from the various sources to the ***entire*** tidal Bay are compared in Table 3. The ranges presented for atmospheric deposition, river transport, urban runoff, and shoreline erosion were not calculated similarly, and may be based upon as little as two estimates (Chesapeake Bay Program, 1994a; Velinsky, unpublished data). Point sources are presented as a single point, and may vary by a factor of 30 (Chesapeake Bay Program, 1994a; Warner et al. 1992). Unfortunately, organic data for the various sources are lacking, as there is not a coherent program to measure these parameters, except for the atmospheric and river monitoring studies.

For copper, zinc, and chromium, river transport fluxes are substantially higher than other sources (Table 3). The second largest source of trace metals to the tidal Bay appears to be urban runoff. This is especially true for the flux of cadmium and lead, in which urban runoff is up to 6 to 30 times higher than the other sources. However, the range of estimates for urban runoff is large, and should be an area of future study to help constrain these values. Shoreline erosion, along with river transport, appear to be important sources of chromium and zinc, most likely due to their crustal abundance compared to the other metals. While the fluxes for rivers, urban runoff, shoreline erosion, and point sources appear to be higher or of similar magnitude to atmospheric inputs, the location of these inputs (i.e., along the coast or in specific tributaries) is markedly different than atmospheric deposition which is distributed directly to the surface water of the Bay. Each source, regardless of its overall magnitude however, may have a substantial biological effect in the "local" area (i.e., tributaries).

Generally, there is a lack of adequate data for the quantification of the inputs of most organic contaminants. The river transport flux for total PCBs is approximately ten times greater than atmospheric deposition (Table 3). Unfortunately, there are no data for the other possible sources of these chemicals to the Bay. Urban runoff is the dominant source of the aromatic hydrocarbons, chrysene and benzo[a]pyrene, to the Bay. While there is no estimate of the uncertainty or range in these fluxes, which may be substantial, studies from other areas (National Academy of Sciences, 1975; Hoffman et al. 1983; 1984) also indicate that urban runoff is a significant source of petroleum hydrocarbons to coastal urban areas. For both chrysene and benzo[a]pyrene, atmospheric deposition is a slightly greater source to the tidal portion of the Bay than point sources. However, the data available to determine the point source load are very limited and the rates presented are most likely an underestimation of the "true" loadings.

Table 3. Summary of contaminant loads to the entire tidal waters of Chesapeake Bay.

Chemical	**Atmospheric Deposition**	**Urban Runoff**	**River Transport**	**Shoreline Erosion**	**Point Sources**
Metals					
Cadmium	1.3 - 1.6	0.95 - 5.3	37 - 71	1.0 - 1.9	0.62
Chromium	2.2 - 4.2	5.4 - 30	200 - 270	83 - 90	19
Copper	11 - 15	15 - 84	270 - 450	28 - 29	37
Lead	9.5 - 15	190 - 360	310 - 410	27 - 28	5.3
Zinc	31 - 52	84 - 460	130 - 220	96 - 120	160
Organics					
Benzo[a]pyrene	0.054 - 0.13	0.094	0.19 - 0.36	ND	0.044
Chrysene	0.093 - 0.19	0.24	ND	ND	0.007
Total PCBs	0.030 - 0.039	ND	0.37 - 0.38	ND	ND

Loads are in metric tons per yr. Adapted from Chesapeake Bay Program (1994a), Baker et al. (1994), and Velinsky (1994). ND - No Data.

These data illustrate the current status of the loading information available as part of the *Chesapeake Bay Basinwide Toxics Loading and Release Inventory* (Chesapeake Bay Program, 1994a). While there are many assumptions and problems with the current data set, this exercise highlights areas that need further study in order to synthesize a more complete understanding and quantification of the sources of potentially toxic chemicals to Chesapeake Bay. This will be further illustrated in the next section. Recommendations for future loadings studies include: 1) for all sources determine a consistent chemical fraction (e.g., total, total recoverable, dissolved), 2) use lower detection limit methods for both dissolved and particulate analyses, 3) include urban stations in the atmospheric deposition network, 4) undertake a comprehensive sampling of major point source dischargers, and 5) initiate site specific studies to better estimate the urban flux of chemical contaminants. These studies should be coupled with the determination of the removal rates (i.e., burial, gas exchange, degradation) from Chesapeake Bay to help understand the fate and cycling with in this environment.

A PRELIMINARY MASS BALANCE FOR THE MARYLAND PORTION OF THE TIDAL CHESAPEAKE BAY: AN ILLUSTRATIVE EXAMPLE

To illustrate some of the problems, pitfalls, and usefulness of constructing a simple input-output mass balance, information and data from various sources were collected and compared for the Maryland portion of tidal Chesapeake Bay. This balance considers only chemical contaminants coming into this region from sources mentioned in the previous section and the amount of contaminants buried in the sediment. Only specific trace metals (e.g., copper, lead, and zinc) were quantified due to a larger existing database for these metals than for organic contaminants (e.g., PCBs) or other trace metals. For this study, only the tidal area from the mouth of the Susquehanna River (RM 156) to south of the Potomac River (RM 55) was selected due to the greater amount of available data compared to the Virginia portion of the Bay. The exchange of water and sediment from the southern portion of the Bay also were not considered in these calculations. Additionally, microbial processes affecting metal speciation were not quantified because only bulk "total" concentrations were used. The approach to calculating the sediment burial of trace metals is similar to that described in Officer et al. (1984) for sediments and Nixon (1987) and Boynton et al. (1995) for nitrogen and phosphorus.

Inputs of Metals

Sources of copper, lead, and zinc were adapted from the data in Chesapeake Bay Program (1994a). Shoreline erosion estimates were modified from Velinsky (1994) to adjust the loads for the Maryland portion of the Bay and important tributaries (e.g., Potomac, Patuxent, and Choptank rivers). While not all areas or tributaries were quantified directly, this exercise most likely accounts for a majority of the inputs to the tidal waters of Maryland (Table 4).

The ranges listed in Table 4 for atmospheric deposition (wet+dry), urban runoff, and river transport are derived differently. The ranges for atmospheric deposition were related to the uncertainty in the dry deposition flux (see Baker et al. 1994), while the ranges for river transport were the low and high fluxes over a four year time period (1990-1994) and are related mainly to the variations in water discharge. While there are no ranges presented for either shoreline erosion or point source loads, the data in Chesapeake Bay Program (1994a), Velinsky (1994), and Warner et al. (1992) indicate that the fluxes could vary by an order of magnitude.

Similar to the inputs for the entire Chesapeake Bay, river transport and urban runoff are the two dominant sources to the Maryland portion of the Bay. Inputs from atmospheric deposition

Table 4. Summary of trace metal loads to the Maryland portion of the tidal waters of Chesapeake Bay. Loads are in metric tons per yr.

Chemical	Atmospheric Deposition	Urban Runoff	River Transport	Shoreline Erosion	Point Sources
Copper	2.0 - 3.6	10 - 56	130 - 240	13	31
Lead	4.7 - 7.6	44 - 240	160 - 270	11	4.7
Zinc	12 - 14	56 - 310	180- 780	45	140

Adapted from Chesapeake Bay Program (1994a), Baker et al. (1994), and Velinsky (1994).

directly to the surface waters of the upper bay and shoreline erosion appear to be of similar magnitude, but how and where these sources enter the Bay differ markedly. The sediments from the headlands and shoreline of the Bay (e.g., Calvert Cliffs), derived from erosion, are not easily transported and mixed throughout the Bay, yet atmospheric deposition occurs over the entire Bay, even in remote waters. Point source loads, while most likely underestimated, are similar to shoreline erosion in that they are introduced into specific areas and over a specific time period. However, becasue a portion of the point source load may be in the dissolved phase, it will either stay in the dissolved phase or partition to suspended material and be transported with the water more rapidly than erosional sources.

Metals Burial in the Sediments

The inputs of these metals to the water column or suspended sediments are balanced against the burial of particulate metals in the sediments of the Bay (see previous discussion on particle-reactivity of metals). The burial rate of a contaminant (B; kg metal/yr) can be determined by using the concentration of a metal in the sediment that is buried (C; µg Metal/g dry weight), the dry bulk sediment density (ρ_s; g dry sediment/ cm^3 of total sediment), and the vertical sedimentation rate (ω_v; cm/year). From this information, the burial rate of a metal can be determined via the following equation (Berner, 1980; $B = C\cdot\square_s\cdot\omega_v$). Studies that provide a mass sedimentation rate (ω_m; g dry sediment/cm^2-year) for a given area of the Bay can also be used with concentrations of metals to provide a burial rate ($B = C\cdot\omega_m$).

Additionally, areas within the Bay must be classified as depositional, erosional, or at equilibrium. For each area or segment of the Maryland portion of the Bay, this type of information is combined and summed to provide an estimate of the removal of a contaminant via sediment burial. This method is similar to that for both nitrogen and phosphorus deposition as described in Boynton et al. (1995).

To accomplish this calculation, data were obtained from many studies that spanned over 15 years. First, the surface area of the upper bay (Cronin and Pritchard, 1975; Boynton et al. 1995) was broken into upper and lower Maryland segments, with the three major tributaries were treated separately (Table 5). The fraction of each segment or tributary that is depositional was taken from Kerhin et al. (1983; 1988) and ranged from 0.8 in the tributaries to 0.5 in the lower portion of the Maryland mainstem (Table 5). Areal mass depositional rates were obtained or derived from the studies of Kerhin et al. (1983; 1988), Brush et al. (1982), Officer et al. (1984), and Boynton et al. (1995). High and low mass depositional rates for the different areas are presented in Table 6. The information presented in Table 5 was then used with the mass sedimentation rates presented in Table 6 to derive a dry sediment flux in the Maryland portion of Chesapeake Bay.

Next, sediment contaminant concentration data for Chesapeake Bay and its tributaries (Table 7) were applied to the sediment depositional rates for the given area and the burial of metals was calculated. The contaminant data were obtained from the comprehensive report by Eskin et al. (1995, unpublished report) and represent surface sediment concentrations from samples collected over various years. If available, concentrations of contaminants below the surface layer should be used to account for possible diagenetic remobilization of metals into the overlying waters; however this is not always possible. Also, while median concentrations were used to calculate the burial of trace metals, there is substantial spatial variability in the concentration of metals throughout all areas (Eskin et al. 1995 unpublished report and references within).

In addition to the mainstem bay and the three tributary estimates, there are two recognized areas within this study area, the Anacostia River and Pataspco/Back River system, that have extremely elevated concentrations of trace metals (Velinsky et al. 1994; Eskin et al. 1995 unpublished report). These two areas have been declared as Regions of Concern by the Chesapeake Executive Council and Regional Action Plans are being drafted to help manage and remediate these areas (Chesapeake Executive Council, 1994). For each of these areas, a preliminary assessment was made of the deposition rate of these metals to the sediments.

For the tidal Anacostia River, a similar technique as described above was used to determine the burial of metals in the sediments. This was accomplished using recent surface sediment concentrations (Velinsky et al. 1994; Sampou, 1990; Pinkney et al. 1993) and sediment deposition rates from Scatena (1987). From this preliminary analysis, the sediment burial of copper, lead,

Table 5. Surface areas and depositional fractions for Maryland portion of Chesapeake Bay.

Location	Surface Area (m^2)	Fraction Depositional
Total Bay	1.15×10^{10}	0.52
Maryland Mainstem[a]	5.15×10^{9}	0.72
Upper MD portion	1.69×10^{9}	0.72
Lower MD portion	3.82×10^{9}	0.54
Patuxent River	1.36×10^{8}	0.80
Potomac River	1.13×10^{9}	0.80
Choptank River	3.60×10^{8}	0.80

[a] Includes all tributaries from RM 55 to RM 156. Upper MD portion is from RM 125 to RM 156 and the lower portion is from RM 55 to RM 125. Data taken from Cronin and Pritchard (1975), Officer et al. (1984), Kerhin et al. (1983; 1988), Hobbs et al. (1992), and Boynton et al. (1995).

Table 6. Mass sedimentation rates for various areas of Chesapeake Bay.

Location	Mass Sedimentation	Reference
Total Bay (weighted average)	0.23	Officer et al. (1984)
Upper MD portion	0.39	Kerhin et al. (1983; 1988)
Lower MD portion	0.17	Kerhin et al. (1983; 1988)
Upper Bay	0.30 - 1.2	Officer et al. (1984)
Mid-Bay	0.10 - 0.30	Officer et al. (1984)
Lower Bay	0.10 - 0.80	Officer et al. (1984)
Upper Patuxent River	0.24 - 0.27	Khan and Brush (1994)
Lower Patuxent River	0.15 - 0.20	Brush (1984)
Upper Potomac River	0.69 - 1.5	Brush et al. (1982)
Lower Potomac River	0.07 - 0.47	Brush et al. (1982)
Upper Choptank River	0.34	Yarbo et al. (1983)
Lower Choptank River	0.09	Yarbo et al. (1983)

Mass sedimentation rates in units of g dry sediment/cm^2-yr.

Table 7. Trace metal concentrations for areas within the Maryland portion of Chesapeake Bay

Location	Copper	Lead	Zinc
Upper	3.7 - 56 (33)	13 - 86 (61)	19 - 500 (220)
Lower	2.5 - 48 (24)	6 - 76 (35)	25 - 350 (140)
Patuxent River	12 - 34 (23)	8.0 - 52 (29)	99 - 172 (150)
Potomac River	28 - 43 (36)	15 - 73 (33)	130 - 270 (190)
Choptank River	3.0 - 31 (15)	2.0 - 55 (29)	29 - 170 (110)

Data from Eskin et al. (1995, unpublished report). Concentrations are low and high concentrations with median values in (   ).

and zinc was estimated to be 3.8, 8.4, and 17 metric tons/year, respectively (Velinsky et al. 1993). These fluxes are within 1 to 3 times the loads for the Anacostia watershed (Velinsky, unpublished data; Olsenholler, 1991).

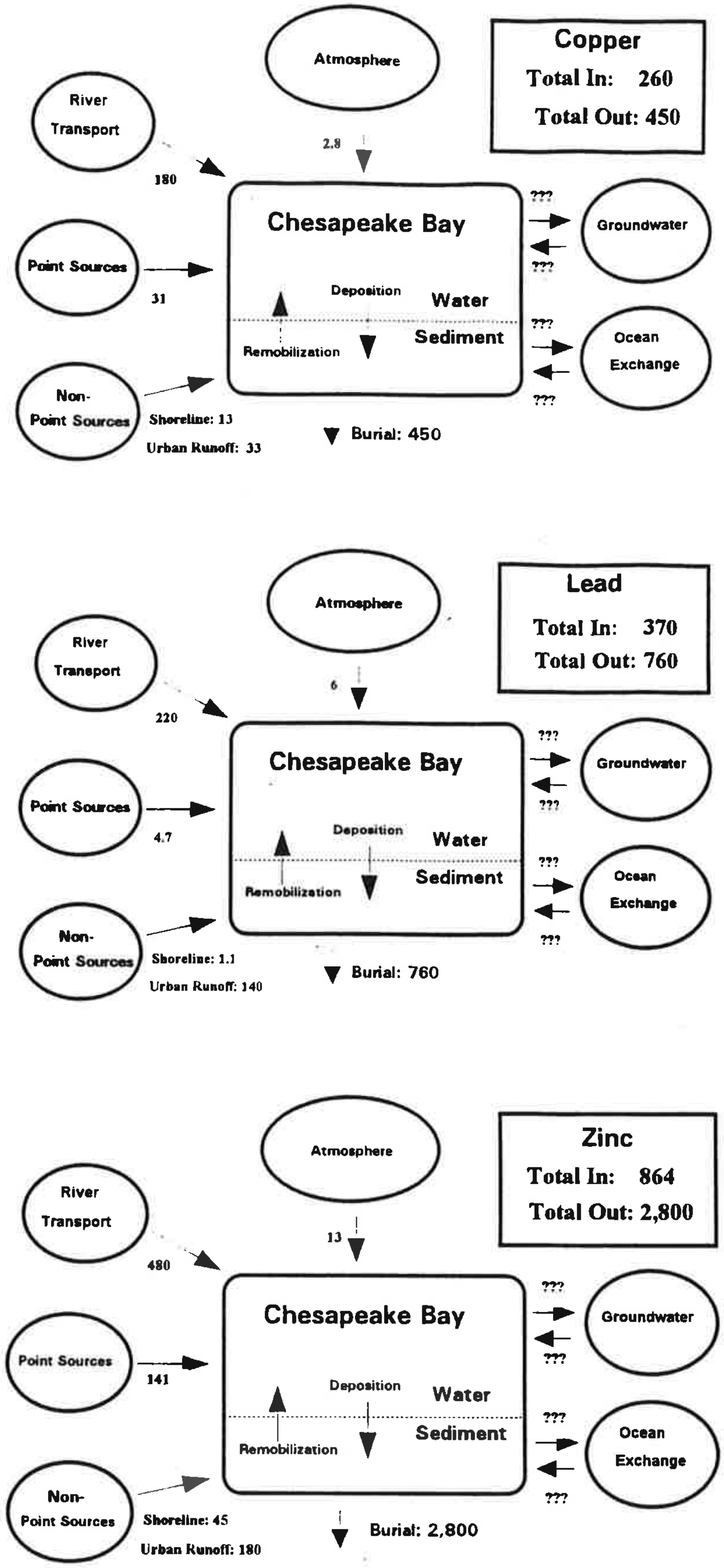
For the Pataspco and Back River system, a similar approach was used. Using data from Eskin et al. (1995 unpublished report) and Warner et al. (1992), sediment burial was estimated to range from 9.6 - 43 metric tons/yr, 9.9 - 44 metric tons/yr, and 36 - 140 metric tons/yr for copper, lead, and zinc, respectively. This range is based on the range in sedimentation rates and median Baltimore Harbor metal concentrations from Eskin et al. (1995 unpublished report). However, this estimate does not account the removal of sediments with elevated levels of trace metals from the extensive dredging in the Baltimore Harbor area. These rates were compared to the loadings calculated by Warner et al. (1992) for both point and nonpoint sources. They estimated copper lead, and zinc loads to the harbor area of 26, 37, and 130 metric tons/yr, respectively. Helz (1976) also estimated the annual input of zinc in 1970 to this area of 650 metric tons/yr; evidently the annual load of zinc has decreased over the past 20 years (Sinex and Helz, 1982). These two estimates (loads vs burial) are in reasonable agreement suggesting that most of the metals that enter the system are retained in the sediments as proposed by Sinex and Helz (1982).

This method of calculating the removal of metals via sediment burial is fraught with many problems. At each point in these calculations assumptions were made, usually involving temporal and spatial scaling issues (i.e., taking short term data and applying them to longer and larger temporal and spatial scales). For example, while there have been many studies on the sedimentation rate within the Bay, these studies have focused on specific areas and not a systematic sampling of the entire Chesapeake Bay area. The study by Officer et al. (1984) summarized a collection of about 20 cores taken throughout the Bay region. These studies used geochemical tracers such as ^{210}Pb or ^{137}Cs for sediment dating. Sedimentation rates derived using ^{210}Pb or other geochemical tracers are usually averaged over an approximately 100 year time period and do not separate short term episodic events that can be important in sediment deposition. For example, Gross et al. (1978), using a sediment budget, estimated that the majority of sediment introduced to the Bay from the Susquehanna River for a ten year period was derived from two major storm events, Tropical Storm Agnes and Hurricane Eloise. Hirschberg and Schubel (1979) further suggested that sediment profiles of ^{210}Pb from their study indicate a massive deposition of sediments derived from Agnes and other storms. These episodic events in sedimentation are averaged out using tracer studies and could underestimate sediment accumulation. Other methods for calculating sedimentation rates, such as sediment budgets and bathymetric depth changes yield slightly different rates than geochemical tracer studies. Without a systematic approach of sampling and measuring sedimentation rates within the Bay and tributaries, mass balance budgets for contaminants will remain uncertain.

Comparison of Inputs and Burial

Using the above estimates, yearly burial rates of copper, lead, and zinc to the Maryland portion of the Bay ranged from 220 to 680 metric tons/yr, 360 to 1,200 metric tons/yr, and 1,400 to 4,300 metric tons/yr, respectively. Interestingly, the burial of these metals in both the Anacostia River and the Baltimore Harbor region accounts for between 4 and 7% of the total deposition (using the mid-points of the ranges) even though these areas constitute only approximately 2% of the total surface area of the Maryland portion of the Bay.

The midpoint of these ranges were compared to the total inputs to this region (Figure 3). For both copper and lead there is a reasonable agreement between quantified inputs and burial, while for zinc the output via sediment burial is approximately three times as high as the inputs. It is



All fluxes are in Metric tons/yr

Figure 3. Inputs and outputs of trace metals to the Maryland portion of Chesapeake Bay.

unclear why the burial of zinc is much higher than its input, compared to either copper and lead (i.e., all sources and sinks were estimated similarly). Variations in the concentration of surficial concentration of zinc may require further study. Conversely, there may be many unaccounted or underestimated sources that also need to be assessed or re-assessed. It appears that the total load introduced to this area can be balanced by what is lost or buried in the sediments, and very little is transported to the southern portion of the Bay. However, while the closeness of these fluxes may be real, there are many areas of uncertainty, both for sources and sinks, that prohibit any definitive conclusions at this point.

Uncertainty in source estimates comes from several factors. First, there are currently no estimates for the inputs of contaminants from groundwater, sediment/water transport, and the coastal region to the Bay. These sources could be important for specific contaminants depending on their mobility and transport rate. Studies by USGS, U.S. EPA and others indicate that nutrient inputs via groundwater can be significant (Chesapeake Bay Program, 1993), and research by Cerco (1994) and Boynton et al. (1995) suggests that the Bay is a net importer of phosphorus from the coastal areas. However, depending on the reduction-oxidation potential within the sediments and aquifer, many contaminants which are particle-reactive may not be transported through the groundwater to the same extent as more water soluble contaminants. Second, there are large uncertainties associated with load calculations for most of these sources. There are not sufficient monitoring data of sufficient quality to evaluate annual concentrations and fluxes of metals from many river systems. For example, only the Susquehanna River has sufficient data to evaluate annual loads to the Maryland portion of the Bay. The Susquehanna River flux was then extrapolated to the unmonitored Maryland portion of the Bay. While this river accounts for the majority of the total flow, other smaller watersheds could have an impact on the Bay, especially on the waters which directly receive the river's flow. Third, Warner et al. (1992) suggest that point source loads can vary substantially depending on the calculation method. These estimates can vary by orders of magnitude. Lastly, similar variations can be shown for estimates via urban runoff and possibly shoreline erosion, both of which are major inputs to tributaries and the Bay.

The only output considered in this budget was the burial of contaminants in the sediments. As pointed out earlier, there are also many areas for uncertainty in these calculations. For example, variations in trace metal concentrations within the northern Bay can be substantial (Eskin et al. 1995 unpublished report and references within). However, the majority of the uncertainty most likely lies with the estimates of the depositional rates and the areas of the Bay that are depositional. Kerhin et al. (1983; 1988) studied the pattern of erosion and deposition for the mainstem northern Bay, giving little attention to some of the tributaries. Although these tributaries are probably more depositional than the mainstem Bay, more information is needed.

There are different ways to compute the sedimentation rate of a given area; either by use of geochemical tracers such as ^{210}Pb (Officer et al. 1984; Owens and Cornwell, 1995) or use of a sediment budget (Kerhin et al. 1983; 1988; Hobbs et al. 1992). Officer et al. (1984) showed a trend of high sedimentation rates in the upper bay of 0.3-1.2 g/cm^2-yr with lower rates in the mid-Bay region of 0.1-0.3 g/cm^2-yr. Mass sedimentation rates in the lower Bay were slightly higher than mid-Bay sites. While there was substantial variation between areas, these sedimentation rates are in general agreement with other studies (Hobbs et al. 1992; Helz et al. 1985; Cooper and Brush, 1993; Owens and Cornwell, 1995). With better coverage of sedimentation rates of the tributaries as well as the mainstem Bay, a more precise estimate can be derived for this sink of metals.

TOWARDS A CHESAPEAKE BAY CHEMICAL CONTAMINANT MASS BALANCE

The simple input-output mass balance analysis for copper, lead and zinc appears to be consistent in that there is a reasonable agreement between total inputs and the loss of these metals via burial. Unfortunately, due to the lack of data it is impossible to quantify the uncertainty for these estimates. However, while the amount of uncertainty in this analysis is most likely large, this study does allow a focusing of monitoring efforts on specific sources and geographic areas that would greatly improve and expand a mass balance. For example, in many areas urban runoff is a dominant source. The method used to calculate the urban runoff load (Olsenholler, 1991) should be updated carefully with newer chemical and land use data. Also, it became apparent during the development of this input-output mass balance that there is little information available concerning the transport of organic contaminants into and within the Bay. If an expanded mass balance is sought, especially for other inorganic or organic contaminants, much more monitoring is warranted.

Overall, basic monitoring information is needed for almost all sources and sinks identified in this document. While these monitoring data will not provide information as to the effects of chemical contaminants, they do provide the needed information as to where and how much a reduction in a particular source load is needed. Until both sources and sinks are better quantified, future input-output balances will remain uncertain and of limited quantitative use.

The input-output model derived for the Maryland portion of the Bay is a simplistic form of a time dependent mass balance. Other types of mass balances would be much more complex. For example, a model could be developed to include a water transport component which would be coupled to a nutrient-driven eutrophication model. This framework would then generate the organic carbon-related solids information which would be coupled to a bulk solids transport model. This section would be an input to a contaminant exposure/food chain model. This type of modeling framework would be used if fish or benthic organism exposure is an endpoint. Once verified, this model could be used to answer "what if" questions such as; if specific sources are reduced, how much reduction is needed and how long will it take to lower the concentration of a specific contaminant in the water column or an organism to a given level? This type of modeling is currently under development for specific areas within the Great Lakes for PCBs.

For a more complete mass balance model to be useful, its development must be driven by the objectives that *both* managers and scientists decide upon. Also, there are many questions concerning the feasibility of using a mass balance approach to manage or evaluate chemical contaminants in Chesapeake Bay. For example, if a concerted effort is applied to determine the absolute inputs and outputs from significant sources and sinks, will enough specific information exist to help managers of the various sources of contaminants (e.g., point source regulators or urban planners) determine the need for potential additional regulation of these sources? Also, if additional regulatory actions are taken, will living resources that are affected by contaminants respond and show some improvement (e.g., fewer fish advisories)?

As can be seen from the simple input-output model for Maryland, the data needs for any of these tasks are enormous and would therefore be very expensive. However, the development of a simple input-output mass balance could be a first step and would be less expensive while providing useful information to Bay managers. For example, current load estimations to the Bay could be evaluated and judged for accuracy by also estimating the outputs. This would help managers and scientists determine any unrecognized source(s) to the Bay. When an accurate assessment of the relative loading exists, the importance of each source can be determined, and a determination can be made of the possible measures in controlling these sources in an overall context. The results generated from such a project would also be a part of the initial data requirements for a larger modeling framework, if developed. This information is needed to help focus clean-up efforts and the limited dollars to areas and sources that will make the biggest difference in the overall health of Chesapeake Bay.

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