Puget Sound Estuary Program

Evaluation of the Atmospheric Deposition of Toxic Contaminants to Puget Sound

August 1991

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INTRODUCTION

Evaluation of the Atmospheric Deposition of Toxic Contaminants was a study conducted to more fully understand the contribution of airborne toxic contaminants to water quality problems in Puget Sound. The study was managed by the Puget Sound Water Quality Authority, with major funding provided by the National Estuary Program of the EPA through the Region 10 office. The Puget Sound Air Pollution Control Agency (PSAPCA) also contributed to the study.

One of the main concerns that prompted the study was a growing recognition of the problem of cross-media transfer of pollutants. The deposition of airborne particles and gases may be responsible for contributing certain heavy metals, polycyclic aromatic hydrocarbons (PAHs), and other organic compounds to Puget Sound. Deposition can occur directly as particles settle onto the water surface, or indirectly as they settle on land and are subsequently washed or blown off the land into the Sound. These toxic chemicals are then added to the chemicals in the surface water layer (microlayer) of the Sound, the water column, and/or the sediments. The resultant increase in toxicity from this deposition is a concern because of its potential effect on the health and survival of aquatic life in the Sound, and ultimately, through the food chain, on human health.

Atmospheric deposition of toxic contaminants has received only limited attention in the Puget Sound region, but these studies pointed towards this pathway as a potentially important contributor to the total loading of lead (Pb), arsenic (As), PAHs and other organic compounds to the Sound. Atmospheric deposition has been found to be a major source of particulate metals and PAHs in the Southern California Bight; a source of metals, polychlorinated biphenyls (PCBs), DDT, and other pesticides in the Great Lakes region; and a source of one-quarter of the nitrogen compounds that cause serious eutrophication problems in Chesapeake Bay.

STUDY DESIGN

Commencement Bay, an embayment near Tacoma, Washington, was selected for a pilot-scale study to address the following objectives:

▶   Develop a better understanding of the importance of atmospheric deposition relative to other inputs of toxic contaminants to Commencement Bay.

▶   Develop efficient and cost-effective tools for assessing this question in other reaches and embayments of Puget Sound, and other water bodies as well.

Commencement Bay was selected to represent a "worst case" test area, because it is a heavily industrialized area with a complex mix of air pollution sources and documented high concentrations of Pb, PAHs, and other chemicals in both the sediments and sea-surface microlayer. The study design was focused on sampling and analysis of metals (e.g. lead, zinc, arsenic, manganese) and combustion PAHs (three- to five-ring compounds). Low molecular weight PAHs, PCBs, aliphatic hydrocarbons, and nutrients were also sampled and analyzed. PAHs are of concern because some are persistent in the environment and are potent cancer-causing and mutagenic agents. Metals are of concern because they are toxic to aquatic life at certain elevated concentrations.

The "tools" employed for the study consisted of four field sampling components and two modeling efforts. Some general capabilities and limitations of the tools were known in advance: field measurements are resource-intensive and therefore cannot be used realistically to cover a large or dense grid of sites, modeling can provide larger area coverage, but its accuracy is dependent on the input data and the assumptions used to develop the model. In applying these tools in concert in a single embayment, the aim was to compare and validate their effectiveness and determine whether some more limited combination of tools would provide an adequate assessment of the contribution of atmospheric contaminants to the water.

The field components consisted of:

▶ Six-month meteorological data acquisition -- temperature, solar radiation, precipitation, and wind speed and direction collected at one site.

▶ Six-month aerosol and deposition sampling -- twice per week (three- or four-day) aerosol samples (collecting particles up to 25-50 μm in diameter) at six sites [broken into intensive (five-site) and non-intensive (three-site) sampling periods], and two-week deposition samples at five sites (no definite upper particle size limit).

▶ 18-day sampling for receptor modeling -- aerosol sampling for particles up to 10 μm and volatile organic compounds (VOCs) at two sites.

▶ Source testing of the Simpson Tacoma Kraft pulp mill -- sampling and analysis of metals and PAHs in the emissions.

The modeling efforts, which complemented the field studies and provided the tools for interpreting and extrapolating from the field study results, included:

▶ Receptor modeling -- using a mathematical method to attempt to match patterns in chemicals released from sources with patterns of chemicals collected at receptor sites in order to apportion the ambient aerosol to its sources (focusing on particles less than 10 μm).

▶ Diffusion/transport modeling (including a mobilization coefficient model) -- using emissions data, emissions stack parameters, and meteorological data in a physical model to estimate the aerosol and deposition concentrations over a 91.5 km^2 region and then further estimating the percentage of the deposited contaminants that are washed off the land (rather than held in the soil) into Commencement Bay (focusing on the less than 10 μm particles).

An emission inventory was a necessary data input for both models. The emission inventory was prepared compiling previous direct measurements and estimates of both point source and area source emissions in the Tacoma Tideflats.

A field sampling network was established, centered in the industrialized Tacoma Tideflats. Six sites were located along two different transects through the study area: one transect crossed the main industrial sector roughly southwest to northeast, the other stations were located along the path of the prevailing wind through the area (southeast to northwest). The upwind and downwind sites were selected to provide an indication of the background contaminant levels. Stations were located either near or over the water.

The field program was conducted from July 1989 through January 1990, encompassing six months with a range of meteorological conditions and emissions scenarios.

Following completion of the individual studies, paired comparisons of the data were conducted to bridge between the studies (particularly where different particle size fractions had been investigated) to attempt to reconcile results and fill data gaps.

STUDY RESULTS

An important result of the investigation was a much more coherent picture, for the Tacoma Tideflats/Commencement Bay region, of the contributing sources of atmospheric contaminants and the temporal and spatial variations in the ambient aerosol and the amounts of contaminants deposited. Some of the more significant findings include:

▶   The summer and winter high-concentration[2] aerosols were qualitatively different. The high-concentration summer aerosol appears to have consisted largely of resuspended larger particles, such as fugitive dust. The highest concentrations of metals were found in the industrial area, particularly at the Sea-Land site (Pb and Zn). The highest concentrations of PAHs were measured at the Alexander Avenue site. The set of meteorological conditions favoring transport of these high-concentration aerosols consisted of prolonged periods of dry weather followed by moderate-to-high wind speeds.

▶   The 18-day study showed that on average the late fall/winter PM_{10} (particles less than 10 μm) aerosol consisted largely of "fine" particles (particles less than 2.5 μm). A large percentage of the total fine-particle mass consisted of organic compounds. The similar aerosol concentrations throughout the sampling area suggest a substantial influence of regional sources relative to local sources. High concentrations of the particles were most often associated with air stagnation episodes and low wind speeds predominantly from the southeast.

▶   During the summer/early fall sampling period, when larger particles appear to have been an important component of the aerosol, earth-moving and construction activities (with accompanying exhaust and road dust from heavy machinery) occurred in the vicinity of the industrial area sampling sites. Also during the study period Kaiser had at their site approximately eight acres of wet scrubber sludge containing PAHs, some of which had the potential of becoming airborne dust during the dry season. Ore offloading operations occurring near the Sea-Land site included offloading of "black ore" (ore from which lead, zinc, silver, and gold are extracted by smelting) into open rail cars. These sources are inferred based on the patterns of chemicals in the deposition samples and their proximity to these industrial sites.

▶   The major source of the late fall and winter high-concentration fine-particle aerosol (less than 2.5 μm) appears to be woodsmoke that drains downslope and downwind from residential areas into the industrial area. This unexpected result was supported by the receptor modeling, a tracer rose analysis (which projects concentrations of contaminants measured at a receptor as vectors pointing upwind) and comparisons between the diffusion model simulations and data collected at Puget Sound Air Pollution Control Agency (PSAPCA) monitors in the Tideflats.

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[2]High-concentration aerosol refers to episodes during the study period when the highest concentrations of aerosol were observed.

► The sampling times and locations may not have been adequate to accurately reflect the relative influence of the Simpson Tacoma Kraft mill, the largest emissions source for PM_{10} in the study area.

► The deposition rates for metals and PAHs were higher in the summer than in the fall. High concentrations usually occurred after periods of dry weather and were associated with moderate wind speeds. The substantial concentration gradients that were detected between sampling sites reflected the proximity of the contaminant sources to the sampling sites. These facts indicate that resuspended large particles were most likely a major part of the deposition. Deposition rates for all the metals were greater at the industrial sites than the background sites and were probably the result of nearby industrial practices. PAH deposition rates were five to 10 times higher at the Alexander site than at Tyee Marina, Morse, and Sea-Land. PAH deposition was probably dominated by large particles from the Kaiser emissions or resuspended dust from the Kaiser site.

► The diffusion model simulations predicted that one to three percent of the PM_{10} emissions would be deposited and reach Commencement Bay during normal rain event runoff. More than 90 percent of the emissions would be advected beyond the boundaries of the 91.5 km^2 modeling domain. Based on knowledge of the dynamics of small particles, and the topography and meteorology of Puget Sound, another three to four percent of the emissions are expected to be deposited farther downwind in Puget Sound.

Based on the study results some first order estimates of atmospheric loading to Commencement Bay were computed and compared with other sources of contaminants to these waters. With the data available only limited conclusions and conjectures can be drawn:

► Using deposition rates as measured at the Riverside School (low rate) and Sea-Land (high rate) sites, and an assumed area of Commencement Bay of 10 km^2, mass loading rates for metals and combustion PAHs were calculated and compared with measured loadings from municipal and industrial point sources and the Puyallup River. The metals loadings from the atmosphere were considerably lower than the point source and the river loadings. Similar data was not available for comparison of the PAH loadings. These deposition estimates did not include runoff from land.

► Computing mass loading from the diffusion model simulations and the estimated mobilization of contaminants into runoff also resulted in metals loadings that were minor compared to the point sources and the river inputs. However, these estimates are probably low because of the low assumed deposition velocities (0.1 cm/s) and mobilization coefficients.

► Comparing estimates of the predicted microlayer concentrations of metals and PAHs, based on deposition rates measured at Tyee Marina and Sea-Land, with measured microlayer concentrations demonstrated that it was possible to account for the measured concentrations with the estimated atmospheric inputs.

CONCLUSIONS AND RECOMMENDATIONS

The study was successful as a pilot-level effort in developing first order estimates of atmospheric deposition and in providing a test and evaluation of a comprehensive set of field sampling and modeling tools that can be used (with modifications) to study atmospheric deposition elsewhere. The conclusions set atmospheric deposition in perspective relative to other sources of contaminants in a heavily industrialized region of Puget Sound, where overall

contaminant loading is high. It should not be assumed that the relative contribution of atmospheric deposition is the same elsewhere in the Sound.

Relative Importance of Atmospheric Deposition

▶ Direct atmospheric deposition of metals appears to be a small contributor, in terms of mass loading, relative to point source water discharges of metals to Commencement Bay.

▶ The data available do not allow definitive conclusions on the relative importance of atmospheric inputs of PAHs. The deposition measurements of PAHs suggest that Kaiser may be an important local source of PAHs. [Note: Since the sampling conducted for the study, Kaiser has covered PAH-contaminated scrubber sludges on their property that had the potential to become part of the fugitive dust loading of PAHs to the Bay.]

▶ Woodsmoke, another source of PAHs, is an important contributor to the ambient aerosol during winter periods of air stagnation. However, PAHs generally make up less than 1 percent of the woodsmoke emissions mass. In addition, woodsmoke emissions are predominantly in the less than 2.5 μm particle size fraction, therefore they are not expected to settle nearby and be an important component of atmospheric deposition to Commencement Bay.

▶ The total input from atmospheric deposition cannot be assessed from the results of this study because of uncertainty in the estimates of atmospheric deposition on land and its subsequent runoff to the Bay.

▶ Atmospheric deposition may be significant relative to other inputs in particular zones, especially close to large sources of fugitive dust, near discharge pipes for stormwater, and at the sea surface microlayer (the top 50-100 μm of the water column). These focused entry points into the water, coupled with pulsed inputs create periodic conditions where atmospheric deposition may be the dominant source of toxic contaminants.

▶ It is not possible from the data to make a definitive prediction of deposition in the far field (Puget Sound). Emissions that are likely to be carried beyond Commencement Bay are generally made up of vapors and particles less than 2.5 μm in diameter. For this size particle there is a rapidly decreasing probability of deposition with distance from the source.

Effectiveness of the Tools

▶ Direct aerosol and deposition measurements are central to estimating the atmospheric contributions to the water. The experience in this study suggests that important considerations for future application of these sampling approaches include: 1) consistency in particle size fractions sampled; 2) length of the sampling period; 3) the number of samples chemically analyzed; 4) sampling protocol and amount for PCBs, aliphatic hydrocarbons, nutrients, and vapor PAHs; and 5) sampling locations relative to winds and primary sources.

▶ Receptor modeling was effective in discerning important sources of the ambient aerosol, particularly the woodsmoke advected into the study area. For future modeling applications, important considerations are: 1) the temporal and spatial representativeness of the sampling; 2) accurate information on the chemical signatures of sources and their variability with time; and 3) sample quantity for organic analysis.

▶ Diffusion modeling showed promise and performed best when compared with measurements of PM_{10} mass. Model refinements should address: 1) accurate information on chemical and particle size characteristics of emissions; 2) size of the model domain relative to location of sources; 3) particle size fraction modeled; 4) deposition velocities relative to particle sizes.

▶ Mobilization coefficient modeling was entirely theoretical for this study. For future applications particular attention should be devoted to: 1) field validation of coefficients; 2) mobilization during severe storm events; and 3) size of the model domain relative to runoff sources.

Recommendations

Further basic research is needed (not necessarily in Puget Sound) to improve some critical technical methods and the understanding of important physical processes, including:

▶ Aerosol particle distribution and chemistry;

▶ Fugitive dust transport and its controlling parameters;

▶ Particle dynamics related to size and chemistry;

▶ Deposition sampling techniques;

▶ Chemical and physical dynamics of contaminant mobilization;

▶ Hybrid dispersion modeling.

If a more definitive analysis is desired for Commencement Bay and Puget Sound, the following additional studies might be pursued either independently or as part of a larger program:

▶ More detailed characterization of ambient and source particle size distributions and chemistry;

▶ Sampling of the microlayer and nearshore zones to complement deposition sampling;

▶ Combined sewer overflow (CSO)/stormwater monitoring;

▶ Refined emissions inventories, including temporal variations;

▶ Vertical and horizontal wind profiling;

▶ Hybrid dispersion modeling;

▶ More detailed monitoring of discharges of toxic substances from permitted air and water discharges.

Chapter 1. Introduction and Background

INTRODUCTION

This report presents the findings of a study that was conducted to more fully understand the contribution of airborne toxic contaminants to water quality problems in Puget Sound. Commencement Bay, an embayment near Tacoma, Washington, was used as a case study to: 1) determine the importance of atmospheric deposition relative to other sources of toxic contaminants; and 2) develop and test tools for assessing the contribution of atmospheric deposition in other reaches and embayments of the Sound. Both field sampling and modeling were conducted, focusing on the six-month period from July 1989 to January 1990. The study was managed by the Puget Sound Water Quality Authority, with major funding provided by the National Estuary Program of the EPA through the Region 10 office. The Puget Sound Air Pollution Control Agency (PSAPCA) also contributed to the study. Academic, agency, and private sector scientists were involved in designing and conducting the study.

The Problem

One of the main concerns that prompted the study was a growing recognition of the potential for cross-media transfer of pollutants. The atmosphere contains contaminants in the form of particles and gases that originate from exhaust from cars, trucks, and other mobile sources; woodstove smoke; smoke from slash burning; emissions from commercial and industrial processes and materials storage; and dust from soil erosion. The deposition of airborne particles and gases may be a key mechanism for contributing certain heavy metals, polycyclic aromatic hydrocarbons (PAHs), and other organic compounds to Puget Sound. Deposition can occur directly as airborne particles and gases settle onto the water surface, and indirectly as they settle on land and are subsequently blown off the land or washed via surface-water runoff and storm sewers into the Sound. These toxic chemicals are then added to the chemicals in the surface-water layer (or microlayer) of the Sound, the water column, and/or the sediments. The resultant increase in toxicity from this deposition is a concern because of its potential effect on the health and survival of aquatic life in the Sound, and ultimately, through the food chain, on human health.

Atmospheric deposition of toxic contaminants has received only limited attention in the Puget Sound region, but these studies point towards this pathway as a potentially important contributor to the total loading of lead (Pb), arsenic (As), PAHs and other organic compounds in the Sound. During the early 1980s researchers measured the concentrations of toxic chemicals in airborne particulates at several coastal locations (Prahl, Crecelius, and Carpenter, 1984). During the mid 1980's other scientists related concentrations of toxic chemicals in marine sediments to elevated rates of fish disease and altered populations of bottom-dwelling animals like worms, clams, and shrimp, that serve as food for fish. They identified concentrations of toxic chemicals above which they always saw biological harm (Barrick et al., 1988). In 1988, the Washington Department of Ecology released draft sediment criteria for managing the quality of Puget Sound sediments. A comparison of the annual average concentrations of five organic compounds in airborne particles collected by Prahl et al. with the draft sediment criteria revealed that the airborne particles from Seattle significantly exceeded the draft sediment criteria. This comparison, while overly simplified, suggested that deposition of airborne particles has the potential to create sediments that are toxic to marine life. The current study therefore was designed to better assess the atmospheric inputs.

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The State of our Knowledge

Prior to undertaking the study described in this report, an extensive literature review was conducted of relevant research in Puget Sound and other coastal waters, including the Great Lakes (see Appendix A). The intent was to identify how the design of this study could benefit from prior experience and also to determine how this study could best contribute new knowledge about the potential significance of atmospheric deposition as a source of toxic contaminants to coastal waters. Most previous research performed in the Puget Sound area has involved indirect measurements or estimates of atmospheric deposition. Left unanswered are key questions about the rates of deposition and the amount of land-deposited material that actually makes its way to the receiving water. These are difficult questions to answer quantitatively.

A mass balance calculation done by Paulson et al. (1988b) estimated that municipal and industrial water dischargers and atmospheric sources contributed roughly equivalent amounts of Pb to the main basin of Puget Sound, for a total of 66% of the Pb. Romberg et al. (1984) interpolated from TSP (total suspended particulate) maps of the region, assuming a constant Pb/TSP relationship, and concluded that atmospheric deposition may account for one-quarter of the total lead input to the Sound. Romberg et al. made similar calculations for PAHs and concluded that atmospheric input of combustion-derived PAHs is significant.

Stormwater runoff is thought to be a primary mechanism for transporting toxic chemicals to Puget Sound after they have been deposited on land. Galvin et al. (1984) found that street dust and dirt on urban impervious surfaces were major contributors of toxics found in stormwater [particularly phosphorus (P), lead (Pb), and zinc (Zn)]. However, they found no correlations between metals and organics sampled in atmospheric suspended particles and those sampled in street dust. Pitt and Bissonette (1984) suggested that airborne PAHs are combustion products (from vehicles and other sources) while the street dirt PAHs are from petroleum product spills. These studies clearly illustrate the complexity and difficulty of accurately determining the amount and fate of deposited toxics.

Some of the more provocative studies that implicate atmospheric deposition and surface runoff as sources of toxics to the Sound focus on the contamination measured in the sea surface microlayer (approximately 50 to 100 μm boundary layer between the atmosphere and the water column). Scientists studying the microlayer have found pollutant enrichments at concentrations 100 to 10,000 times greater than in the water column. The concentrations of metals in the microlayer were found to be two to 15 times greater in Elliott Bay (industrialized) than Sequim Bay (rural) (Hardy et al., 1985a). Metals concentrations in the microlayer were found to be six to 65 times greater than in water columns for both bays. The concentrations of the metals measured in the study agreed well with predictions of atmospheric deposition [based on using [7]Be as a tracer for the behavior of submicron particles (Crecelius, 1981)]. Hardy estimated that up to half the total input of combustion PAHs and particulate metals entering coastal waters in some areas of the U.S. originates from atmospheric deposition (Hardy et al., 1986b). Lead, benzo(a)pyrene, and PCBs were reported in relatively high concentrations in the microlayer (Hardy and Antrim, 1988a).

Studies in other areas of the country have shown that atmospheric deposition is a major source of particulate metals and PAHs in the southern California Bight (Patterson and Settle, 1974); a source of metals, polychlorinated biphenyls (PCBs), DDT, and other pesticides in the Great Lakes region (Eisenreich, et al., 1979-1985); and a source of one-quarter of the nitrogen compounds that cause serious eutrophication problems in Chesapeake Bay (Fisher, et al., 1988).

Organization of this Report

The remainder of this chapter provides background information on atmospheric deposition and contaminant transport processes to assist the reader in understanding and interpreting the findings of the study. Chapter 2 provides a discussion of the overall study design, including the rationale for site selection, target chemicals, and the individual study components. Chapters 3 - 7 each address a specific study component and present the methods employed, the results, and discussion. Chapter 8 compares and integrates the results of the separate studies. Chapter 9 synthesizes the results and discusses how these findings might apply to Commencement Bay and Puget Sound. Chapter 10 presents conclusions and recommendations.

BACKGROUND

Toxic Contaminants in the Atmosphere

Toxic contaminants exist in the atmosphere in the form of aerosols (a suspension of colloidal particles in a gas) and vapor. The principal contaminants investigated in this study are trace metals -- such as chromium, manganese, iron, nickel, lead, titanium, copper, and zinc -- and polycyclic aromatic hydrocarbons (PAHs). Due to coagulation, condensation, and gas adsorption processes in the atmosphere, a single aerosol particle can contain many different materials, including metals and PAHs.

PAHs are a class of complex organic compounds of natural and anthropogenic origin that are widely-distributed around the world. They are of concern because some are persistent in the environment and are potent cancer-causing and mutagenic agents. PAHs are produced largely by the incomplete combustion of fossil fuels (gasoline, kerosene, coal, diesel fuel), waste incineration, and burning of wood products (woodstoves, forest fires and slash burning). Burning produces small (<3 μm) airborne particulate matter (soot and fly ash) on which PAHs are adsorbed. Lower molecular weight PAHs (2-3 fused aromatic rings) are acutely toxic, causing illness or death to aquatic organisms. Within the group of higher molecular weight PAHs, 20 to 30 are proven carcinogens (Neff, 1979). The fate and composition of deposited PAHs are affected by the processes of sorption, biodegradation, photolysis, and volatilization (Mills et al., 1985).

Trace metals are found naturally in the environment in crustal materials from which they are released by erosion and other mechanical activities. Metals are also generated by human activities and released as an emission from industrial processes and combustion of leaded fuel. Although many metals are required in small quantities for biological processes, metals such as mercury, lead, nickel, zinc, and cadmium are of environmental concern because they are toxic to aquatic life at certain elevated concentrations. As chemical elements, metals are persistent over time. Many trace metals are soluble in sea water and therefore could be available to marine food webs (Hardy et al, 1985).

The size distribution of ambient aerosols is distinctly bi-model: fine (<2.5 μm diameter) and coarse (>2.5 μm diameter). The two modes are relatively independent with respect to origin and differ in their physical and chemical character. Coarse particles are generated mechanically by weathering of crustal materials and biomass, by disturbance of soil or industrial process material, or by droplet formation from seaspray. Fine particles are formed mainly from condensation of hot gases or chemical conversion of gases in the atmosphere to particulate species. They are typically associated with anthropogenic sources such as combustion or industrial processes. Fine particles may grow in size to about 0.5 μm by coagulation. Fine particles are removed by rainout (processes taking place within clouds, such as the formation of condensation nuclei), washout (removal of materials below cloud level by falling ice or

rain), or turbulent mixing to the surface. By contrast, coarse particles are removed mainly by gravitational settling. The residence time of particles in the atmosphere is at a maximum for particles in the 0.1 - 1.0 μm range (see Figure 1-1).

Atmospheric contaminants are sampled by techniques that are optimized to collect a specific size range of particles from ambient air. A PM_{10} sampler collects particles less than approximately 10 μm, which can in some samples be further split into coarse (2.5 - 10 μm) and fine (0 - 2.5 μm) fraction. A PM_{25-50} sampler collects particles up to approximately 50 μm, depending on the wind speed. A TSP, or Total Suspended Particulate, sampler is capable of collecting particles up to about 75 μm in diameter. Organic vapors are typically collected by capture in an adsorbent medium, such as XAD-2 resin or polyurethane foam.

Atmospheric Deposition Processes

Deposition of contaminants from the atmosphere onto the surfaces of a watershed is known as dryfall and wetfall. Within each of these two general categories, a number of specific processes can be identified, depending on the particular contaminant.

Dry deposition consists of the settling of atmospheric particles and the condensation and adsorption of trace gases onto the watershed surface. The settling velocity of a particle is a function of many factors, including the particle mass, its surface area, and the ambient air conditions. While gravity plays a key role in the deposition of larger particles, smaller particles (<2.5 μm) are deposited as a result of turbulent mixing bringing the particles into direct contact with the surface on which they are being deposited.

Wet deposition or washout involves water vapor, rain, or solid phase water (snow, ice) as a medium to transport atmospheric particles and condensed vapor to the land or water surface. Some studies have found the deposition of PCBs to be dominated by wet deposition (Eisenreich et al., 1981).

A number of studies have found that, overall, dry deposition dominates the input of contaminants to the aquatic environment (McVeety and Hites, 1988; Webber, 1986). This cannot be assumed to be the case during the wet winter months in the Pacific Northwest. Accurately estimating deposition rates is exceedingly difficult because of shortfalls in our understanding of the underlying physics, incomplete characterization of the particles and their distribution, and insufficient empirical evidence (due to relatively primitive sampling techniques).

Transport Processes

The question of how much airborne toxic material reaches a particular water body is difficult to answer quantitatively. There are large uncertainties beyond the deposition rates, including how much of the airborne toxic chemicals deposited on the land finds its way to the water. Three of the processes affecting the fate of airborne contaminants deposited on land are discussed below: surface water transport, groundwater transport, and fugitive dust.

Surface Water Transport:

Both bottom sediments and suspended matter in rivers contain significantly more trace metals than are found in the dissolved phase (Horowitz, 1984). Equilibrium between metals in solution and in the sorbed phase is attained on the order of seconds to minutes for most metals. Binding of metals to the sediment is a consequence of sediment surface chemistry reactions. In general, highest metals concentrations are associated with fine sediments having a large surface area to

Figure 1-1. Formation and Deposition of Fine and Coarse Particles (courtesy of R. Stevens)
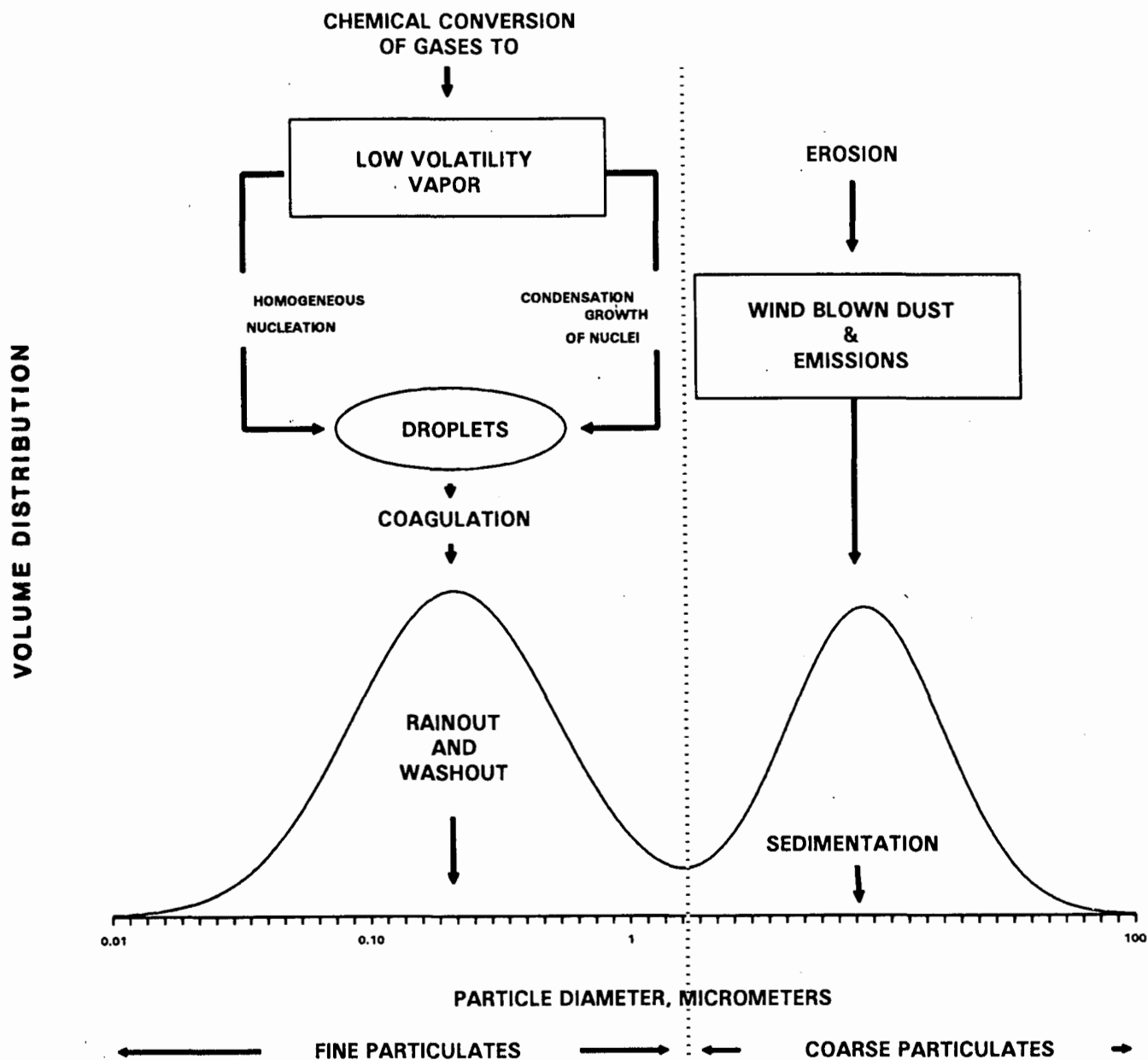
CHEMICAL CONVERSION
OF GASES TO

LOW VOLATILITY
VAPOR

HOMOGENEOUS
NUCLEATION

CONDENSATION
GROWTH
OF NUCLEI

EROSION

WIND BLOWN DUST
&
EMISSIONS

DROPLETS

COAGULATION

RAINOUT
AND
WASHOUT

SEDIMENTATION

VOLUME DISTRIBUTION

0.01   0.10   1   100

PARTICLE DIAMETER, MICROMETERS

FINE PARTICULATES   COARSE PARTICULATES

5

volume ratio. Metals in surface water runoff, like metals in rivers, are largely transported while they are sorbed to suspended and bed sediments.

PAHs also generally tend to sorb to particulate matter in the aquatic environment. Because of their low aqueous solubilities, sorption of PAHs in natural waters occurs rapidly (Neff, 1979); however sorptive equilibrium takes longer to attain for PAHs than for metals, and may not be attained with overlying waters before transport occurs in rivers and streams.

The partitioning of metals and PAHs between the particulate and dissolved phase in surface waters can have a large effect on their transport. In urban areas fine sediment particles can be readily transported by the flow regimes normally encountered in drainage and sewer pipes. In rural areas or developing areas, significant removal of sediment-bound contaminants can occur through a combination of settling and filtration of particulates from overland flow and shallow, concentrated flow, especially if the ground cover consists of fine-leaved vegetation.

Photolysis (chemical breakdown in the presence of light) can significantly reduce the levels of PAHs present on dry watershed surfaces and at shallow depths in surface waters. Environmental factors influence the rate of photolysis, and photolysis rates also vary among PAHs. Biodegradation (breakdown by biological activity) could also significantly degrade PAHs if the period between washoff events is on the order of several days. Many of the processes that act to degrade PAHs can produce intermediate compounds and end products that may be more harmful than the parent PAH compounds.

Groundwater Transport:

PAH concentrations in groundwater are about one-tenth the concentrations found in most rivers in the United States (Neff, 1979), due to both the increased time of contact between PAHs and sediments and biodegradation. Groundwater flow velocities are much lower than those associated with either riverine or overland flow, allowing more time for PAHs to reach equilibrium with the bulk water. In addition, in the case of groundwater, sediment sorption sites are generally not limiting.

In situ biodegradation of toxic organic compounds by soil bacteria and fungi is well documented. Under proper conditions of moisture, pH, temperature, and nutrients, significant degradation of a variety of organic compounds, including PAHs, has been demonstrated. Except for biodegradation, all of the processes listed above, which act to reduce concentrations of PAHs in groundwater, also act to reduce the concentrations of metals in groundwater relative to surface water.

Fugitive Dust Transport:

Airborne particles that settle on land, become available for the fugitive dust load in the watershed. Some of these particles may agglomerate, forming coarse particles which require higher wind speeds for resuspension. Lead, zinc, chromium, copper, nickel, arsenic, cadmium, and beryllium have been detected in street dust samples from both residential and commercial areas (Cooper et al., 1985).

PAHs associated with regional (area-wide) aerosols differ in their sources and their dominant chemistry from PAHs associated with street dust. PAHs associated with regional aerosols tend to be associated with very small soot particles, less than or equal to 1 μm in diameter (Neff, 1979; Pederson et al., 1980, Thomas et al., 1968), and therefore can travel hundreds or even thousands of miles before they are deposited. Some of the fugitive dust particles in which PAHs are found are several orders of magnitude larger than the fine airborne particulate matter

and therefore tend to be transported to areas relatively close to the point where they last resided. Regional aerosol PAHs are largely composed of combustion-derived PAHs, while PAHs associated with street dust are largely composed of higher molecular weight compounds thought to originate from uncombusted petroleum leaked from automobiles (Galvin and Moore, 1984).

Local wind gusts repeatedly suspend and redistribute fugitive dust until the dust particles reach some short- or long-term resting place, such as incorporation into larger, relatively immobile particles or deposition onto the surface of a nearby body of water. PAHs may be volatilized or degraded during this local, wind-blown transport.

Chapter 2. Study Plan

The following discussion presents the overall plan for the atmospheric deposition study and a brief summary of the sampling and analytical scheme for each study component. Chapters 3 - 7 provide details on the methodology and results for the discrete study components.

STUDY OBJECTIVES

▶ Develop a better understanding of the importance of atmospheric deposition relative to other inputs of toxic contaminants to Commencement Bay.

▶ Develop efficient and cost-effective tools for assessing this question in other reaches and embayments of Puget Sound, and other water bodies as well.

Atmospheric deposition of concern in this study includes both direct and indirect (deposition on land and subsequent runoff) inputs to Puget Sound. Both point sources (industrial emissions) and area or regional sources (woodstoves, cars, etc.) are included.

STUDY AREA SELECTION

To make the multi-component study tractable, a single site was selected for intensive investigation. The Technical Work Team evaluated a matrix of information pertaining to eight embayments in Puget Sound and selected Commencement Bay near Tacoma, Washington (Figure 2-1), as the most appropriate study area for the following reasons:

▶ Commencement Bay and its watershed is one of the most studied embayments in Puget Sound. Therefore, databases exist for this embayment for ambient air quality, air emissions, municipal/industrial discharges, wind speeds and directions, and marine sediment quality.

▶ The matrix of air pollution sources is complex and diverse, including both large industrial point sources and pervasive area sources, such as cars and woodstoves.

▶ Both lead and combustion-derived PAHs have been measured at high concentrations in the sediments and the sea-surface microlayer in this embayment.

▶ Commencement Bay is a Superfund site with numerous environmental problems and elevated chemical levels on land and in bottom sediment.

Commencement Bay therefore represents a "worst case" test area for determining if cross-media (air to water) transfer of toxic contaminants is significant.

TARGET CHEMICALS

The study design was optimized for sampling and analysis of metals (e.g. lead, zinc, arsenic, manganese), and combustion PAHs (three- to five-ring compounds). Low molecular weight PAHs, PCBs, aliphatic hydrocarbons, and nutrients were also sampled and analyzed. Metals and combustion PAHs were targeted because:

▶ Lead, some other metals, and combustion-derived PAHs originate from both large individual sources, such as industrial and commercial emissions, and pervasive sources, such as cars and woodstoves.

Figure 2-1. Commencement Bay in Puget Sound, Washington
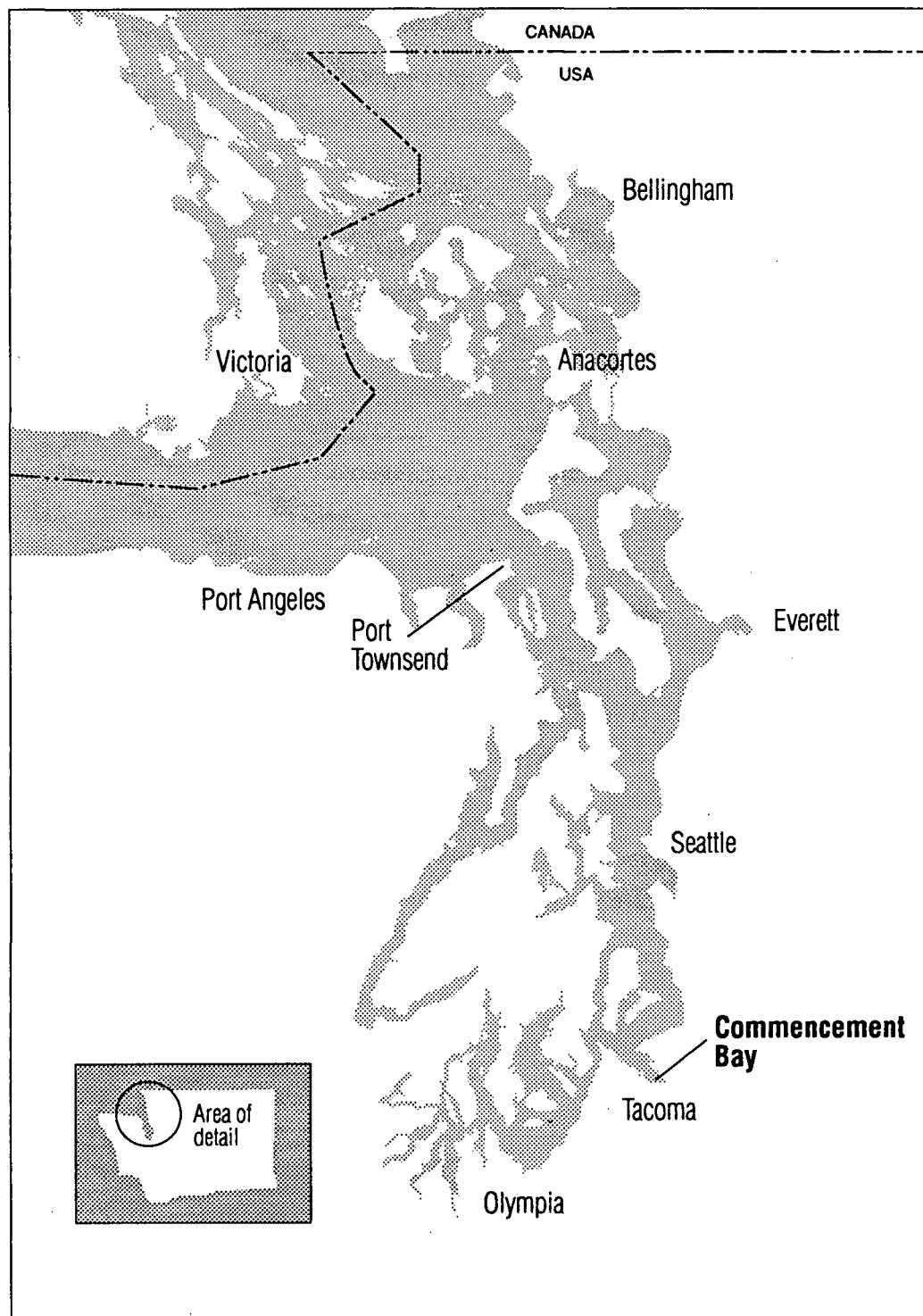
▶ Based on previous studies, atmospheric sources have been estimated to contribute significant amounts of these chemicals to Puget Sound and elsewhere.

▶ Metals and PAHs have been shown to be toxic to marine ecosystems and human health.

▶ Both lead and combustion-derived PAHs have been measured at high concentrations in the sediments and sea-surface microlayer in Puget Sound.

STUDY COMPONENTS

The study consisted of four field components:

▶ Six-month meteorological data acquisition;
▶ Six-month aerosol and deposition sampling;
▶ 18-day field sampling for the receptor modeling; and
▶ Source testing of Simpson Tacoma Kraft pulp mill.

Two modeling efforts complemented the field studies and provided the tools for interpreting and extrapolating from the field study results:

▶ Receptor modeling; and
▶ Diffusion/transport modeling (which also included a mobilization coefficient model).

In addition an emission inventory was prepared compiling previous direct measurements and estimates for both point sources and area sources.

The field sampling network was established in the early summer of 1989 and data were collected from July 1989 through early January 1990. The 18-day study was performed in December 1989 and January 1990. The source test was also performed during January 1990. The intent in selecting this six-month period was to encompass a range of meteorological conditions (precipitation, temperature, winds) and emission scenarios such that results could be used to characterize and extrapolate to other unsampled portions of the year.

Each study component focused on a specific particle size fraction or aspect of atmospheric deposition. These distinctions will be explained below and will again be highlighted in Chapter 8, which compares and integrates the results from all the studies.

The scientists responsible for conducting each study component are listed at the front of this report.

Sampling Network

Figure 2-2 presents the network of sampling sites that was set up in the Tacoma Tideflats. The grid of stations included one transect across the industrial waterfront, roughly southwest to northeast [Morse Industrial Supply (MS), Sea-Land Service, Inc. (SL), and Alexander Avenue (AS)]; and another transect along the path of the prevailing wind through the area (southeast to northwest), starting upwind of the industrial area in the Puyallup River and extending to a site on the Puget Sound shoreline well downwind of the industrial area [Riverside School (RS), Tyee Marina (TM), Brown's Point (BP)]. The far upwind and downwind sites (RS and BP) were selected to provide an indication of background contaminant levels, while the industrialized sites were chosen to represent contaminant levels within a heavily industrialized area.

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FIGURE 2-2

AEROSOL and DEPOSITION
SAMPLING SITES

Tacoma, Washington

SAMPLING SITES

- (BP) Brown's Point
- (TM) Tyee Marina
- (MS) Morse Industrial Supply

- (SL) Sea-Land Services, Inc.
- (AS) Alexander Site
- (RS) Riverside School

OTHER FEATURES

- [FS] Fire Station No. 12

MAJOR INDUSTRIAL SOURCE AREAS

- ■ Kaiser Aluminum & Chemical Corp.
- ■ Simpson Tacoma Kraft Company

LINE FEATURES

- Major Roads
- Other Roads
- Shorelines
- Streams

Brown's Point

Marine View Drive

Commencement Bay

Tacoma

Pacific Ave.

Tideflats
Industrial
Area

Pacific Highway

Taylor Way

I-5

I-5

Puyallup River

| 0 | 1 | 2 | 3 |

Miles
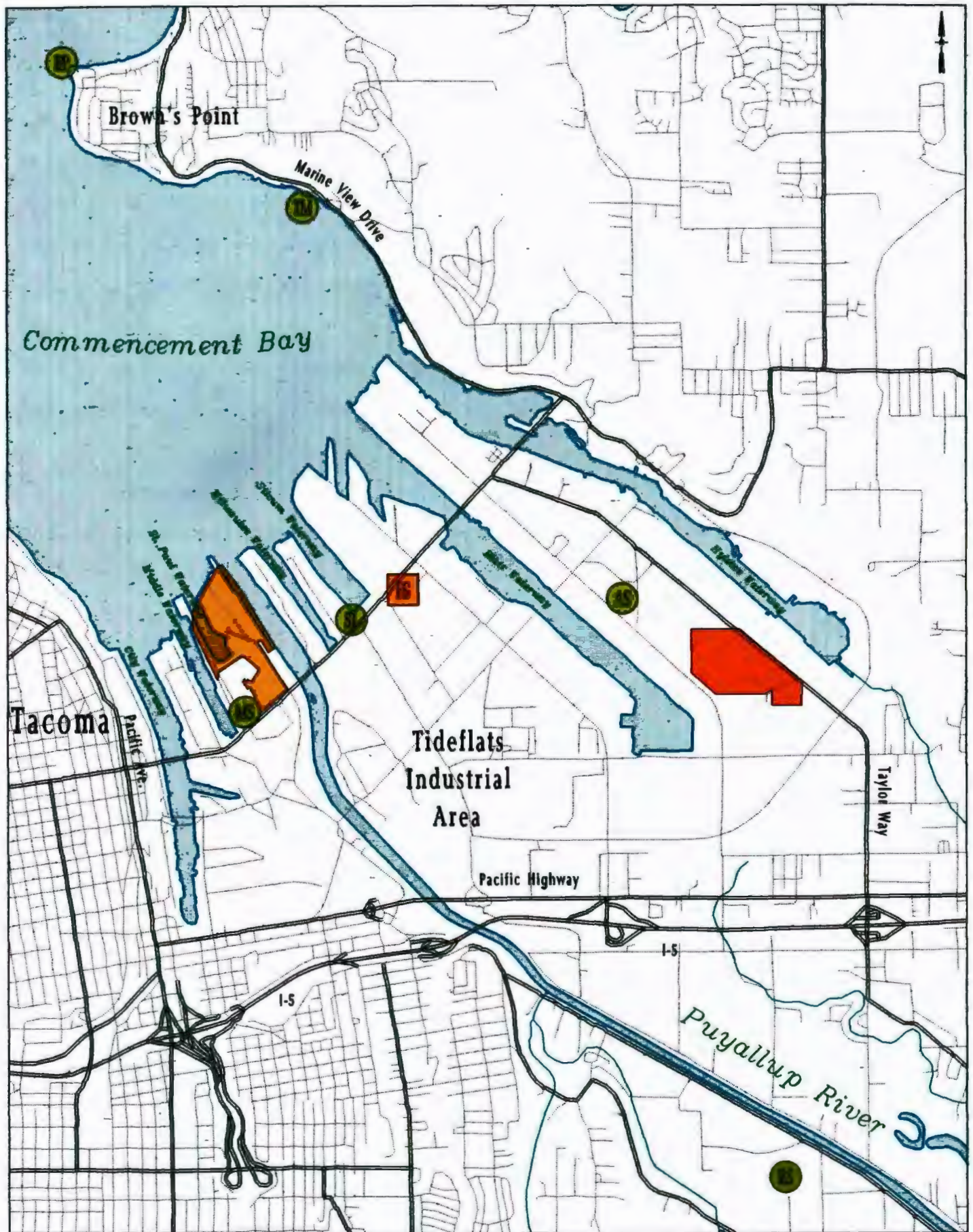
To evaluate deposition to Commencement Bay, stations were located either near or over the water. The sampling instruments at the Morse Industrial Supply, Sea-Land, Alexander Avenue, and Riverside School were located on buildings. The Brown's Point instrument was located on the ground floor of a lighthouse, and the Tyee Marina sampling site was located on top of a grounded barge that is used by the marina for a breakwater. The height of the samplers off the ground or water surface is presented in Table 2-1.

Table 2-1. Height of Samplers Above Surface

Sampling Site	Height Above Surface (feet)
Brown's Point	3
Tyee Marina	12
Morse Industrial Supply	20
Sea-Land	30
Alexander Avenue	10
Riverside School	12

To acquire representative samples of ambient air in the Tideflats area, stations were located at least several blocks away from major point sources such as pulp mills, aluminum refineries, and oil refineries. Figure 2-3 shows some of the industrial sites with air toxic emissions in the Tacoma Tideflats. The map only includes those industrial sources required to report under Section 313 of the Emergency Planning and Community Right-to-Know Act (EPCRA) of 1986. (Reporting is required if the source manufactures, imports, processes, or uses certain toxic chemicals in amounts greater than a specified threshold quantity. Fugitive emissions are not included in the emissions indicated on the map.)

Two PSAPCA monitoring stations are located within the region of this sampling network: Fire Station #12, which samples PM_{10}, TSP, $PM_{2.5}$, $PM_{1.0}$ (nephelometer), and wind speed and direction; and the Alexander Avenue site, where PM_{10} and wind speed and direction are measured. Samples from these stations were used during the study for comparative data checks and to provide a context for comparing conditions-encountered during the study period against those occurring in other seasons and years.

Meteorological Data Collection

An integral part of the overall monitoring program was the collection of meteorological data in the Tideflats during the entire six-month study period. Wind speed and direction, precipitation, temperature, and solar radiation data were collected for input to the diffusion/transport model and to provide information on the ambient environment for interpretation of the other field study results. A meteorological tower was located atop the one-story PSAPCA monitoring trailer at the Alexander Avenue site.

The meteorological measurements were recorded over two different averaging times. Five-minute averages were recorded for wind speed, standard deviation of wind speed, wind direction, standard deviation of wind direction, and precipitation. Hourly averages included temperature at two meters above the ground, temperature difference (the temperature at ten meters minus the temperature at two meters), and solar radiation.

Figure 2-3. TACOMA TIDEFLATS
Stack Air Emissions
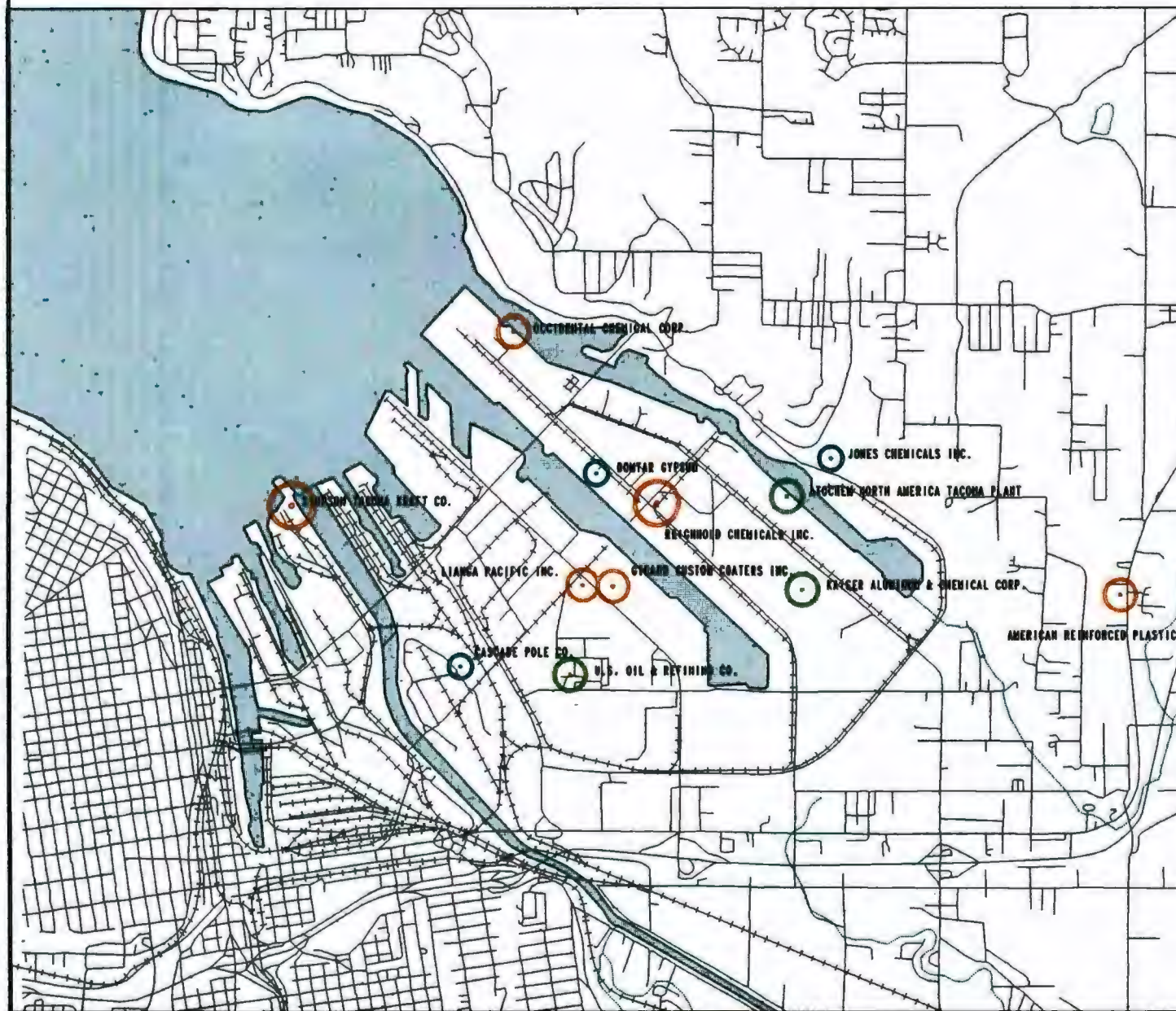
Toxics Release Inventory

Data submitted to EPA by facilities regulated under the Emergency Planning & Community Right-to-Know Act

Pounds Released in 1989

⊙	1 - 1000
⊙	1,001 - 10,000
⊙	10,001 - 100,000
⊙	100,001 - 1,000,000

DRAFT:
facility locations approximate

OCCIDENTAL CHEMICAL CORP.

JONES CHEMICALS INC.

DOMTAR GYPSUM

ATOCHEM NORTH AMERICA TACOMA PLANT

SIMPSON TACOMA KRAFT CO.

REICHHOLD CHEMICALS INC.

LIANGA PACIFIC INC.

CYGARD CUSTOM COATERS INC.

KAISER ALUMINUM & CHEMICAL CORP.

AMERICAN REINFORCED PLASTICS

CASCADE POLE CO.

U.S. OIL & REFINING CO.

Scale 1 : 51150
0 200 400 600 800 1000

Meters

EPA
EPA Region 10 — Seattle
Geographic Information Section

Six-Month Aerosol and Deposition Sampling

The objective of this study was to conduct long-term (six-month) measurements of the ambient aerosol and the deposition of atmospheric contaminants to sites adjacent to Commencement Bay. Aerosol sampling was conducted at all six of the sampling network sites, although not all sites were sampled during each time period. Deposition sampling was conducted at five of the sites (Brown's Point, the background aerosol site, was not used for deposition).

Aerosol sampling collected vapor and particles up to a maximum diameter of approximately 50 μm. Deposition sampling had no upper size limit.

Sampling intervals and frequencies were determined as a function of the following factors: the number of chemical analyses that could be run within the project budget, the minimum required temporal resolution of the data, and the chemical detection limits of the analyses. The sampling schemes were as follows:

▶ Deposition sampling--samples collected every two weeks at each of the five sites during the entire six-month study period.

▶ Intensive aerosol sampling--samples collected twice per week (three- and four-day samples), at five deposition sites (Brown's Point not included) during two sampling periods: July 20 to August 24, 1989 -- primarily dry weather; and November 16 to December 21, 1989 -- primarily wet weather.

▶ Nonintensive aerosol sampling--samples collected twice per week, at two primary sites (Alexander Avenue in the industrial area and Tyee Marina, downwind of the industrial area) and Brown's Point during the remainder of the six-month study period.

The aerosol sampling was timed so that it ran in parallel with the deposition sampling.

All of the aerosol sample filters collected were weighed to determine total mass. Due to budget constraints it was necessary to limit the number of samples that were chemically analyzed. The samples selected were analyzed for metals and particulate PAHs. In addition, ten of the aerosol samples were analyzed for both vapor and particulate PAHs, PCBs, and aliphatic compounds. Selected deposition samples were analyzed for metals, particulate PAHs, and nutrients. Ten of the deposition samples were also analyzed for PCBs and aliphatic compounds.

Field Study for Receptor Modeling

This study was comprised of short-term aerosol sampling focused explicitly on the PM_{10} fraction in the ambient air. These data were needed as input to the receptor modeling. Separate samples were obtained of two size fractions of particles: fine (less than 2.5 μm) and coarse (2.5 - 10 μm). To allow comparisons between the six-month aerosol and deposition monitoring and the receptor modeling, two of the six-month sites were selected as the sites for acquiring ambient receptor modeling data. One site was set up at Morse Industrial Supply; the second receptor model sampling site was located at Alexander Avenue. Two dichotomous samplers (capable of the size-fractionation noted above) were located at each site. In addition, a single volatile organic compound (VOC) canister sampling unit was located at each site.

Concurrent ambient air sampling for PM_{10} particles and volatile organic compounds was conducted for 18 days, split into two sampling periods: 7 a.m., December 5, 1989 to 7 a.m., December 16 1989; and 7 a.m., January 2, 1990 to 7 a.m., January 9, 1990. Twelve-hour sampling was conducted for daytime (7 a.m. to 7 p.m.) and nighttime (7 p.m. to 7 a.m.)

periods. During the December sampling period, the Simpson Tacoma Kraft plant was not fully operating due to routine maintenance as well as unscheduled downtime. Because of Simpson's schedule, there was no ambient sampling for the receptor modeling study for the period from December 16, 1989, to January 1, 1990.

All samples were analyzed for total mass, trace metals and other elements (silicon, sulfur, bromine, chlorine, calcium, potassium). The fine fraction (<2.5 μm) was selected for further chemical analysis (organic carbon, elemental carbon) and was the focus of the receptor modeling, because it constitutes those particles that are transported most broadly in the atmosphere (thereby allowing for area-wide modeling) and because it is made up primarily of combustion products from anthropogenic activities.

Emission Inventory

To provide input data for the diffusion/transport and receptor modeling, a detailed emission inventory was compiled for the Tideflats area. Information was acquired from PSAPCA's registration files for point sources, the source profile library, and relevant source tests. Emission data for the metals and PAHs of interest for this study were acquired for point sources (industrial emissions) and area sources (mobile sources such as cars, trucks, ships; woodstoves; and road dust).

Source Test of Simpson Tacoma Kraft Pulp Mill

The Simpson Tacoma Kraft pulp mill is the major point source of particles less than 10 μm in diameter (PM_{10}) in the Tideflats. Prior to this study, source-specific data on the emissions of metals and PAHs were not available. In order to gather this data, a source test was performed on the Simpson facility.

Particulate samples were collected from the hogged fuel boiler, one of the lime kilns and the No. 3 recovery furnace. Each source test included three separate runs. Testing was accomplished between January 2, 1990, and January 6, 1990. Laboratory analyses were conducted on the samples to determine the relative concentrations of metals and PAHs.

Receptor Modeling

Receptor or chemical mass balance (CMB) modeling was used to relate the ambient sample data to the potential point and area emission sources. CMB modeling is a mathematical method that attempts to match patterns of chemicals released from sources with ambient patterns collected on filters or in canisters (presumably representing multiple sources) at the receptor site. The mathematical model apportions the total amount of chemicals that are collected to the various sources. Unless source-specific information (such as a unique tracer) is available, the CMB can only distinguish source types, not individual culpable sources. This type of model does not address spatial variations unless performed at a number of sites. One of the advantages of the model, however, is that it does not require meteorological or stack parameter data (e.g. height, diameter, and emission velocity and temperature).

In order to use this type of model, the sources that may be identified as contributors must be known and chemically characterized (i.e., the chemical pattern or "fingerprint" of each source must be known). Data from the Simpson Tacoma source test, from emission studies conducted in other regions on area sources, and from the 18-day ambient study were analyzed. Because carbon was not analyzed in the coarse particles collected by the 18-day study, the fine fraction was the focus of the receptor modeling. The model was run using three alternative tracers for vehicle exhaust, and the fine mass was apportioned to the source contributors.

Diffusion/Transport Modeling

Diffusion/transport modeling was used in this study as a means of estimating the aerosol and deposition concentrations in 91.5 km^2 of the Tideflats area, based on the known emissions and the ambient meteorological conditions. The modeling focused on the PM_{10} size fraction of the atmospheric particles, because this was the only size fraction for which there was a detailed emissions inventory. Existing modeling capability was enhanced in order to develop a useful set of tools with which to estimate the contribution of atmospheric sources of contaminants to Commencement Bay. The model developed for this study used the emission inventory, stack parameters, and meteorological data gathered in the field study to produce maps of aerosol concentrations.

Additional data were needed to estimate the deposition of contaminants from the aerosol. The amount of deposition was based on estimates of the rates of transfer for each contaminant from air to land and from air to water determined from the literature and other field studies. These rates were added to the model in order to estimate the amount deposited.

It was also necessary to estimate the fraction of each air toxic deposited on the land which would eventually find its way to the Sound. To do this, theoretical mobilization coefficients were developed to represent the fraction of land-deposited pollutants that would be carried by surface water runoff, by groundwater, or through a series of pipes into the waterway.

Chapter 3. Meteorological Study

METEOROLOGICAL DATA COLLECTION PROGRAM

The purpose of this study was to obtain a high-quality, representative, and complete meteorological data base to aid in interpreting and understanding the air quality and deposition monitoring results. Meteorological data is required for operation of the diffusion/transport model and is also critical to interpretation of the receptor modeling results.

Monitoring Site

The meteorological sensors were located at a single monitoring station set up at the Alexander Avenue site atop the one-story PSAPCA monitoring trailer. The site is in a relatively open area of the Tideflats, between the Blair and Hylebos waterways. The bluff along the northeastern boundary of the Tideflats is a little more than one kilometer northeast of the site. The area in the immediate vicinity is free from significant meteorological influences so that the data collected are considered representative of the Tideflats area. The site is surrounded on three sides (west, south, and east) by open fields, mostly mixed dirt and gravel, with minimal low vegetation (grasses and weeds) cover. The Reichhold chemical plant is located to the north of the site. The area between the site and the Reichhold structures, is an asphalt-covered, truck-loading area.

Sensors

The wind measurements were made with a Wind Monitor-RE, Model 05701, manufactured by the R. M. Young Company of Traverse City, Michigan. This sensor is a low-threshold, fast-response, propeller-vane anemometer. Key specifications of this sensor include a speed threshold less than 0.2 meters per second (m/s), direction threshold less than 0.4 m/s, a damping ratio of 0.65, and a maximum delay constant of 1.0 meter. The wind sensor was mounted on top of a 10-meter tower.

Precipitation was measured by a Texas Electronics tipping bucket rain gauge, Model 525. Each bucket tip measures 0.01 inch of rainfall, with an accuracy of one percent at a rate of two inches of rainfall per hour or less. The rain gauge was mounted on a one-meter pole, which was mounted on top of the monitoring trailer. The gauge was located approximately five meters from the tower to avoid any potential influence from the trailer and the tower. The inlet height was 4.5 meters above the ground.

Solar radiation was measured by a Li-Cor silicon-photocell pyranometer, Model 200. Absolute error is nominally ± 3 percent. The sensor response is linear with a maximum deviation of one percent over the full range. The pyranometer was mounted to the tower on a specially designed mounting arm. The arm extended approximately one meter from the tower in a southerly direction in order to avoid any shadow influences. The sensor was about 4.75 meters above the ground.

Temperatures were measured at two and 10 meters above the ground with Campbell Scientific Model 107 thermistor probes. The sensors' nominal accuracy is $\pm 0.2°C$ from -30 to +45°C. The probes were mounted in the radiation shields attached to the tower. The specific purpose of the temperature measurements was to obtain measurements of temperature difference (ΔT)

in the lower atmosphere. However, it was discovered that this was not an optimum sensor arrangement for accurate measurements of ΔT, because the sensors were not electronically matched to a common temperature reference (as is typically done for ΔT measurements). Therefore, the system was unable to achieve the required ΔT accuracy of 0.1°C. Data quality is considered further below.

All meteorological sensors were attached to a Campbell Scientific Model CR10 datalogger. The datalogger was housed in a weatherproof shelter mounted to the tower. The datalogger interrogated each sensor once per second, and converted the signals to appropriate units. Further, the datalogger calculated averages over five minutes or one hour, as appropriate, and archived the results in its internal memory. The data were summarized into hourly averages and are listed in Appendix B-1.

Operation

New instruments were obtained for this meteorological data collection program. All sensors were checked for proper operation. The temperature probes were calibrated together in an ice bath for a one-point calibration. Installation was completed and monitoring began on July 6, 1989.

After startup of the meteorological instruments, the site was visited weekly to verify the good condition and proper operation of the instrumentation and to download the data from the internal datalogger memory to a portable computer. The data were then transported back to the office where they were permanently archived.

Monitoring was continuous until approximately 10:00 AM PST on January 9, 1990, when the meteorological instrumentation was dismantled. Data recovery rates for the program were greater than 99 percent. A few hours of data were invalidated due to performance checks on the instruments; the invalid data were replaced by a value of -999.

Data Quality

A number of instrument checks were performed during the monitoring program to assess the adequacy of system performance. The variables that were assessed during the data quality checks are discussed below.

Wind

Within 10 days of program startup, the wind direction orientation was checked and found to be in error by 11°. At installation, the orientation of the wind direction sensor was aligned using a compass. Subsequent checks of orientation with a compass confirmed that the compass was subject to magnetic interference. Thus, the sensor had been misaligned, and the wind direction data were subject to a systematic 11° error. The sensor was realigned to correct the error. Two weeks later, the wind direction orientation was rechecked by an independent auditor using a solar azimuth method. The orientation was found to be correct within 1° -- well within the system accuracy specification of ±5°. Based on the results of these checks, the wind direction data for the first week of the program were corrected for the error by adding 11° to each value. The wind direction orientation was checked again at the end of the program and found to be within specification. Wind speed zero checks were also performed when the wind direction checks were performed. Wind speed and direction thresholds were checked halfway into the study, and again at the end of the program, and were found to be within manufacturer's specifications.

Precipitation

The performance of the rain gauge was checked at the beginning and at the end of the program by introducing the equivalent of 0.50 inches of rain into the gauge. The performance check showed the gauge was low by four percent, but still within the system accuracy guideline of ± 10 percent.

Solar Radiation

The pyranometer was calibrated by the manufacturer just before the program began. Normally, pyranometers only require annual calibration, so no further calibrations were performed. The only checks on the performance of the pyranometer were zero checks, which were done frequently throughout the program. In addition, the sensor surface was cleaned regularly during the weekly site visits.

Temperature

As mentioned above, the instrumentation employed to measure ΔT was incapable of achieving the required accuracy. This was determined at the completion of the project after a two-point calibration was performed, and the results were discussed with the manufacturer. Based on the last two-point calibration, a linear correction to the lower temperature sensor is possible (with all temperatures in °C):

T (corrected) = T (uncorrected) - (0.16/13.0) • T (uncorrected).

Even with this correction, however, the ΔT measurements are not considered accurate to within ± 0.1°C because the thermistor probes were not matched to a common temperature reference, and the accuracy of the individual sensors was ± 0.2°C.

Another problem was encountered with the temperature measurements during the program. The instantaneous readings from the upper sensor were observed to fluctuate within a range of about 0.0 - +0.5°C. The problem was never solved, even after considerable troubleshooting efforts, including replacement of the top thermistor probe. The effect of this fluctuation is to bias the upper (10 m) temperature measurements on the high side by approximately 0.1°C. As a result of the above problems, and even though the values appear reasonable, the ΔT measurements must be considered outside the range of accuracy desired for this program.

Results

A listing of the hourly meteorological data is presented in Appendix B-1. A summary of daily wind, solar insolation, and precipitation data is found in Appendix B-2.

In addition, Appendix E-5 contains 12-hour averages of meteorological data for the December 5 to 15 and January 2 to 8 sampling intervals (to coincide with the 18-day PM_{10} ambient monitoring study). How conditions during the study period compare with previous years is addressed in Chapter 8, Comparison of Studies.

Of particular interest for interpreting monitoring and modeling results, is a characterization of the study period in terms of air stagnation episodes. To do this analysis both surface and upper air meteorological data are required. Data collected at Quillayute, Washington, were used, as this is the closest upper air station to the Puget Sound area which would be representative of Puget Sound conditions. The methodology used to categorize air stagnation

episodes was based on a method developed by Holzworth (1972) and modified by Region 10 EPA to incorporate a method for computing mixing heights in marine climates.

Holzworth's method categorizes air stagnation episodes in terms of urban air pollution potential. The more severe the episode, the more potential for urban air pollution. Holzworth's model uses three meteorological parameters to predict the severity of stagnation events:

▶ Mixing height (depth of layer through which pollutants can mix);
▶ Average wind speed in mixing layer (sometimes called ventilation); and
▶ Precipitation (any precipitation event automatically terminates an episode).

Higher pollution potential exists when mixing depths are low and wind speeds are light. Holzworth's method uses eight categories, with level one being the most severe. (Region 10's modification added two additional levels, nine and ten.)

Appendix B-3 includes tables showing level 1, 2, and 3 air stagnation episodes during the entire study period. Appendix B-4 contains the meteorological data for the analysis, including actual mixing depths, wind speeds, and precipitation events. Figures 3-1 (a) and (b) display the results of the analysis for the November 1989 through January 1990 portion of the study period, when there was the greatest potential for air stagnation episodes. Two points (a.m.: midnight-noon; p.m.: noon-midnight) are plotted for each date. If the air stagnation level was constant over that day, only one point was plotted.

The only episode of category 1 was of 48 hours duration and occurred from the afternoon of December 25, 1989, through the morning of December 27, 1989. The most severe episode in terms of duration was a category two of 180 hours length which occurred from the afternoon of December 11, 1989 until the morning of December 19, 1989. At category three this episode began 12 hours earlier, with a total length of 192 hours. The only episode in the summer was a category two of 36 hours length, from the morning of July 26, 1989, through the morning of July 27, 1989.

Figure 3-1(a). Air Stagnation Episodes (November - December)

SOLID LINES REPRESENT STAGNATION SEVERITY
1 (MOST SEVERE) THROUGH 10 (LEAST SEVERE)
FIGURE ONE

Figure 3-1(b). Air Stagnation Episodes (December - January)

SOLID LINES REPRESENT STAGNATION SEVERITY
1 (MOST SEVERE) THROUGH 10 (LEAST SEVERE)
FIGURE TWO

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Chapter 4. Six-Month Aerosol and Deposition Study

OBJECTIVES

▶ Establish a network of stations with co-located samplers for monitoring ambient aerosol and the deposition of atmospheric contaminants;

▶ Monitor continuously for six months (July 1989 to January 1990); and

▶ Analyze samples for total mass and specific chemical constituents (metals, PAHs, PCBs, aliphatic hydrocarbons, and nutrients).

SAMPLING NETWORK

Chapter 2 contains a description of the six sites established for aerosol sampling--Morse Industrial Supply (MS), Sea-Land Service, Inc. (SL), Alexander Avenue (AS), Riverside School (RS), Tyee Marina (TM), and Brown's Point (BP)--and a map illustrating station placement (Figure 2-2.). Aerosol sampling was split into two five-week intensive periods (July 20 to August 24, 1989--primarily dry weather; and November 16 to December 21--primarily wet weather) when all stations except Brown's Point were sampled; and a non-intensive sampling scheme for the remainder of the six months when samples were only collected at Alexander Avenue, Tyee Marina, and Brown's Point (background reference station). Aerosol samples were collected twice per week (one three-day and one four-day sample). Deposition samples were collected every two weeks at all of the above sites except Brown's Point (Table 4-1).

Table 4-1. Aerosol and Deposition Sampling Plan

Sample Type	Sampling Frequency	Locations	Length of Study
Aerosol (intensive study)	2 per week	AS, MS, SL, TM, RS	10 weeks
Aerosol (non-intensive)	2 per week	AS, TM, BP	16 weeks
Deposition	2 per month	AS, MS, SL TM, RS, + one duplicate	6 1/2 months

EXPERIMENTAL METHODS

Aerosol Sampling

Aerosol samples were collected with General Metal Works Model PS-1 aerosol samplers (Figure 4-1). The upper size limit of particles captured by the PS-1 sampler is 25 to 50 μm, depending on the wind speed. The samplers were equipped with 102 mm-diameter quartz (high purity) filters and backed up with 6 cm-diameter, 8 cm-long polyurethane foam plugs (PUFs) for collection of organic vapor. The quartz filters were used because they work well for particulates and organics and are resistant to clogging.

Figure 4-1. PS-1 Aerosol Sampler
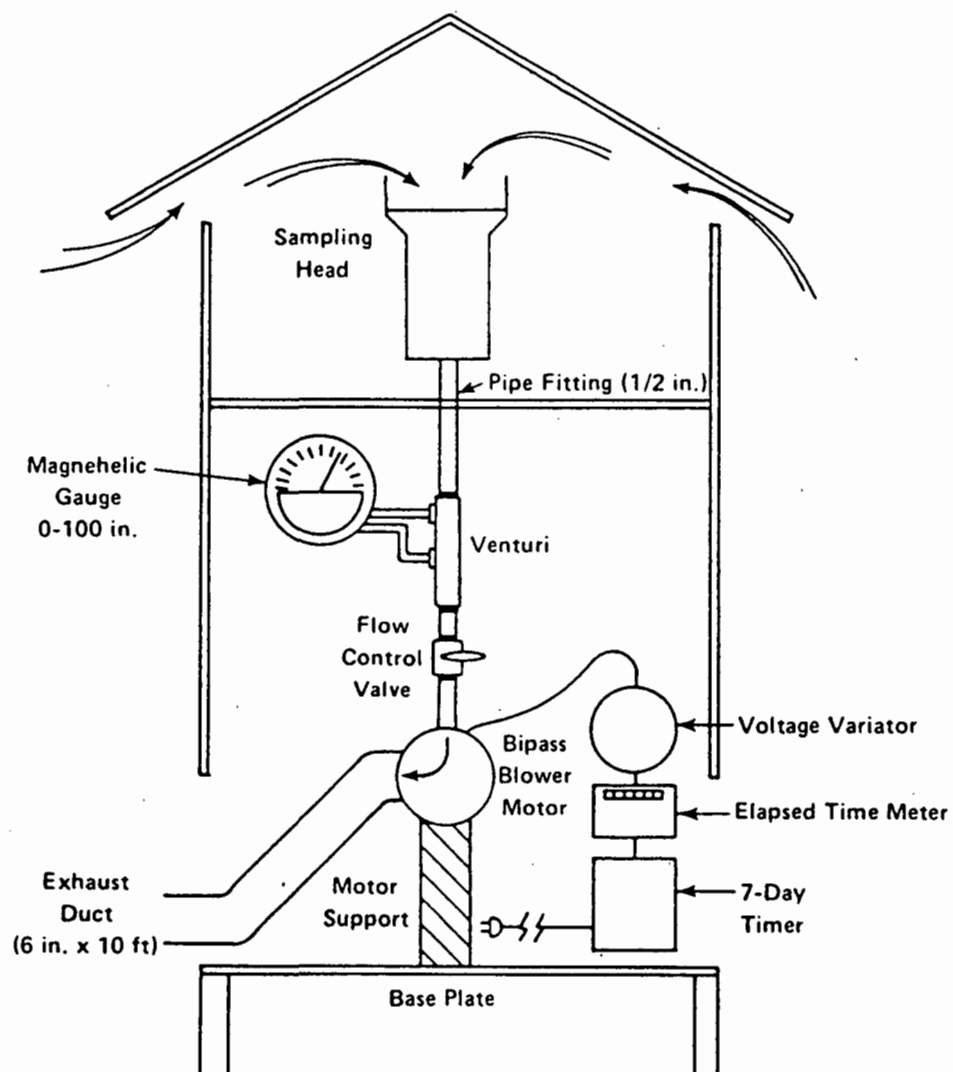
Air was drawn through the sampler at about 0.25 m^3 per minute and the sampling period was three or four days (twice weekly). The sampling period and flow rate were chosen to provide adequate sample for quantitative chemical analyses without overloading the air pump or the filters. (During periods of air stagnation alerts, filters were changed daily to avoid plugging.) This sampling frequency minimized the number of samples to be collected over the six-month continuous sampling period. PS-1 samplers were operated following standard operating procedures prescribed by EPA Region 10.

The PUFs and filters were cleaned before use following methods taken from the U.S. EPA (1988) *Compendium Method TO-13*. All PUFs were cleaned with solvent (pesticide grade acetone) in a Soxhlet extractor. Filters were cleaned in methylene chloride, dried, and ashed. An amplified discussion of these procedures is presented in Appendix C-1.

Filters were conditioned and weighed before field use following procedures in the EPA guidance document for PM$_{10}$ (U.S. EPA, 1987a). Clean filters were conditioned for 24 hours at 20° during the summer and in a desiccator at 4°C in the fall, then weighed within 30 seconds after removal from the desiccator. In the field, filters and PUFs were handled only with clean nylon gloves and acid-cleaned, solvent-rinsed, Teflon-tipped forceps. Quartz filters and the PUFs collected from the field were stored individually in a low-temperature (-70°C) freezer until analyzed.

Deposition Sampling

A large water-filled Pyrex pan with a surface area of 0.12 m^2 was used as a deposition collector (Figure 4-2). The pan contained a 1-cm layer of high purity water, simulating the surface of Puget Sound. The water prevented dry deposited material from blowing out of the pan during dry windy weather. A reservoir of water was used to maintain a constant level of water in the pan in dry weather and an overflow drain and reservoir collected the excess water in wet weather. The contents in the deposition pan were transferred biweekly to the deposition reservoir container and taken to the laboratory for storage in a refrigerator. Deposition samples were acidified to a pH of less than two with hydrochloric acid and held at 4°C in the dark until analyzed. All deposition sampling equipment was made of glass or Teflon. See Appendix C-1 for cleaning and handling procedures.

Each pan was located on a 60 cm high table to reduce the input of resuspended dust and soil. Vertical glass rods surrounded the pan to keep birds off and eliminate contamination from bird droppings. The overflow reservoir was located under the table. The table was located near the aerosol sampler, but protected from possible contamination from the aerosol sampling motor by a plastic hose that directed the exhaust away from the deposition collector. Materials such as feathers, leaves, and large bugs were removed with clean forceps.

Chemical Analysis of Aerosol and Deposition Samples

The particulate load on filters was determined by accurately weighing the air filter before and after use. The filters were conditioned in a desiccator before weighing to prevent weighing errors due to humidity. During the fall and winter, filters were conditioned at 4°C instead of 20°C to reduce the loss of volatile hydrocarbons.

Filters were subsampled for metals and organic compounds after being cut into pie-shaped sections with a solvent-cleaned knife on a clean Teflon surface. These subsections were weighed so that the percentage of the particulate load on the subsection could be calculated.

Figure 4-2. Deposition Sampler
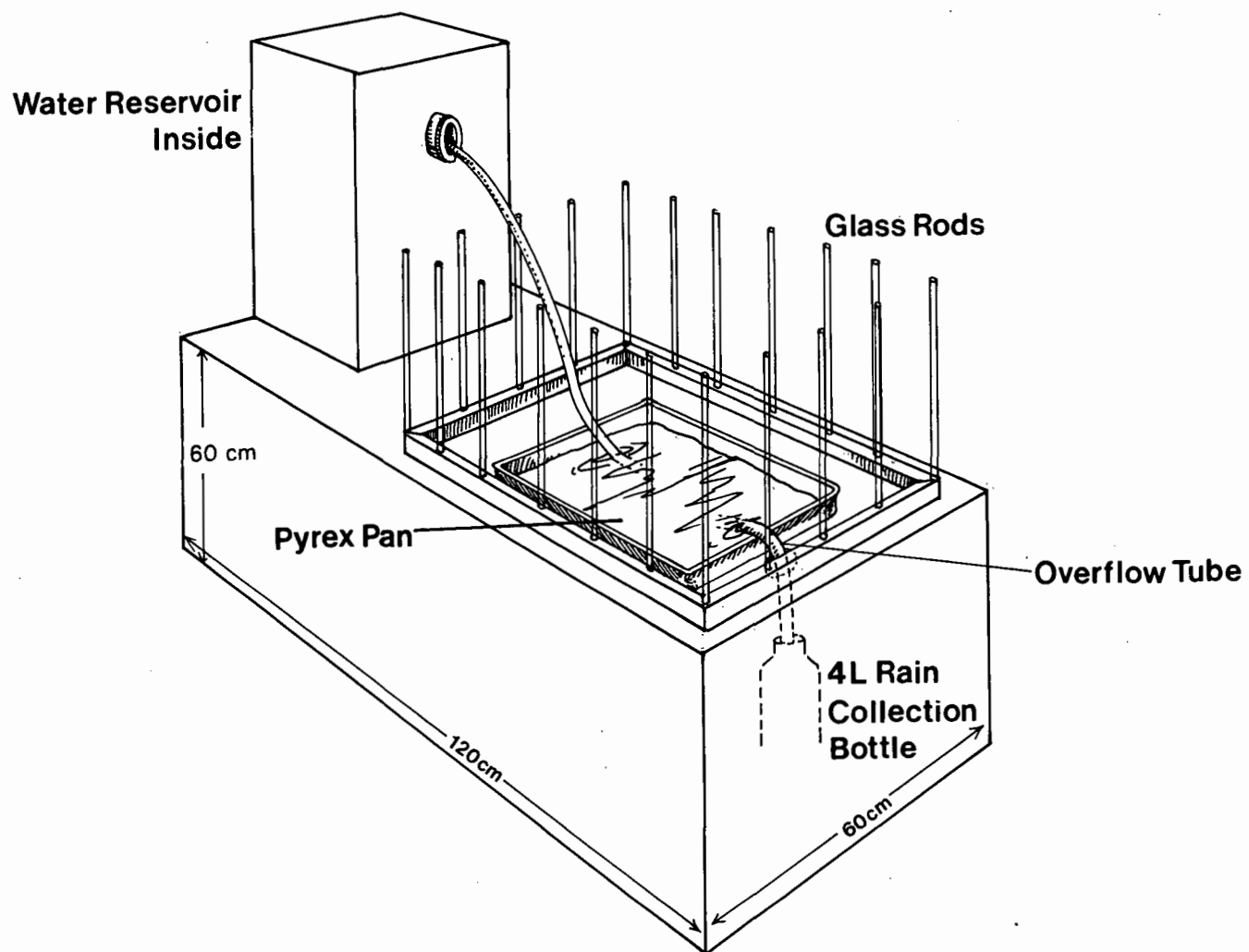
Extraction procedures and analytical methods used are summarized in Table 4-2. Air filters were analyzed for sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), bromine (Br), titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), vanadium (V), nickel (Ni), lead (Pb), arsenic (As), selenium (Se), copper (Cu), and zinc (Zn). The minimum quantifiable limit was about 0.5 ng/m^3, which was usually sensitive enough to quantify most of the elements on the air filters. The minimum quantifiable limit for metals in water was about 1 μg/L. The metals that were quantified in the deposition samples included As, Cu, Pb, Zn, Ni, Mn, and Cr.

Quality control samples for metals included a field blank, a certified water sample, and a spike blank sample containing metals concentrations comparable to the deposition samples. These samples were also acidified and stored, and metal recoveries determined. Precision was estimated from field duplicate samples.

Approximately 17 individual PAH compounds (Table 4-3) were quantified from filter, PUF, and deposition samples. Before the filters, PUFs, and deposition samples were extracted, a known amount of three deuterated PAH surrogates was added to each sample to determine method recovery. Detection limits were about 0.1 ng/m^3.

PAH compounds lower in molecular weight than phenanthrene exist primarily in the vapor phase. While the PUF is intended to trap vapor phase compounds, studies have documented significant sample breakthrough (escape through the PUF) as a function of vapor pressure, temperature, and volume of air sampled (You and Bidleman, 1984; Chuang et al., 1987). Therefore, ambient concentrations of low molecular weight compounds are likely to be underestimated by the methods and sampling schemes used in this study. However, measured concentrations of the 11 PAH compounds, anthracene through benzo(g,h,i)perylene, are expected to be representative of the ambient concentrations.

Extracts were analyzed for selected PCB congeners (18, 33, 49, 52, 77, 97, 101, 105, 118, 126, 138, 149, 169, 180, 187, 194, and 195). These congeners were chosen because they span a wide range of chlorination, molecular weight, solubility, and vapor pressure, and also because they are prominent in aerosol samples and contribute significantly to the mass of commercially sold PCBs (Aroclors). Surrogates and injection standards were used to verify analytical recoveries.

Sample Selection

Due to budget constraints, it was necessary to limit the number of sample analyses. All of the aerosol samples collected were weighed for determination of total mass. The Alexander Avenue site was selected for the most comprehensive analysis, because it has a substantial record of existing data from the PSAPCA monitoring co-located there, and because it is the site where extensive meteorological measurements were made during this study. Aerosol samples from the two highest, the two lowest, and the two weights closest to the mean were analyzed from the Alexander Avenue site for each of the intensive monitoring periods (July 20 to August 24, and November 16 to December 24) and also the non-intensive period. The selection of these samples determined the set of dates from which aerosol samples were selected from the remaining sites. Time periods corresponding to the intensive aerosol monitoring were chosen for the deposition sample analysis. The sample sites and dates selected for analysis are contained in tables in Appendix C-2.

Table 4-2. Extraction Procedures and Analytical Techniques for Aerosol and Deposition Samples

Sample	Chemical	Extraction Method	Chemical Analysis Technique
AEROSOL			
Filter	Metals		Energy-dispersive x-ray fluorescence (XRF) (Nielson, 1977)
PUF & Filter	Organics	Methylene chloride (filter) Hexane-Ether (PUF) (Compendium Method TO-13, EPA, 1988)	
	-PAHs		Gas chromatography/ mass spectrometry (GC/MS)
	-PCBs		Gas chromatograph/ electron capture detection (GC/ECD) (similar to Method 608)
	-Aliphatic Hydrocarbons		Gas chromatograph/ flame ionization detection (GC/FID)
DEPOSITION	Metals	Acid-digested for total recoverable metals (Method 3005, EPA, 1986c)	Atomic absorption flame spectrophotometry (EPA, 1986c)
	Organics	Methylene chloride (Method 610)	(same as above for aerosol samples)

Table 4-3. Study PAHs (listed in order of ascending molecular weight)

Naphthalene	Benzo(a)anthracene
Acenaphthylene	Chrysene
Acenaphthene	Benzo(b)fluoranthene
Fluorene	Benzo(k)fluoranthene
Dibenzothiophene	Benzo(a)pyrene
Phenanthrene	Indeno(1,2,3-c,d)pyrene
Anthracene	Dibenzo(a,h)anthracene
Fluoranthene	Benzo(g,h,i)perylene
Pyrene	

In addition the following samples were analyzed specifically to assist in comparison and interpretation of the results of various studies:

▶ Samples collected from November 27 to 30 from the Alexander Avenue and Riverside School sites: these samples were taken during the highest aerosol readings that occurred during the study. The samples were analyzed to determine from the chemical patterns which sources were the major contributors to the high readings.

▶ Samples collected from September 7 to 11 and September 14 to 18 from the Alexander Avenue site: these samples were analyzed to composite the results with the September 11 to 14 and September 18 to 21 samples to compare the aerosol and deposition measurements for the same time period during a two-week dry period.

▶ Samples from November 2 to 6 and November 13 to 16 from the Alexander Avenue site: these samples were analyzed to composite the results with the November 6 to 9 and November 9 to 13 samples to compare the aerosol and deposition measurements for the same time period during a two-week period of heavy and continuous rain.

▶ November 30 to December 4, December 4 to 7, December 7 to 11, and December 12 to 13 samples were analyzed to composite their results with the December 11 to 12 and December 13 to 14 samples. This was done to compare the results with the aerosol results from the receptor modeling study.

Numbers of samples collected and analyzed are summarized in Table 4-4.

Table 4-4. Aerosol and Deposition Sample Analysis Summary

Sample Type	Locations	Samples Collected	Samples Analyzed
Aerosol (intensive study)	AS, TM, SL, MS, RS	140	45
Aerosol (non-intensive)	AS, TM, BP	93	16
Deposition	AS, TM, SL, MS, RS + one duplicate	78	50

RESULTS AND DISCUSSION

Aerosol Results

Particulates

The concentrations of suspended particulates were usually in the range of 20 to 100 $\mu g/m^3$. The data for each air filter are presented in Appendix C-3, and the mean concentrations for each site are presented in Table 4-5.

Table 4-5. Mean Particulate Concentrations (μg/m^3) at Six Tacoma Sites[a]

	Alexander Avenue (AS)	Tyee Marina (TM)	Brown's Point (BP)	Sea-Land (SL)	Morse Supply (MS)	Riverside School (RS)
Entire Sampling Period 6-29-89 to 1-9-90	62	41	35[b]	77[c]	64[c]	50[c]
Summer Intensive Period 7-20-89 to 8-24-89	66	22	No Data	50	42	42
Autumn Intensive Period 11-16-89 to 12-21-89	73	62	No Data	100	82	56

(a) The estimated error in particulate concentrations is approximately $\pm$ 2.6 percent based on duplicate samples collected at one site.
(b) Sampling period is 7-10-89 to 11-6-89, and does not include summer intensive period
(c) Summer and autumn intensive periods only

The suspended particle results for Alexander Avenue and Tyee Marina are plotted versus time in Figure 4-3. The particulate concentrations at Alexander Avenue were three times higher than those at Tyee Marina during the summer. During the fall there are similar particulate patterns at these two sites. The highest particulate concentrations occurred during periods of air stagnation. During the fall intensive sampling period, the two highest particulate concentrations for the entire data set were measured at all of the five primary sites for filter periods that began either on November 27 or December 11. On November 27 all of the filters were clogged due to the high particulate concentrations. (To prevent this from happening again, filters were changed daily during air stagnation periods.) During the periods of highest particulate concentrations, similar particulate concentrations (121 to 174 μg/m^3) were observed at all five primary sites.

The difference in particulate concentrations between Alexander Avenue and Tyee Marina during the summer may have been due to a massive ditch digging and earth moving construction project that took place during July and August 1989 within 200 meters of the Alexander Avenue site. Under dry summer conditions resuspension of dust is more likely to occur. The more even gradient in particulate concentrations among all the sites during the period of highest concentrations in the fall suggests that the samples were more heavily influenced by a regional source, most likely dominated by fine particles rather than a nearby source of coarse particles.

Elemental Concentrations

The concentrations of elements in air samples appear to be correlated with particulate concentrations. The concentrations of elements are generally lowest during wet, windy periods and highest during air stagnation episodes. The concentrations of 15 elements in the air samples are presented in Appendix C-4, and the mean concentrations for each site are presented in Table 4-6. High and variable concentrations of copper in air filter samples resulted from air contamination by the air sampler motor armature, even though a plastic tube was used to divert motor exhaust away from the sampler. Consequently, the copper data from the air filters were not usable. Based on the limited number of filters from each site, the pattern is composed of

Figure 4-3. Suspended Particulate (PM$_{2.5-50}$) Concentrations, Alexander Avenue and Tyee Marina Sites
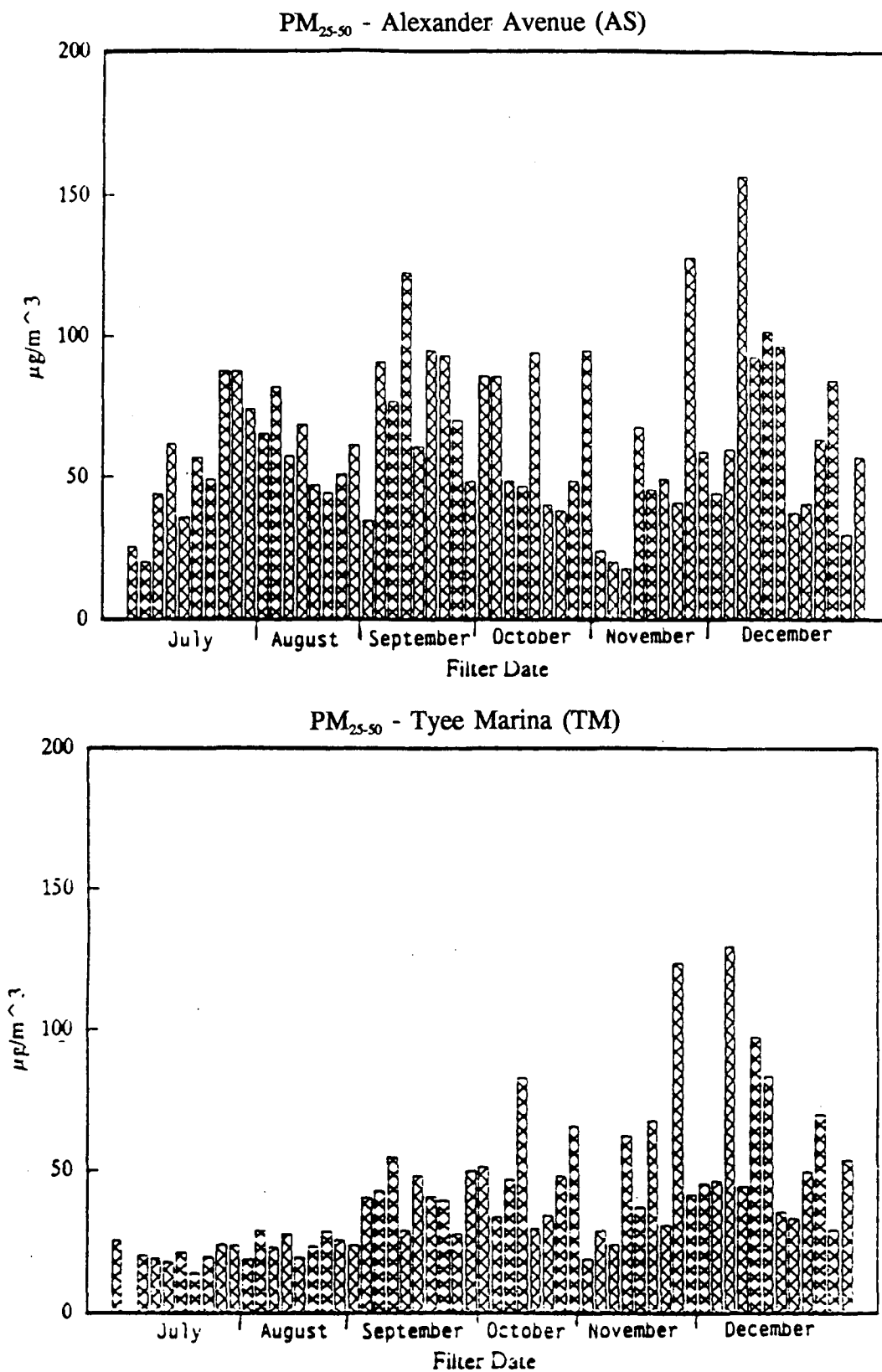
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Table 4-6. Mean Elemental Aerosol Concentrations at Six Tacoma Sites (ng/m^3)[a]

	Site (Number of Samples)					
Element	AS (26)	TM (9)	BP (3)	SL (5)	MS (6)	RS (7)
S	2600	2200	1400	2000	2000	1400
Cl	650	800	300	380	470	300
K	350	200	160	330	320	310
Ca	1600	740	540	980	970	360
Ti	100	54	40	100	84	64
V	10	9.6	7.6	9.1	6.4	8.4
Cr	5.6	3.3	0.87	6.8	8.6	6.8
Mn	45	31	18	43	45	37
Fe	1400	860	510	1400	1300	770
Ni	12	9.9	5.9	10	10	9.9
Zn	94	78	27	130	90	72
Se[b]	0.58	0.75	0.68	0.7	0.6	0.47
Pb	39	27	15	62	45	52
As	5.8	2.6	2.7	6.6	4	3.6
Br	7.8	6.2	5.0	8.8	7.2	9.3

(a) The estimated error in metal concentration is approximately ±10 percent based on chemical analyses of duplicate samples collected at one site.

(b) Where selenium (Se) was undetected in samples, the detection limit of about 0.5 ng/m^3 was used to calculate an estimated mean.

higher concentrations of crustal elements (Ca, Fe, K, Mn, and Ti) at the industrial sites (AS, MS, and SL) and the rural site (RS) than at the marine sites (TM and BP). The Sea-Land site had the highest lead and zinc concentrations. Crustal metals such as iron and potassium were generally highest during the summer at the Alexander Avenue site (Figures 4-4 and 4-5). During the fall air stagnation episodes, the concentrations of lead and zinc at both Alexander Avenue and Tyee Marina were much higher relative to crustal metals than in the summer (Figures 4-6 and 4-7).

The probable source of lead and zinc at the Sea-Land site is a facility nearby at Terminal 7 where ore containing these metals is off-loaded from ships and loaded into open rail cars. The peak in crustal metals concentrations at the Alexander Avenue site may reflect construction and earth moving activities during dry summer weather.

Particulate PAHs

The concentrations of PAHs collected on air filters were approximately an order of magnitude higher during air stagnation episodes, when total particulates were high, than during other periods. The dominant five compounds are fluoranthene, pyrene, chrysene, benzo(b)fluoranthene, and benzo(a)pyrene. The concentrations of these individual compounds range from 0.1 to 10 ng/m^3. These five compounds are often referred to as combustion PAHs (CPAHs) because of their probable source. The PAH concentration data for 17 compounds are presented in Appendix C-5 and the mean concentrations for each site are presented in Table 4-7. The PAH compounds listed from naphthalene through anthracene are relatively volatile and usually not detected on air filters and only partially recovered from PUF samples. Because of the long sample collection period (three to four days) some particulate PAHs may also have partitioned off the filter and onto the PUF. The mean total CPAH particulate concentrations [sum of the ten compounds, fluoranthene through benzo(g,h,i)perylene] are relatively uniform among the sites, except for Brown's Point, which has much lower concentrations.

Vapor PAH

The concentrations of volatile PAH compounds, such as naphthalene, acenaphthalene, acenaphthene, and fluorene in air samples were severely underestimated by the sampling and analytical methods used in this study. The two main causes are breakthrough of volatile PAHs on PUF plugs and low recoveries of PAHs during the chemical analyses.

The vapor penetration of PAHs through PUF plugs has been studied by You and Bidleman (1984). Their results indicate an air sample volume of about 1,000 m^3 (as used in this study) would result in approximately 50 percent breakthrough of phenanthrene in the PUF plugs. Compounds more volatile than phenanthrene, such as fluorene or naphthalene, will break through at an air volume of less than 200 m^3. Therefore, the concentrations of fluorene and more volatile PAH compounds will be underestimated for vapor PAHs in this study by at least 50 percent.

The analytical chemistry recovery results for the lower molecular weight PAH compounds were estimated using two surrogates, naphthalene-d8 and acenaphthene-d10. The recoveries of the surrogate for PUF samples were in the range of 10 to 40 percent for this study, indicating that the lower molecular weight PAH compounds, which are volatile, are partially lost during the evaporation step of the analysis. Results of surrogate recoveries are in Appendix C-6.

Figure 4-4. Aerosol Iron (Fe) Concentrations, Alexander Avenue and Tyee Marina Sites

Iron - Alexander Avenue (AS)

Iron - Tyee Marina (TM)
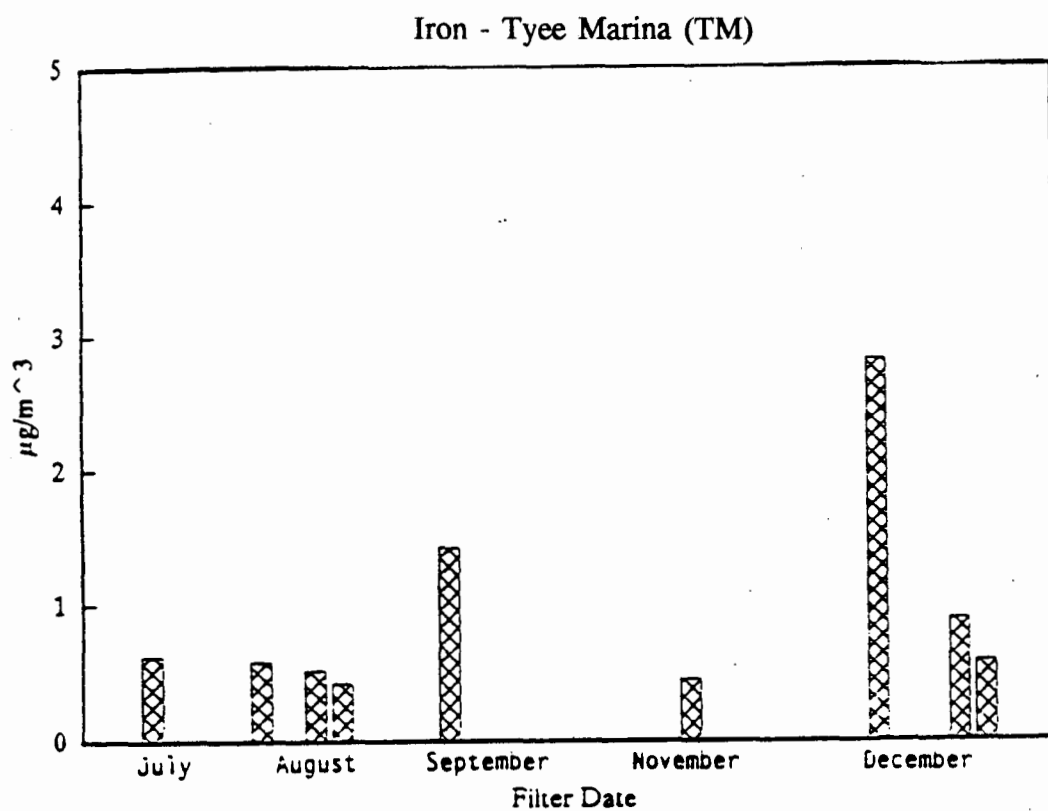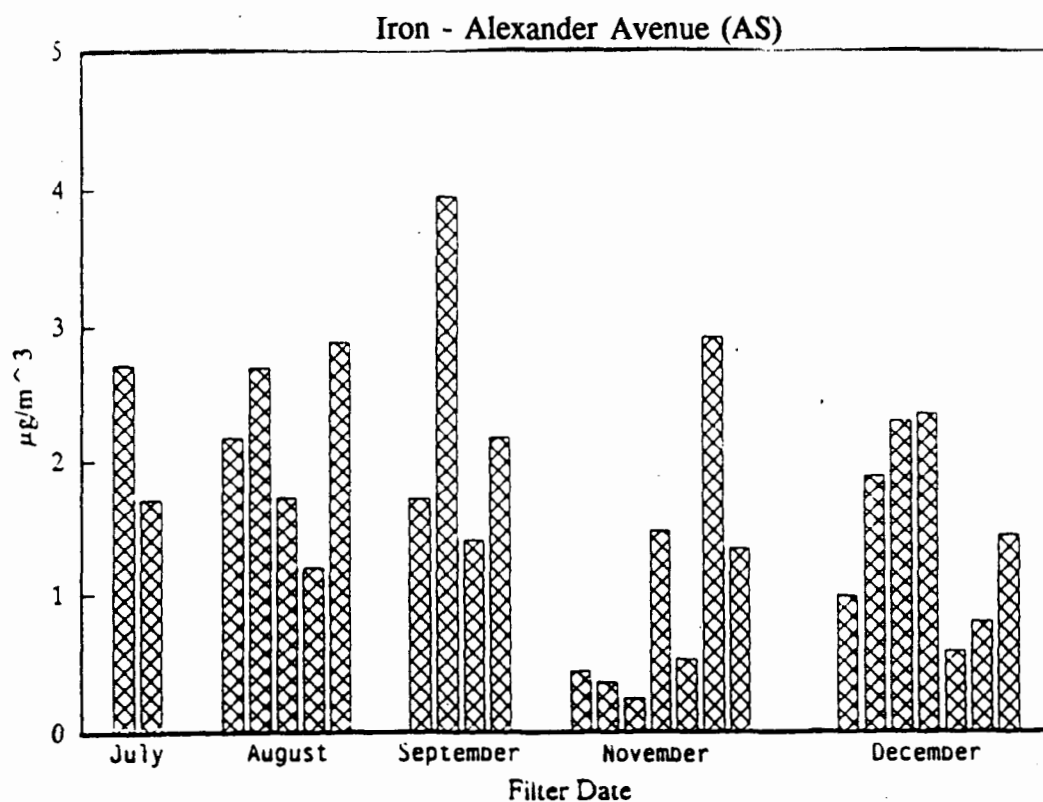
Figure 4-5. Aerosol Potassium (K) Concentrations, Alexander Avenue and Tyee Marina Sites
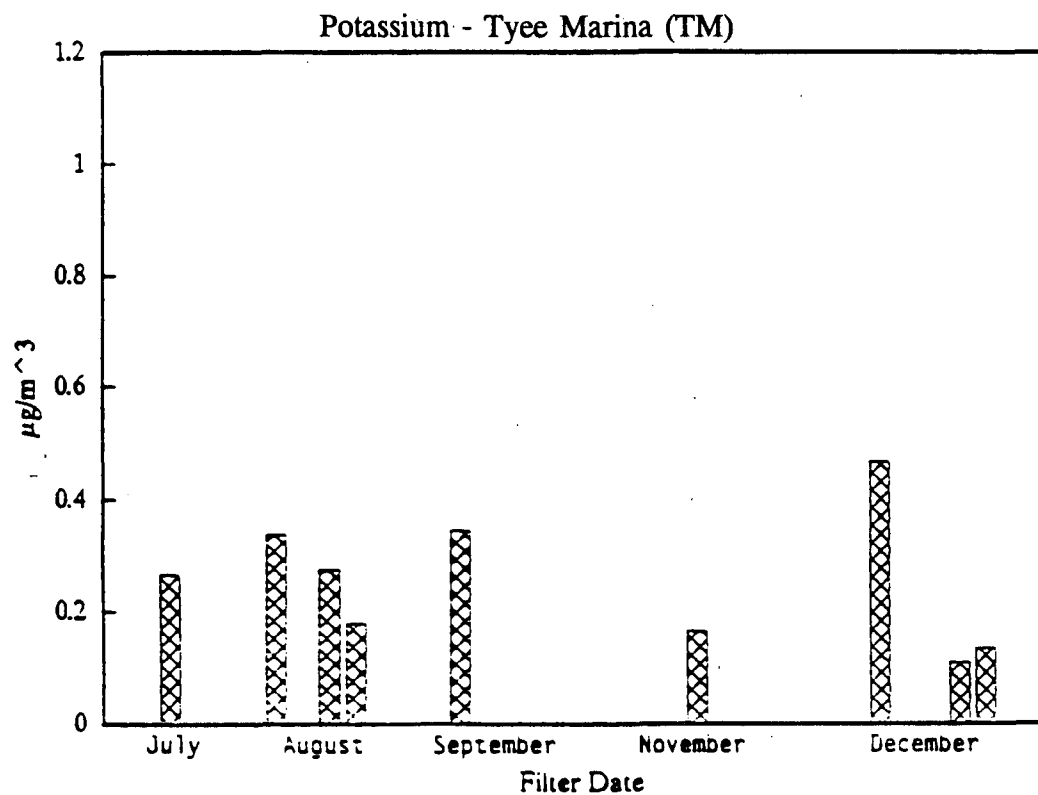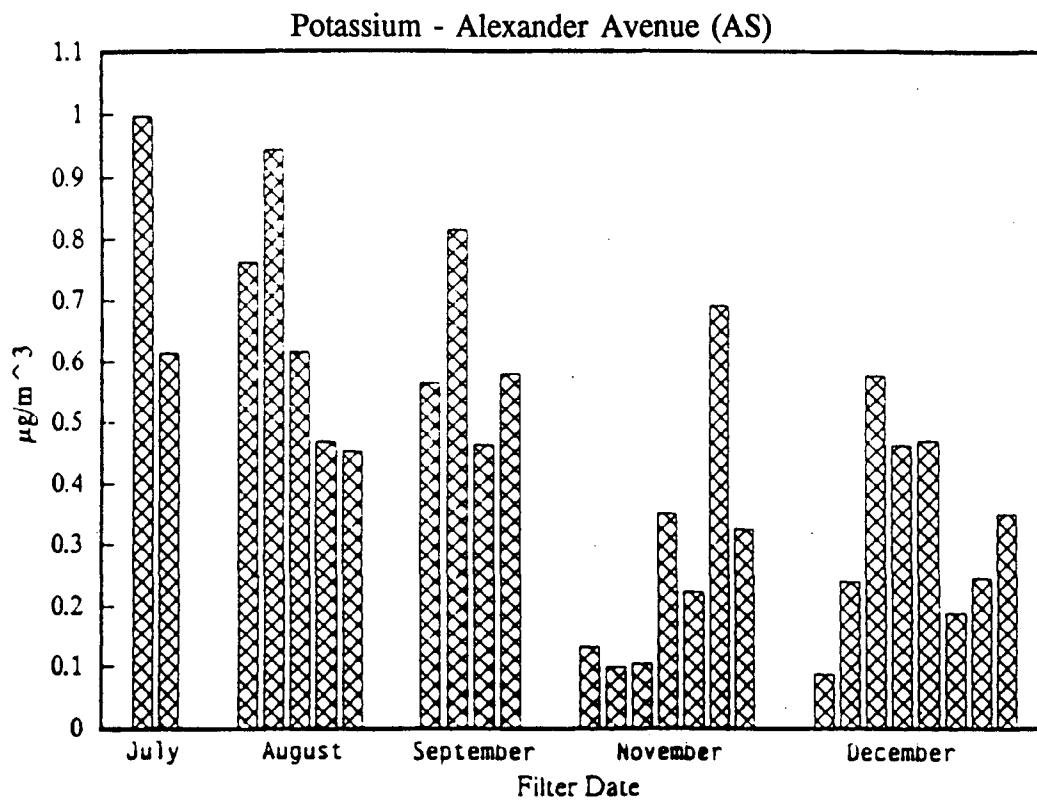
Potassium - Alexander Avenue (AS)

Potassium - Tyee Marina (TM)

Figure 4-6. Aerosol Lead (Pb) Concentrations, Alexander Avenue and Tyee Marina Sites

Lead - Alexander Avenue (AS)
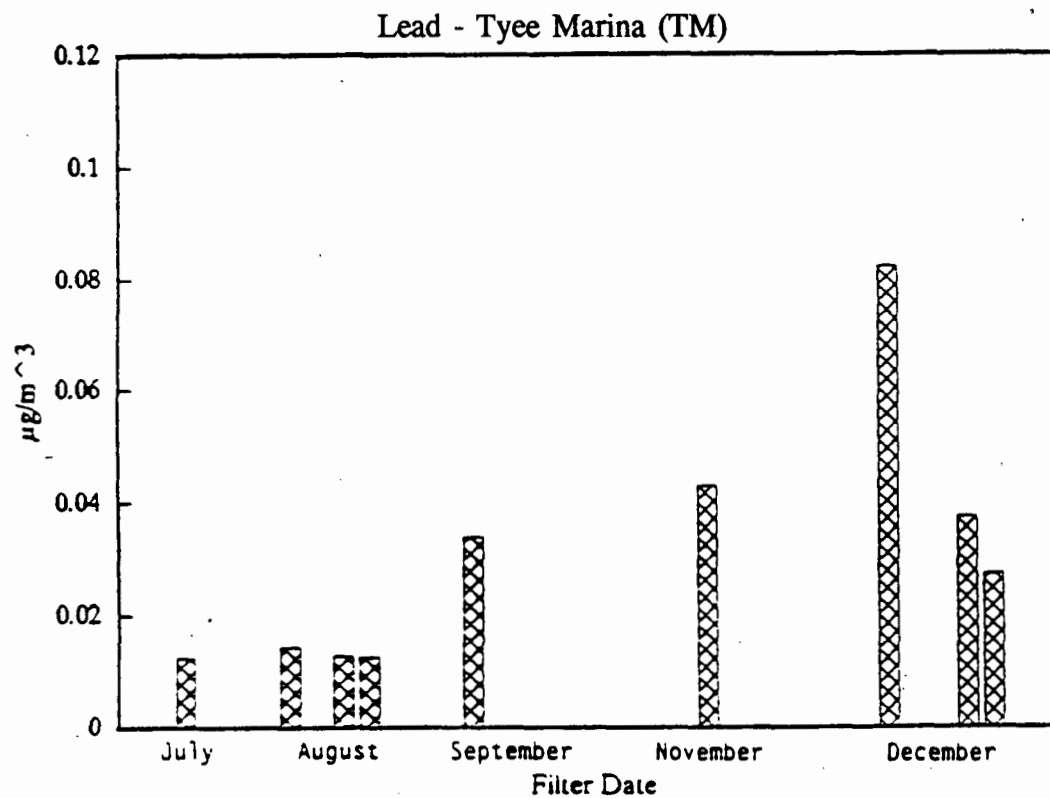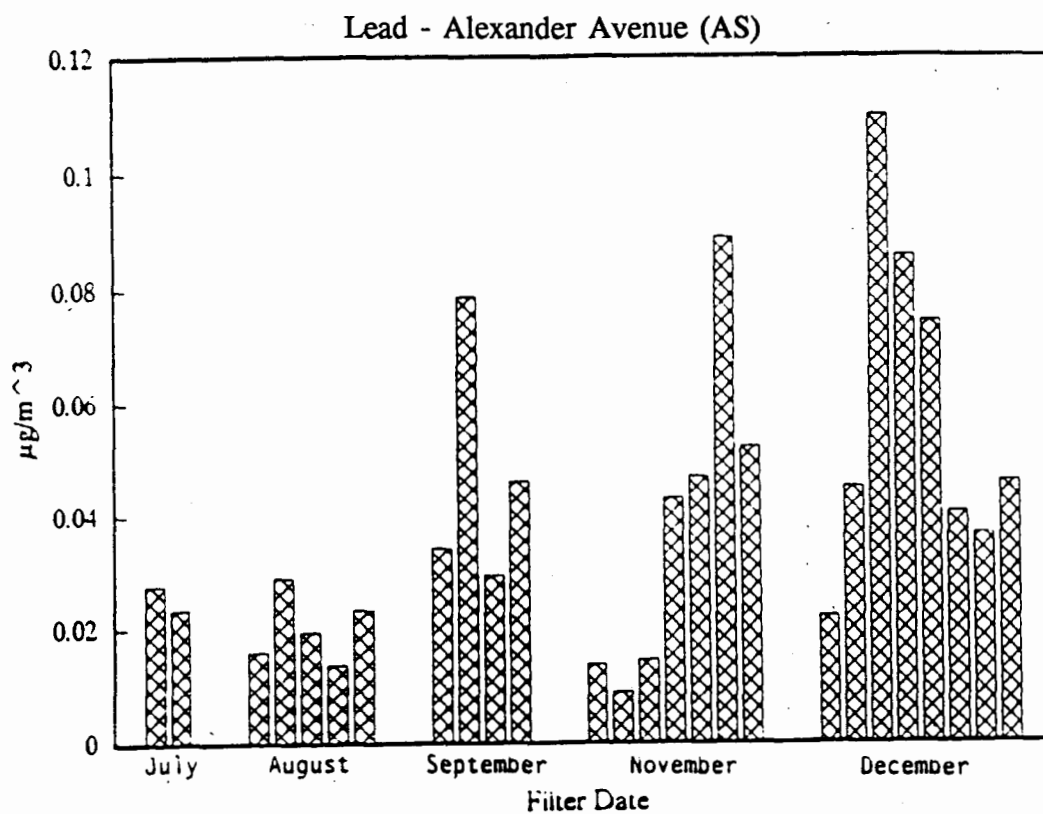
Lead - Tyee Marina (TM)

Figure 4-7. Aerosol Zinc (Zn) Concentrations, Alexander Avenue and Tyee Marina Sites
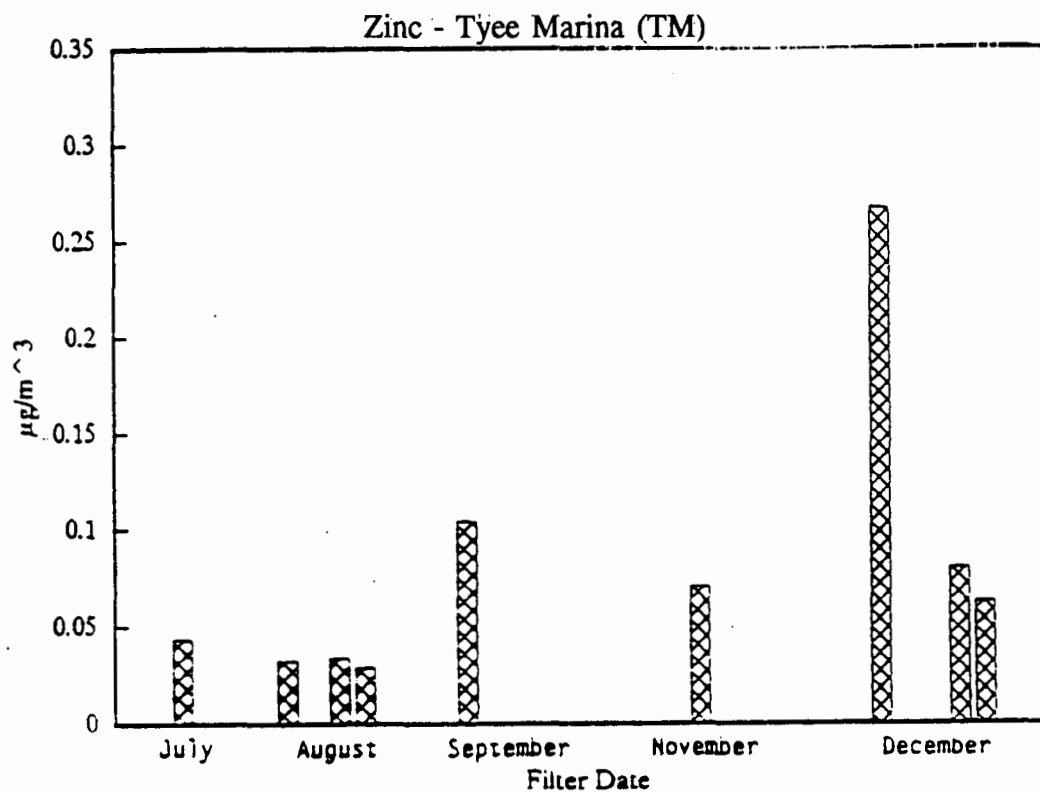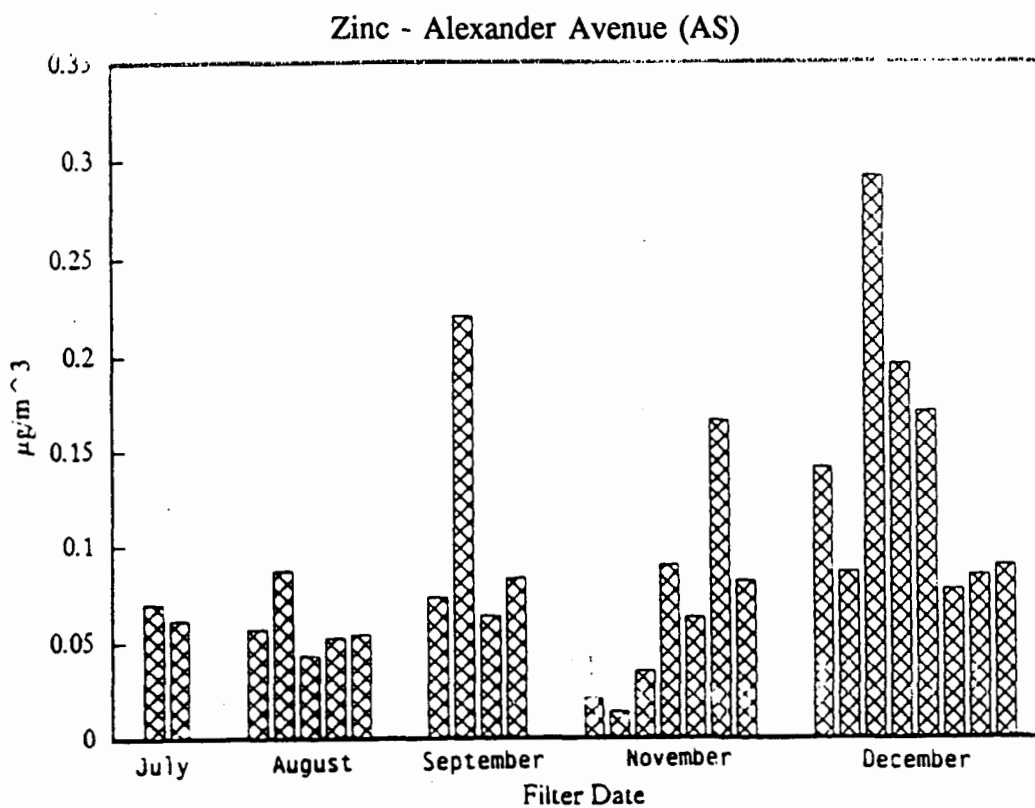
Zinc - Alexander Avenue (AS)

Zinc - Tyee Marina (TM)

Table 4-7. Mean Particulate PAH and Total Combustion PAH[a] Concentrations at Six Tacoma Sites (ng/m³)[b]

Compound	Site (Number of Samples)					
	AS (26)	TM (5)	BP (3)	SL (5)	MS (6)	RS (7)
Naphthalene	0.037	0.16	0.093	0.091	0.22	0.11
Acenaphthalene	ND[c]	ND	ND	ND	ND	ND
Acenaphthene	ND	ND	ND	ND.	ND	ND
Fluorene	0.001	ND	ND	ND	ND	ND
Dibenzothiophene	0.005	ND	ND	ND	ND	ND
Phenanthrene	1.2	0.79	0.11	1.2	0.81	1.1
Anthracene	0.034	0.082	ND	0.084	ND	ND
Fluoranthene	4.4	4.7	0.34	4.0	3.0	3.2
Pyrene	3.3	4.5	0.28	3.8	3.0	3.5
Benzo(a)anthracene	3.1	4.2	0.24	2.9	2.4	4.3
Chrysene	7.3	10.2	0.84	5.6	4.6	6.9
Benzo(b)fluoranthene	4.3	5.9	1.8	3.9	3.4	5.1
Benzo(k)fluoranthene	2.8	2.1	0.024	2.6	1.8	3.4
Benzo(a)pyrene	2.7	1.9	0.23	2.7	2.2	4.4
Indeno(1,2,3-c,d)pyrene	2.0	1.2	0.29	1.9	1.5	2.7
Dibenzo(a,h)anthracene	0.42	0.46	0.10	0.40	0.33	0.60
Benzo(g,h,i)perylene	2.5	1.5	0.40	2.4	2.2	3.1
Total CPAHs	32.9	36.8	4.55	30.1	24.4	37.3

(a) Combustion PAH concentrations are the sum of ten compounds (fluoranthene through benzo (g,h,i) perylene)

(b) Samples usually three to four days, few one-day samples
Sample volume approximately 1,000 m³

(c) ND = Not detected

Given both the sample capture and analytical recovery errors discussed above, the vapor PAH results presented below must be treated carefully and considered as only qualitative at best. The biases in the sampling and analysis may mean that as little as 5 - 20% of the original vapor PAH load was measured.

Despite the sampling and analytical losses the mean concentrations of vapor PAHs measured are considerably higher than the mean concentrations of particulate PAHs. (As noted above, the PUF may have sampled some of the particulate PAHs that broke through during the long sampling period.) The mean total vapor PAH concentrations for all six sites except Brown's Point are in the range of 101 to 237 ng/m³ (Table 4-8). The data for each PUF sample are provided in Appendix C-6. Brown's Point concentrations are very low, but include only two samples. The dominant four compounds are fluorene, phenanthrene, fluoranthene, and pyrene. The latter two compounds are also present on the filters, however, only at levels one-fifth of the concentration found in the vapor phase. Compounds that are higher in molecular weight than pyrene are generally not detected or, if they are detected, they have lower concentrations in the vapor phase than in the particulate phase.

Individual mean concentrations of the four dominant PAH compounds range between 2 and 124 ng/m^3. A plot of monthly average vapor PAH concentrations at the Alexander Avenue and Tyee Marina sites is shown in Figure 4-8. The highest concentrations at Tyee Marina occurred during the December air stagnation episodes when the concentrations of particulates, metals, and particulate PAHs were highest. However, the highest concentration at the Alexander Avenue site occurred in August with lower, but fairly similar concentrations in September, November, and December.

Table 4-8. Mean Vapor PAH Concentrations at Six Tacoma Sites (ng/m3)[a]

Compound	Site (Number of Samples)					
	AS (21)	TM (7)	BP (3)	SL (5)	MS (6)	RS (7)
Naphthalene	2.4	0.54	0.63	1.0	1.2	2.4
Acenaphthalene	2.2	1.3	0.25	2.2	3.0	5.2
Acenaphthene	4.3	3.3	0.80	3.1	2.0	1.7
Fluorene	12	9.2	2.2	12	9.5	7.1
Dibenzothiophene	9.2	8.4	1.0	8.1	7.8	3.8
Phenanthrene	124	101	27	57	54	49
Anthracene	14	7.1	1.1	5.0	5.6	5.9
Fluoranthene	40	29	13	16	15	14
Pyrene	25	21	8.4	11	12	11
Benzo(a)anthracene	0.84	0.62	0.63	0.25	0.26	0.37
Chrysene	2.4	1.7	3.1	0.66	0.51	0.80
Benzo(b)fluoranthene	0.07	0.18	0.10	0.01	0.02	0.10
Benzo(k)fluoranthene	0.01	ND[b]	ND	0.00	ND	ND
Benzo(a)pyrene	ND	ND	ND	ND	ND	ND
Indeno(1,2,3-c,d)pyrene	ND	ND	ND	ND	ND	ND
Dibenzo(a,h)anthracene	ND	ND	ND	ND	ND	ND
Benzo(g,h,i)perylene	ND	ND	ND	ND	ND	ND
Total Vapor PAHs	237	183	55	115	110	101

(a) Samples usually three to four days, few one-day samples
     Sample volume approximately 1,000 m^3
     Data not corrected for breakthrough or recovery efficiency
(b) ND = Not detected

Figure 4-8. Average Monthly Vapor PAH Concentrations, Alexander Avenue and Tyee Marina Sites[a]
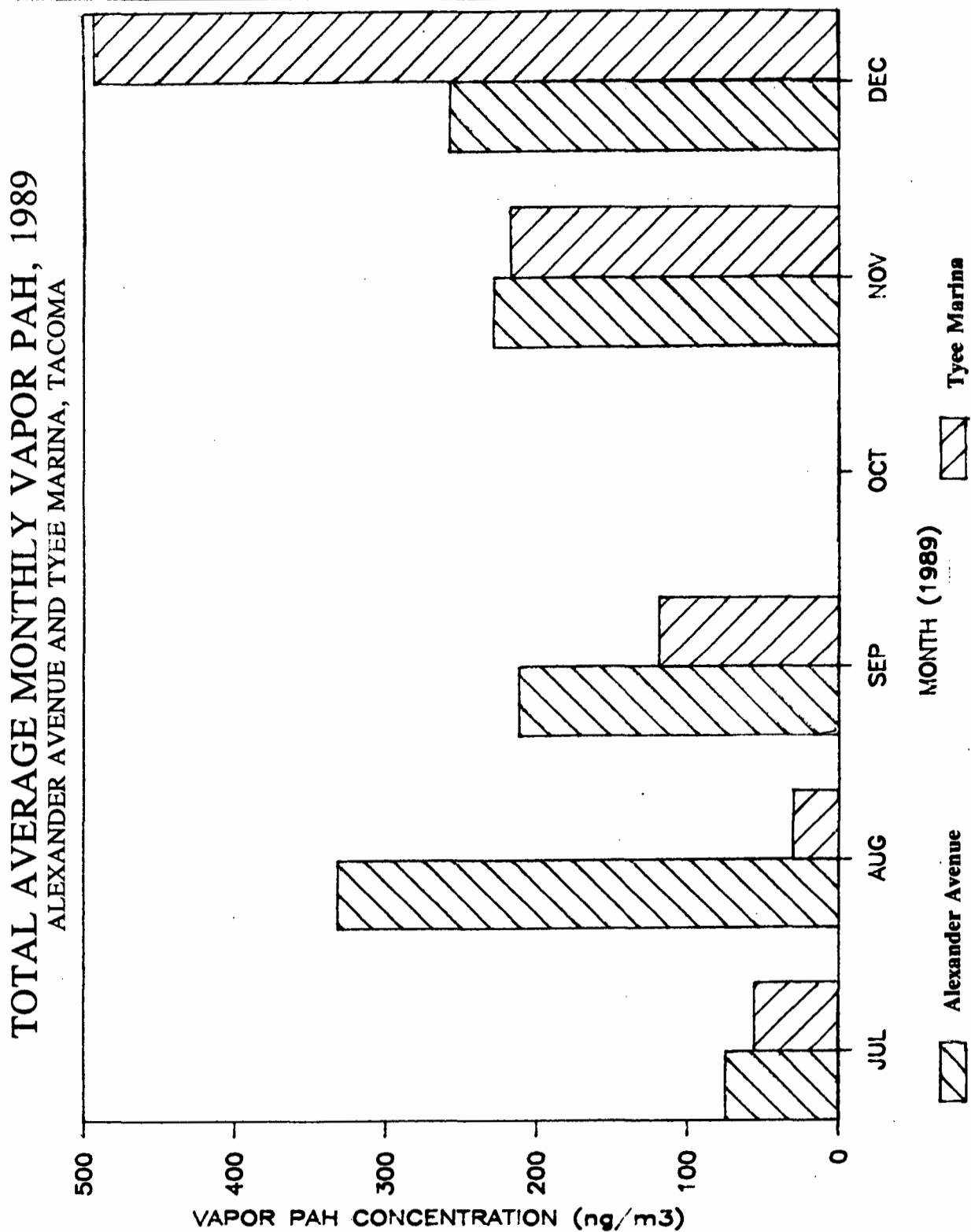
(a) Data not corrected for breakthrough or recovery efficiency

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Particulate and Vapor Aliphatic Hydrocarbons and PCBs

The mean concentrations of particulate and vapor aliphatic hydrocarbons and PCBs are summarized in Table 4-9, and the results for the individual filter and PUF plug samples are included in Appendix C-7. Four air samples collected in July and five air samples collected in December were analyzed for 27 aliphatic hydrocarbon compounds (AHC, C9 to C36) and 21 PCB congeners. The concentrations of the AHCs and PCBs were frequently below detection limits for the sample sizes used in this study.

The general pattern is that the total AHCs (vapor and particulate) detected in December, when air stagnation existed, were approximately four times higher than the total AHCs in July. There usually were higher concentrations of vapor than particulate AHCs. This could reflect some partitioning of particulates from the filter onto the PUF.

The total PCB concentration was approximately five times higher in December than in July. The PCBs were present predominantly in the vapor phase. However, due to breakthrough, the measured values may be low. Because of the limited number of samples analyzed and the limited number of congeners that were detected, the data set is not of quantitative value, however, the proportion of vapor to particulate is consistent with other studies (Chevreuil et al., 1989; Duinker and Bouchertall, 1989).

Table 4-9. Concentrations of Particulate and Vapor Aliphatic Hydrocarbons (C9 to C36) and PCBs (21 Congeners) (ng/m^3)

	AS	TM	July 27 SL	MS	
Particulate Aliphatics	43	3	11	19	
Vapor Aliphatics	27	130	30	15	
Particulate PCBs	0.05	0.01	<0.02	0.04	
Vapor PCBs	0.01	0.07	0.17	0.04	
	AS	TM	December 11 SL	MS	RS
Particulate Aliphatics	60	270	170	130	20
Vapor Aliphatics	100	350	600	99	120
Particulate PCBs	0.15	0.37	<0.02	<0.02	<0.02
Vapor PCBs	0.35	1.3	1.6	1.3	0.38

Deposition Results

Metals

The concentrations of seven metals (As, Cr, Cu, Mn, Ni, Pb, and Zn) were determined in atmospheric deposition samples collected at five sites for nine two-week intervals, and deposition rates were calculated for each metal in each sample. These results are included in Appendix C-8. The mean metal deposition concentrations for the sampling period are presented in Table 4-10. The deposition concentrations for all of the metals are greater at the industrial sites than at the marine sites. The mean metals deposition rates are presented in Table 4-11.

Table 4-10. Mean Concentrations of Metals[a] in Atmospheric Deposition Samples Collected in Tacoma from July to December 1989

SITE	As	Cr	Cu	Mn	Ni	Pb	Zn
				$\mu g/L$			
Tyee Marina	1.4	4.0	51	39	13	34	103
Tyee Marina (dup)	1.3	3.6	26	33	7.8	30	94
Morse Supply	10.2	7.9	133	206	56	132	326
Sea-Land	20.8	15.0	162	149	41	872	916
Alexander Avenue	13.4	9.8	85	144	42	73	287
Riverside School	0.9	3.0	13	24	6.0	13	26

(a) Mean values for all times

Table 4-11. Mean Metals Deposition Rates

SITE	As	Cr	Cu	Mn	Ni	Pb	Zn
				$\mu g/m^2/day$			
Tyee Marina	1.8	4.1	58	43	17	35	107
Tyee Marina (dup)	1.8	4.0	30	42	8.4	42	125
Morse Supply	9.8	9.2	123	188	49	127	284
Sea-Land	18	17	149	142	41	653	872
Alexander Avenue	11	11	68	112	33	55	230
Riverside School	1.8	4.6	20	42	8.4	22	36

Nutrients
___

The concentrations of nutrients (nitrate plus nitrite, ammonia, total phosphate, orthophosphate, and sulfate) were determined in deposition samples collected at five sites for six two-week intervals. The concentrations measured (mg/L) are presented in Appendix C-9 along with the sampling dates and the volumes collected. The concentrations of all nutrients appear lower during the wet periods of November and December than during the drier periods of summer and early fall due to dilution from rain. The data generally show poor agreement between field duplicates collected in pans 10 feet apart. There could be numerous reasons for the variability observed between duplicates and between stations. A primary concern is the long (two-week) sampling period, which is far from optimal for nutrients subject to microbial uptake and remineralization, as well as degassing from the water. Therefore, the qualitative observations about the data should be considered as only preliminary. Mean deposition concentrations for each nutrient at each site over the July to December 1989 period are summarized in Table 4-12. There do not appear to be spatial trends in the mean data. Appendix C-9 also contains the nutrient data expressed as deposition units of $\mu g/m^2/day$. Seasonal trends are not apparent.

Table 4-12. Concentrations of Nutrients and Chloride in Atmospheric Deposition Samples Collected in Tacoma from July to December 1989 (Mean values)

					mg/L		
Site	Volume (L)	Chloride	Nitrate + Nitrite	Ammonia Nitrogen	Total Phosphate	Ortho- Phosphate	Sulfate
Tyee Marina	4.5	4.2	0.39	0.44	0.07	0.01	55
Tyee Marina (dup)	2.5	2.3	0.58	0.74	0.08	0.05	9.1
Alexander Avenue	4.8	2.9	0.45	1.6	0.24	0.01	33
Alexander Ave (dup)	7.5	1.3	0.36	0.13	0.04	0.00	12
Morse Supply	4.3	1.3	0.25	0.14	0.23	0.06	19
Sea-Land	4.3	2.2	0.29	0.32	0.13	0.00	27
Riverside School	6.4	0.67	0.25	0.32	0.05	0.00	4.7

Aliphatic Hydrocarbons and PCBs

The concentrations and deposition rates for AHCs and PCBs are presented in Appendices C-10 (a) and (b). Deposition samples collected in July (July 11 to 25) and December (November 30 to December 14) were analyzed, and the deposition rates for a total of 27 AHCs and 21 PCB congeners are given in units of ng/m^2/day. AHCs with molecular weight greater than C-18 were frequently present in deposition samples. Based on this limited data, there do not appear to be regional or seasonal trends. The PCBs are rarely detected in the deposition samples and no patterns are apparent. The sample sizes and detection limits were not satisfactory to provide useful quantitative data.

Polycyclic Aromatic Hydrocarbons

The atmospheric deposition of PAHs at the five sites is dominated by four CPAHs: fluoranthene, pyrene, chrysene, and benzo(b)fluoranthene. The mean PAH deposition rates by site and the total PAH deposition rates are presented in Table 4-13. The PAH data for each of the 48 deposition samples are in Appendix C-11. These four compounds were also the four most abundant compounds in the particulate air samples. This relationship is in agreement with other PAH deposition studies, which reported that PAH deposition is due to the particulate, not the vapor phase (McVeety and Hites, 1988). The individual mean deposition rates of the four dominant compounds are in the range of 500 to 3,500 ng/m^2/day at the Tyee Marina, Morse Supply, Sea-Land, and Riverside School sites. The mean deposition rates at the Alexander Avenue site are five to ten times higher than those of the Tyee Marina, Morse Supply, or Sea-Land (see Table 4-13 and Figure 4-9). The maximum deposition occurred at the Alexander Avenue site in September 1989. Deposition rates at Riverside School are about one-third those at Tyee Marina, Morse Supply, and Sea-Land. The highest deposition rates at the Alexander Avenue site are inconsistent with the particulate PAH aerosol data, which indicate similar concentrations at all sites and show the highest concentration in December rather than September.

The high deposition of PAHs at the Alexander Avenue site may be due to resuspension of coarse soil particles which contain high concentrations of PAH. The local construction activity near the Alexander Avenue site could have caused the resuspension of contaminated coarse soil particles that were large enough so that they were not collected by the air sampler.

Table 4-13. Mean PAH and Total Combustion PAH Atmospheric Deposition Rates at Five Tacoma Sites (ng/m²/day)

COMPOUND	Site (Number of Samples)				
	AS (8)	TM (9)	SL (9)	MS (9)	RS (9)
Naphthalene	140	120	120	170	160
Acenaphthalene	21	ND[a]	16	75	10
Acenaphthene	66	3	47	89	ND
Fluorene	150	21	69	150	7
Dibenzothiophene	150	19	46	60	6
Phenanthrene	3,200	520	730	920	260
Anthracene	210	15	90	190	9
Fluoranthene	12,000	2,000	2,900	1,700	820
Pyrene	7,800	1,200	2,100	1,600	510
Benzo(a)anthracene	3,200	420	710	630	170
Chrysene	11,000	2,900	3,400	1,900	1,100
Benzo(b)fluoranthene	7,900	1,800	2,700	1,100	660
Benzo(k)fluoranthene	2,100	39	600	540	16
Benzo(a)pyrene	2,600	210	690	580	87
Indeno(1,2,3-c,d)pyrene	2,000	180	830	470	83
Dibenzo(a,h)anthracene	640	75	270	230	32
Benzo(g,h,i)perylene	1,800	190	920	520	110
TOTAL CPAH	52,000	9,000	15,000	9,300	3,600

(a)   ND = Not detected

ATMOSPHERIC DEPOSITION OF CPAH VERSUS TIME
ALEXANDER AVENUE AND TYEE MARINA, TACOMA

Figure 4-9. Atmospheric Deposition of CPAH versus Time, Alexander Avenue and Tyee Marina Sites
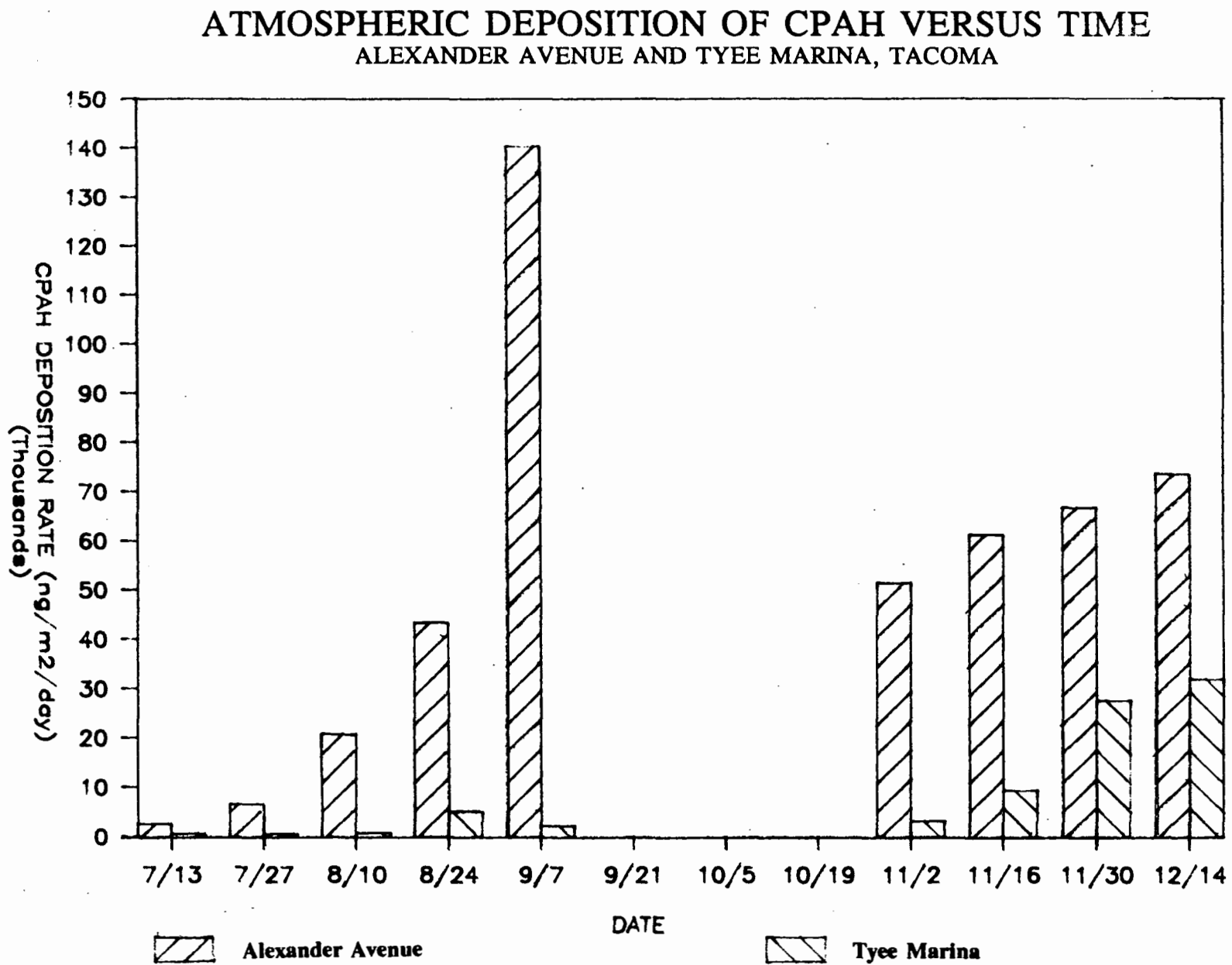
QUALITY CONTROL

Quality Control Results for Field Sampling

Quality control procedures for field sampling included collection of duplicate filters, PUFs, and deposition samples, and field blanks.

Results of field blanks (filters, PUFs, and water) indicate the elements and compounds were either not detected and/or were detected at concentrations that were insignificant (less than 10 percent) compared with the concentrations in field samples.

The results for duplicate samples are limited to only a few filters, PUFs, and deposition samples because a limited number of the field samples were analyzed. All of the particulate duplicate samples were analyzed and the results between samplers were usually very close; for example, the mean difference between 11 particulate samples collected on two PS-1 samplers at the Alexander Avenue site during the fall intensive period was 2.6 percent. There is also good agreement between the particulate concentrations (TSP) measured daily at the PSAPCA Fire Station No. 12 site and those measured for three- or four-day periods in this study.

The concentrations of metals in duplicate aerosol and duplicate deposition samples usually agree within 10 to 20 percent. There is lesser agreement between nutrients in duplicate deposition samples than for metals, which indicates that the nutrient data have higher variances. The duplicates for PAHs in filters, PUFs, and deposition samples usually agree within 20 to 30 percent; however, approximately 10 percent of the PAH compounds in both vapor and particulate samples differ by more than 50 percent between duplicates.

Quality Control Results for Chemical Analyses

Polycyclic Aromatic Hydrocarbons

Quality control samples for chemical analysis of PAH compounds in air filters included field blanks, surrogate recoveries, and filter spikes, as well as analysis of National Institute of Standards and Technology (NIST) certified reference urban dust (SRM 1649). The field blanks did not contain detectable levels of PAH compounds except for naphthalene [Appendix C-12(a)]. The detection limits were about 0.1 ng/m^3 [Appendix C-12(b)]. Surrogate recoveries of three deuterated PAH compounds (naphthalene-d8, acenaphthene-d10, and perylene-d12) that were added to each filter during the extraction were usually in the range of 10 to 40 percent for d8, 30 to 70 percent for d10, and 60 to 120 percent for d12. These recoveries are within acceptable ranges. Blank filter spikes with approximately 1.5 ng/m^3 of all PAH compounds had recoveries in the range of 40 to 80 percent [Appendix C-12(c)]. The results for SRM 1649 averaged 11 percent lower than the certified concentrations [Appendix C-12(d)].

Analysis of PAH PUF plugs and deposition water samples included field blanks, surrogates, and blank spikes. Field blank PUFs contained detectable PAH concentrations equivalent to approximately 2 ng/m^3 [Appendix C-12(a)]. Field blank deposition water occasionally contained five to 10 ng/L of PAH compounds which would contribute about five ng/m^2/day, or only a few percent of the deposition rate for most field samples. Surrogate recoveries of d8 in PUFs and deposition samples were usually in the range of 10 to 20 percent [Appendices C-12 (a) and (c)]. However, the d10 and d12 recoveries were approximately 20 to 40 percent and 60 to 110 percent, respectively. Recoveries of spiked blanks were in the range of 60 to 112 percent for PUF spikes at the level of 2.5 ng/m^3 [Appendix C-12(c)]. Spike recoveries for water were in the range of 38 to 130 percent with the lower recoveries for the most volatile PAH compounds.

PCBs and Aliphatics

Method detection limits for air and deposition samples were estimated by analyzing seven replicates of spiked blanks, then multiplying the standard deviation of the mean by the Student t-test values [Appendices C-12 (e) and (f)]. The concentrations of PCB congeners and AHCs in field blanks were below the method detection limits. The spike recoveries for a blank filter spiked with AHCs were in the range of 45 to 159 percent [Appendix C-12(g)].

Nutrients

Quality control procedures for nutrients included analysis of a field blank, laboratory duplicates, matrix spikes, and matrix spike duplicates. Field blanks (water used to fill the deposition sampler) contained 0.021 mg/L total phosphate, 0.014 mg/L nitrate + nitrite, and 0.013 mg/L ammonia. The other nutrients were below detection limits. Laboratory duplicates usually agreed within 10 percent and matrix spike recoveries were in the range of 83 to 112 percent. Because of the poor agreement between nutrient deposition rates for field duplicate samples and between different sites, the samples appear to have been subject to errors due to the sampling procedure, and therefore the data are considered of lesser quality than the metals and PAH data.

Metals - XRF

The procedure for XRF analysis of aerosol-loaded filters was developed for low atomic weight organic filter material such as Whatman 41, Teflon, cellulose acetate, International Paper Corporation (IPC) filter material, polycarbonate, charcoal, and similar material on which the aerosol loading would represent a significant percentage of the total mass observed by the XRF analytical method. Quartz fiber filters were used because they are acceptable for the collection and analysis of organic compounds. The problem encountered with the relatively high atomic weight of the quartz filters is that the filter itself represents most of the mass defined as sample by the scatter peaks, which results in an over-correction for absorption. The use of the quartz filter also effectively forecloses retrieval of any usable concentration values for the analytes of aluminum (Al), silicon (Si), and P. To deal with the problem of over-correction, a spectrum of a blank filter was collected for one-half the acquisition time of the actual samples and the blank spectrum was subtracted from the sample spectrum. To verify that the corrections were of the proper magnitude, a fusion of a known area of three of the filters was accomplished and analyzed for three analytes (Fe, Ca, and K) by an independent technique, atomic absorption (AA) spectroscopy [Appendix C-12(h)].

Quality control for elements on filters included field blanks and XRF standards. Concentrations of elements in filter blanks were usually below detection limits or at a low uniform level. For several metals (As, Cr, Se, and V), the concentrations in some of the field samples were below detection or, when the field samples were corrected for the filter blank, negative concentrations resulted.

High and variable concentrations of copper in air filter samples resulted from air contamination by the air sampler motor armature even though a plastic tube had been used to divert motor exhaust away from the sampler. Consequently, the copper data for air filters were not usable. The deposition samples, which were not collected as close to the air sampler motor, do not appear to be affected by copper contamination.

Metals - Atomic Absorption

Quality control samples including two certified water samples (SLRS and 1643b), three field blanks, certified urban dust (1648), and two matrix spikes were analyzed along with the

deposition samples [Appendix C-12(i)]. The results of quality control samples indicate the analytical methods provided acceptable results. Except for Cr, Ni, and Zn recoveries from the urban dust standard, the recoveries for metals in other standards and spikes were acceptable. The low recoveries of chromium and zinc indicate the digestion method (total recoverable metal) used was not able to completely dissolve these metals in urban dust. The high recovery of nickel is unexplained. However, nickel recovery was acceptable in other standards and matrix spikes. The concentrations of metals in field transport blanks were low compared with the concentrations of metals in field samples.

SUMMARY

Aerosol (PM$_{2.5-50}$)

▸ During the summer, the total particulate mass concentrations were three times higher at the industrial (Alexander Avenue) site than at the marine site (Tyee Marina).

▸ Higher concentrations of crustal elements were observed at the industrial and rural sites than at the two marine sites (Tyee Marina and Brown's Point).

▸ The highest aerosol concentrations of Pb and Zn were measured at the Sea-Land industrial site.

▸ The mean total CPAH concentrations [fluoranthene through benzo(g,h,i,)perylene] were relatively uniform among the sites, except for the background site at Brown's Point, where CPAH concentrations were lower than at the other sites.

▸ The highest total mass concentrations occurred during periods of air stagnation.

▸ During periods of air stagnation, similar total mass concentrations were observed at all sites.

▸ The concentrations of the metals were highly correlated with the total mass concentrations and were, therefore, generally lowest during wet and windy periods and highest during air stagnation episodes.

▸ Concentrations of crustal metals, such as Fe and K, were relatively higher in the summer at the Alexander Avenue site.

▸ During the air stagnation episodes in the fall, the concentrations of Pb and Zn were much higher relative to the concentrations of crustal metals than they were in the summer.

▸ Concentrations of particulate PAHs in the aerosol were approximately an order of magnitude higher during the fall air stagnation episodes than when the total mass concentrations were low.

▸ The mean concentrations of vapor PAHs were considerably higher than the mean concentrations of particulate PAHs. However, the concentrations of the more volatile PAH compounds (naphthalene through fluorene) were underestimated by the sampling and analytical methods used in this study, and some of the particulate PAHs may have broken through during the sampling and been collected on the PUF.

▸ Nutrient, aliphatic hydrocarbon, and PCB data were not adequate for reliable quantitative results.

Deposition

► The deposition rates for all of the metals were greater at the industrial sites. The highest deposition rates for Pb and Zn were at the Sea-Land site.

► The atmospheric deposition of PAHs at the five sites was dominated by the most abundant compounds in the particulate air samples.

► The PAH deposition rates at the Alexander site were five to 10 times higher than those at the Tyee, Morse, or Sea-Land sites. Deposition rates at the Riverside School site were about one-third those at the Tyee, Morse, and Sea-Land sites.

► The highest maximum PAH deposition occurred at the Alexander site in September, while the highest particulate PAH aerosol concentrations occurred throughout the monitoring network in December.

► Higher metals deposition rates occurred in the summer than in the fall.

Chapter 5. Emissions

EMISSION INVENTORY

An emission inventory is a cataloguing of all emissions sources, with information regarding the total mass and specific chemical constituents emitted by each source. It is important to have as accurate and complete an emission inventory as possible to use as input for modeling studies. The diffusion/transport model uses the emission inventory estimates, along with stack parameters such as height and diameter of the stack, temperature and emission rate of the exit gases, and meteorological data to estimate the ambient concentrations of chemicals via the diffusion equations. The chemical mass balance (CMB) or receptor model compares patterns of chemicals from the ambient data (at the receptor) with patterns of chemicals of the possible contributing sources from the emission inventory.

The inventory was compiled for the PM_{10} fraction of emissions (particles with diameters of 10 μm or less), because this is the focus in regulating emissions (and the size class most responsible for human health effects). Most information is available for this size class. This was the size class used in the diffusion/transport modeling and measured during the 18-day receptor modeling study.

Emissions from point sources (industrial emissions) and area sources (mobile sources such as cars, trucks, ships; woodstoves; and road dust) are included in the inventory. Point source information was taken from the PSAPCA registration files, the source profile library, and relevant source tests. Area source estimates originated from PSAPCA's PM_{10} emission inventory for the Tacoma Tideflats. Despite the substantial database for compiling the inventory, the data are limited in representing the spatial and temporal variations of source emissions. In addition, specific source tests were not available for all point sources, so estimates were derived from "generic" profiles in the source profile library. These limitations affect the accuracy of the modeling and will be discussed further in Chapter 8, Comparison of Studies.

The discussion that follows provides an overview of the emissions inventory. An amplified discussion of the computations for the emissions inventory can be found in Appendix D.

Point Sources

PSAPCA Files

Point-source air emission data were taken from PSAPCA's registration files for industrial sources. The information in these files is a combination of actual measured emissions and estimates based on industrial process and facility specifications. Point sources within 12 km of Fire Station No. 12 (located approximately in the center of the Tideflats industrial area) are listed in descending order of emission quantity in Tables 5-1 and 5-2. In Table 5-1 the sources are listed in descending order of PM_{10} emission quantity, because most of the metals and PAHs exist in the environment in the small particles. Indeed, most of the major sources of concern are listed in Table 5-1. However, a few additional sources, which contained no PM_{10} emissions, but might contain chemical emissions of interest, are listed in Table 5-2 in descending order of VOCs.

From PSAPCA files, additional data were compiled on the metal and PAH emissions for the major contributing sources. This information can be found in Appendix D-1. Limitations in these data were addressed by using available source profiles from similar industrial point sources located elsewhere.

Table 5-1. Point Sources for PM$_{10}$

PM$_{10}$ (T/YR)	NAME	FUNCTION
783.9	Simpson	Paper mill
330.2	Kaiser	Aluminum production
52.4	Woodworth	Asphalt paving
44	Buffelen	Hardwood veneer and plywood
43.7	Puget Sound Plywood	Softwood veneer and plywood
42.5	Lone Star Cement	Minerals and earth
42.4	West Coast Door	Millwork
27.9	Continental Lime	Lime
27.9	U.S. Oil and Refining	Petroleum refining
25.4	Continental Grain	Grain
19.8	General Metals	Scrap and waste
17.8	Coastcraft	Millwork
17.1	Domtar Gypsum	Gypsum production
11.8	USG Interiors	Mineral wool
8.9	Tacoma Port Facilities	Marine cargo handling
6.9	Commencement Bay Mill	Sawmill and planing mill
6.3	Canyon Sand and Gravel	Construction
4.5	Scofield George	Ready-mix concrete
3.8	Sound Refining	Petroleum refining
3.6	Canyon Concrete	Ready-mix concrete
1.4	Pacific International	Concrete products
1.3	Kaiser	Aluminum production
1.3	Lianga	Millwork
1.2	Occidental	Alkalies and chlorine
1.0	Harmon	Millwork
0.8	Simon Joseph and Sons	Secondary smelting and refining of nonferrous metals
0.7	Pacific NW Terminals	Marine cargo handling
0.6	Tacoma Public Works	Asphalt paving
0.3	Nalleys	Pickles, sauces and seasonings
0.3	Tacoma Boatbuilding	Shipbuilding and repairing
0.1	Sierra Sandblasting	Heavy construction
0.1	Reichhold Chemicals	Industrial organic chemicals
0.1	Monitor Inc.	Millwork
0.1	Atlas Foundry	Steel Foundry

Figure 5-1. 12-km Diameter Circle Around Fire Station No. 12
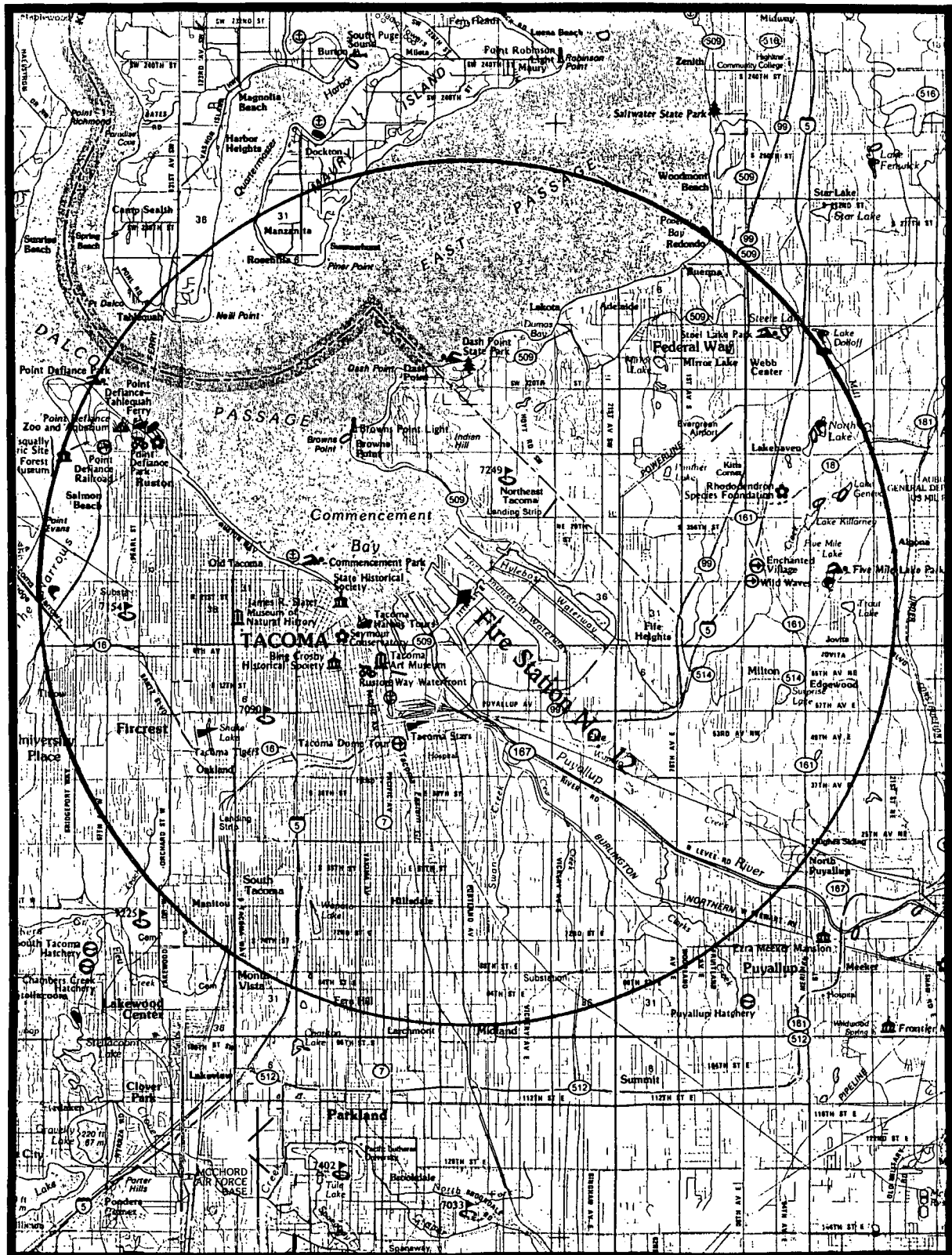
Table 5-2. Point Sources for VOCs

VOC (T/YR)	NAME	FUNCTION
247	Girard Custom Coaters	Wood preserving
41.5	American Reinforced Plastic	Plastic products
28.6	TAM Engineering	Motor vehicle parts/accessory
23.5	Auto Warehousing	Business association
21.1	Overall Laundry	Industrial Launderers
6.0	B.P. Oil	Petroleum bulk station/terminal
4.0	Buckeye Pipeline	Refined petroleum pipeline
3.1	Superior Oil	Petroleum bulk station/terminal
3.0	Unocal	Petroleum bulk station/terminal
2.1	American (Yale)	General industrial machinery
2.3	Pennwalt Inorganic Chemicals	Industrial inorganic chemicals
0.7	Beloit	Fabricated rubber products
0.5	Puget Sound By-Products	Animal/marine fats and oils
0.2	Tacoma Public Works Utility	Sewage systems

Source Profile Library

Source profiles are obtained through emissions testing at the source. A number of sources have been tested in the Northwest and throughout the United States. The source profiles obtained include information on the proportions of various chemicals in the emissions. Source profiles used to estimate metal and PAH emissions in the Tideflats are listed in Appendix D-2. Some of the profiles are based on source tests performed at Tacoma sources. However, some of the profiles are taken from source tests performed at similar sources elsewhere in the country (generic source profiles). Generic source profiles provide some information about metals and PAHs which otherwise may be completely missing from the registration data, but often are not truly representative of the source in question.

Source profiles are usually expressed as a percentage of the total mass contributed by each chemical in the emission. To estimate the emissions of a particular plant, the specific chemical percentages are multiplied by the total mass emissions of the plant to acquire chemical-specific mass emission numbers.

Source Tests

According to the PSAPCA PM_{10} emission inventory, 73 percent of the point source PM_{10} emissions in the Tacoma Tideflats come from the Simpson Tacoma Kraft pulp mill (51 percent) and the Kaiser aluminum refinery (22 percent). Therefore, it seemed particularly important to obtain the best emission information available for these two sources.

There are two sets of chemical source test information for Kaiser Aluminum (see Appendix D-3). Both sets contain general emission information and information on quantities of specific PAHs. Pollution control work has been done at Kaiser to reduce particulate emissions since the 1985 source test. Therefore, the most recent set (1988) is being used to define the emissions from Kaiser. A summary of the Kaiser particle size source test results is included at the end of this chapter.

The source test data on Simpson that were available at the beginning of this project did not have specific information on the PAHs that were of interest for this study. Therefore, a source test was performed on Simpson, with support from Ecology. A discussion of the Simpson source test and the results comprise the second section of this chapter. A description of the sampling procedures and the complete results of this source test are in Appendix D-4.

Area Sources

An area source emission inventory was compiled for the Tideflats industrial area using available 1986 emission estimates from PSAPCA and scaling them up for growth through 1991. To inventory area sources, a grid system was set up for the Tideflats area. The Universal Transverse Mercator (UTM) System was used to define grids with a spatial resolution of 1 km². A detailed discussion and calculations of area source emissions can be found in Appendix D-5.

Residential Heating

Emissions from residential heating are generally correlated with the population density. Therefore, a detailed, block-by-block analysis was made for the Tacoma Tideflats area using the latest census data (1980).

Distillate oil: Data on sales of distillate oil were obtained and adjusted for known usage by all point sources. The remaining fuel was apportioned to each grid by population. PM_{10} emissions were calculated using an emission factor from *Compilation of Air Pollution Emission Factors* (AP-42, Vol. I, pg. 1.3-2 8/82) and assuming a PM_{10} fraction of 50 percent (AP-42, Vol. I, pg. 1.3-6, 10/86) and a population density of 1,000 people per square kilometer.

Residential wood combustion: To estimate PM_{10} emissions from residential wood combustion, data from a study conducted by the Oregon State Department of Environmental Quality was used to derive wood usage. The average usage for all homes was found to be 0.71 cords per year. Emission factors for wood stoves/fireplace inserts and fireplaces were taken from AP-42 (Vol. I, pg. 1.9-3, 5/83), and a PM_{10} fraction of 100 percent was assumed.

To adjust for the colder climate in Tacoma than Portland, the ratio of the climatological average of heating degree days per year was also factored into the calculation.

Railroads

Data on distillate fuel (diesel) usage by switchyard locomotives were obtained from Burlington Northern and Union Pacific. PM_{10} emissions were calculated using these data and an emission factor from AP-42 (Vol. II, pg. II-2-1, 4/73), assuming a PM_{10} fraction of 80 percent.

Ships

Data on ship activity were obtained from the Port of Tacoma. An approximate emission factor from AP-42 (Vol. II, pg. II-3-2, 1/75) and a PM_{10} fraction of 50 percent (AP-42, Vol. I, pg. 1.3-6, 10/86) were used and a 24-hour turnaround time was assumed.

Motor Vehicles

The calculation of exhaust emissions from motor vehicles includes a very slight dependence on the vehicle speed and a strong dependence on the vehicle mix. The emission factors for light-duty cars and trucks are similar. Heavy-duty gasoline vehicles emit roughly three times as much as light-duty vehicles; however, the majority of the total emissions come from heavy-

duty diesel trucks. Even though they constitute only about 10 percent of the vehicles on the road in these areas, they emit nearly 75 percent of the particulate matter.

The method used to compute motor vehicle emissions per grid in the Tacoma Tideflats area involved defining three speed zones (20, 35, and 55 mph), each with its own vehicle mix. The 20-mph zone was chosen to represent downtown and residential traffic (collector streets), and the average vehicle mix that was used was provided by the Washington State Department of Transportation (DOT). The 35-mph zone was chosen to represent the major arterial streets, which, in these areas, have roughly four times as many heavy-duty diesel trucks and twice as many heavy-duty gasoline trucks. The 55-mph zone was chosen to represent highways and freeways, and contained the standard DOT mix.

The procedure used to calculate emission factors is contained in AP-42 (Vol. II, Appendix L, 9/85).

Traffic count data were acquired from the Traffic Engineering Division of the City of Tacoma, and when multiplied by the appropriate length of roadway, these numbers give the vehicle miles traveled (VMT). The product of the VMT per grid and the appropriate emission factors gives the total emissions per grid.

Resuspended Road Dust

The emission factor for road dust is a function of the vehicle speed. High-speed roadways are swept clean by the turbulence induced by the flow of traffic.

Conclusions

Table 5-3 summarizes the results of the PM_{10} area source inventory for the base year 1986. The totals in the table were computed by expanding the example calculations in Appendix D-5 to all area sources for the total Tideflats industrial area. The inventory estimates clearly show the importance of resuspended road dust and motor vehicle exhaust. When calculated as a daily emission rate, the contribution of woodstoves is also important. The emissions from the use of natural gas and distillate oil for residential heating are negligible.

Table 5-3. PM_{10} Area Source Inventory-1986

Source	Tideflats	
	Tons/year	kg/day
Exhaust	58	143
Road Dust	357	887
Ships	9	22
Railroads	6	15
Airplanes	---	---[a]
Woodstoves	18	109
Total	448	1,176

(a) Insignificant

For the 1991 baseline inventory the following growth factors were assumed:

Table 5-4. Growth Factors 1986-1991

Source	Tideflats
Exhaust	+3% per year
Road Dust	+3% per year
Ships	no change
Railroads	no change
Airplanes	N/A
Woodstoves	no change

Growth factors for vehicular sources (i.e., exhaust and road dust) were determined by the Tacoma Traffic Engineering Division based on the rate of growth in traffic volumes over the years 1984-1986.

SIMPSON TACOMA KRAFT SOURCE TEST

Because the Simpson Tacoma Kraft plant is the largest PM_{10} point source in the Tideflats, a source test was performed to update the site-specific metals and PAH emission data. Particulate samples were collected from three emission points at the Simpson plant: the hogged fuel boiler, the No. 1 lime kiln, and the No. 3 recovery furnace. The source testing was started January 2 and completed January 6, 1990.

The methods used were similar to those used for the Pacific Northwest Source Profile Library (PNSPL) study. Samples were analyzed to determine total mass and chemical analyses were performed on the fine fraction using x-ray fluorescence (XRF), ion chromatography, and combustion flame ionization (CFI) for organic and elemental carbon determination.

The PM_{10} size-segregating dilution sampler (SSDS) was used to collect samples from each emission source. Two dichotomous samplers (total of 4 filters) with modified inlet tubes were used to collect both fine and coarse samples from the dilution chamber. In general, the samples were collected downstream of the emission controls on each of the stacks at sample ports routinely used for compliance monitoring. Typical sampling duration was one hour. All source tests included three replicate runs, so that a total of 12 filters were collected for each of the source tests.

The sources were tested under normal operating conditions. The facility had recently gone through a maintenance shutdown, and the sampling was delayed until plant operation returned to acceptable operating conditions. An expanded description of the sampling equipment and sample run conditions can be found in Appendix D-4(a).

Test Results

The laboratory results of the PAH, XRF, and ion chromatography analyses are presented in Appendix D-4(c, d). Laboratory protocols are discussed in Appendix D-4(b).

PAH Analyses

The PAH analyses showed that there was relatively little organic mass in the source test samples. This was indicated by both the organic carbon/total carbon fine mass fraction results and by the mass spectrometer responses. The target quantity for the PAH analyses is 100 μg organic carbon per assay, but there was only 10 μg per assay or less available for the study samples. As a result, most of the analytes were below the lower quantitation limits for the samples, and a limited dynamic range was seen among those analytes that could be detected.

In particular, the five-ring PAH compounds that from previous chemical mass balance analyses were most useful in differentiating among sources of polycyclic organic matter (POM) were below detection limits. This characteristic of these samples is not consistent with previous experience with source tests from Simpson's hogged fuel boilers. It may represent unusually efficient combustion conditions during sampling or some aspect of sample collection or may be the result of major modifications that the Simpson Tacoma Kraft company made to the boilers in 1987 to reduce the emissions of unburned hydrocarbons.

Results from the PAH analyses [Appendix D-4(c)] show very little PAH in the lime kiln samples; n-alkanes in the recovery boiler samples; and carbazole, fluoranthene, pyrene, and retene in the samples from the hogged fuel boiler.

Metals, Ions, and Carbon Analyses

Analysis summaries for metals, ions, and carbon are presented in Appendix D-4(d). All three sources sampled show significant percentages of sodium (26 - 32%), sulfur (9 - 19%), and sulfate (26 - 58%). Of greater interest to this study are the relative emissions of Cu, Pb, Zn, As, and organic carbon (OC).

As shown in Table 5-5, the lime kiln emissions are relatively enriched in lead while the hogged fuel boiler emissions are relatively enriched in the other three metals. Both the hogged fuel boiler and the recovery boiler emissions are relatively enriched in organic carbon.

Table 5-5. Mean Percent of PM$_{10}$ Emissions

Source	Cu	Pb	Zn	As	OC
Hogged Fuel Boiler	.049	.262	.607	.032	2.34
Lime Kiln	.013	.485	.008	.001	.30
Recovery Furnace	.006	.000	.037	.003	1.84

KAISER PARTICLE-SIZE SOURCE TEST RESULTS

Particle-size distribution samples were collected from two roof monitors and units 36 and 37 dry scrubber baghouses at Kaiser Aluminum and Chemical Corporation's plant in Tacoma, Washington, on July 21 through 27, 1988. Three to six particle-size distribution samples were collected at each site. The average sampling period for each of the samples collected was approximately 20 hours. The results of these tests are presented in Table 5-6.

Table 5-6. Kaiser Particle-Size Distribution Source Test Results - July, 1988

Line I Monitor		Line IV Monitor		Dry Scrubber Baghouses	
Run No.	%PM$_{10}$	Run No.	%PM$_{10}$	Unit-Stack-Run No.	%PM$_{10}$
1	13.3	1	32.7	36-2-1	32.6
2	11.5	2	35.7	36-2-1	27.2
3	18.8	3	43.9	36-2-3	28.5
1-Special	18.9			36-2-4	16.9
2-Special	18.0			37-2-1	27.4
3-Special	19.4			37-2-2	32.9
				37-2-3	38.2
				37-2-4	17.5
				36-1-1-Special	25.9
				36-2-2-Special	32.9
				36-2-3-Special	38.2
Average (%)	16.7		37.4		27.7

[Average for Monitors: 27.0%]

The results of the size distribution test show that the average percentage of particulate matter with an aerodynamic diameter of less than 10 μm (PM$_{10}$) was 27 percent. Therefore, the Kaiser emissions consisted mainly (over 70 percent) of particles larger than 10 μm in diameter.

Chapter 6. Receptor Modeling Study

OBJECTIVES

▶ Conduct 18-day ambient monitoring of PM_{10} particulates and volatile organic compounds.

▶ Using source test information and known chemical "fingerprints" for emission sources, run receptor or chemical mass balance (CMB) model to apportion sources of ambient aerosol.

Receptor or chemical mass balance (CMB) modeling uses mathematical tools and chemical information on the ambient aerosol and its sources to determine the contributions of major sources of pollutants to the total particulate mass at a "receptor" site. Receptor modeling generally focuses on the fine particles (<2.5 μm) of the ambient aerosol, as this fraction is transported most broadly in the atmosphere and is primarily a product of combustion or other human activities.

AMBIENT MONITORING

The receptor modeling was supported by an 18-day ambient monitoring study conducted at the Alexander Avenue and Morse Industrial Supply sites from December 5, 1989 to December 16, 1989, and from January 2, 1990 to January 8, 1990. Alexander Avenue and Morse Industrial Supply are located within 3.5 km of each other (Figure 2-2).

Each site was equipped with two dichotomous PM_{10} samplers and a VOC (volatile organic compound) canister sampler. Two dichotomous samplers with two types of filter media (quartz and Teflon) were needed to accommodate the variety of analytical techniques performed. Twelve-hour day and night samples were obtained of fine- (<2.5 μm) and coarse- (2.5-10 μm) particle metals, fine-particle ionic species, fine-particle organic and elemental carbon, and VOCs. VOCs were monitored concurrently with fine particles to determine whether any of the VOCs could serve as a tracer for mobile sources. (Although, lead has been used as a tracer for mobile sources in the past, it is being phased out of the fuel supply, so an alternate tracer is needed.) A detailed discussion of the sampling and analysis equipment that was used and the types of analyses that were performed for this study is presented in Appendix E-1.

Analytical Results of 18-Day Field Study and Discussion

Average Composition

A detailed compilation of all results can be found in Appendix E. Average fine-particle concentrations of organic carbon, elemental carbon and ionic species measured at the two sampling sites are presented in Tables 6-1 (a) and (b). Averages are given for daytime (7 a.m. to 7 p.m.), nighttime (7 p.m. to 7 a.m.), and all samples (day and night combined) for each sampling site. Chemical species with average measurement uncertainty of 30 percent or less for at least one of the sites are included in this summary. A compilation of all fine-particle data can be found in Appendix E-2.

Average coarse-particle species concentrations are presented in Tables 6-2 (a) and (b). Only data on total mass and ionic species are available for the coarse particles. Averages are given for daytime, nighttime, and all samples (day and night combined) for each sampling site. Species with average measurement uncertainty of 40 percent or less for at least one of the sites are included in this summary. All coarse-particulate data can be found in Appendix E-3.

Table 6-1(a). Average Fine-Particle Species Concentrations at the Alexander Avenue Site

Parameter[a]	Method[b]	Mean Concentration, ng/m³			Uncertainty
		Day	Night	All	All
Mass	GRAV	21900	21800	21800	2%
OC	THERM	8500	8700	8500	7%
EC	THERM	2300	1200	1700	19%
NO_3^-	IC	1200	920	1000	17%
$SO_4^=$	IC	2600	1800	2100	12%
Al	XRF	143	816	480	20%
S	XRF	937	709	823	8%
Cl	XRF	173	182	177	10%
K	XRF	105	128	116	9%
Ca	XRF	49	28	39	14%
Mn	XRF	24	15	19	15%
Fe	XRF	181	64	123	13%
Cu	XRF	31	26	28	17%
Zn	XRF	51	33	42	14%
Br	XRF	7.0	7.3	7.2	28%
Pb	XRF	32	23	27	19%

[a]Mass = fine particle mass; OC = organic carbon as carbon; EC = elemental carbon.

[b]GRAV = gravimetry; THERM = thermal-optical; IC = ion chromatography; XRF = X-ray fluorescence.

Table 6-1(b). Average Fine-Particle Species Concentrations at the Morse Supply Site

Parameter[a]	Method[b]	Mean Concentration, ng/m³			Uncertainty
		Day	Night	All	All
Mass	GRAV	24700	23000	23800	2%
OC	THERM	10600	10300	10200	7%
EC	THERM	2400	1500	1900	19%
NO_3^-	IC	1400	1200	1200	11%
$SO_4^=$	IC	2300	1800	1900	22%
Al	XRF	136	148	142	80%
S	XRF	879	708	793	8%
Cl	XRF	226	251	238	9%
K	XRF	146	175	161	8%
Ca	XRF	55	28	41	13%
Mn	XRF	41	18	29	12%
Fe	XRF	289	89	189	12%
Cu	XRF	10	5	8	42%
Zn	XRF	51	30	41	14%
Br	XRF	8.7	7.5	8.1	23%
Pb	XRF	45	27	36	17%

[a]Mass = fine particle mass; OC = organic carbon as carbon; EC = elemental carbon.

[b]GRAV = gravimetry; THERM = thermal-optical; IC = ion chromatography; XRF = X-ray fluorescence.

Table 6-2(a). Average Coarse-Particle Species Concentrations at the Alexander Avenue Site.

| Parameter[a] | Method[b] | Mean Concentration, ng/m^3 | | | Uncertainty |
		Day	Night	All	All
Mass	GRAV	8500	4600	6600	4%
Al	XRF	459	203	331	42%
Si	XRF	1092	428	760	39%
S	XRF	194	137	165	21%
Cl	XRF	358	302	330	19%
K	XRF	64	41	53	16%
Ca	XRF	313	125	219	9%
Mn	XRF	10.4	6.6	8.0	30%
Fe	XRF	450	156	303	11%
Cu	XRF	18	12	15	23%
Zn	XRF	27	17	22	27%
Cr	XRF	3.2	1.0	2.1	148%

[a]Mass = coarse particle mass.

[b]GRAV = gravimetry; XRF = X-ray fluorescence.

Table 6-2(b). Average Coarse-Particle Species Concentrations at the Morse Supply Site

Parameter[a]	Method[b]	Mean Concentration, ng/m³			Uncertainty
		Day	Night	All	All
Mass	GRAV	13000	6900	9600	4%
Al	XRF	1660	1169	1428	30%
Si	XRF	1373	528	951	29%
S	XRF	154	140	147	22%
Cl	XRF	394	370	381	17%
K	XRF	82	58	70	15%
Ca	XRF	336	124	230	9%
Mn	XRF	15	7.2	11	21%
Fe	XRF	636	234	435	10%
Cu	XRF	13	5.2	8.8	33%
Zn	XRF	30	16	22	17%
Cr	XRF	9	4	6	40%

[a]Mass = coarse particle mass.

[b]GRAV = gravimetry; XRF = X-ray fluorescence.

For some of those species with <u>average</u> measurement uncertainty greater than 30 percent, there were individual samples with uncertainties of much less than 30 percent. For example, fine-particle aluminum concentrations during three nighttime sampling intervals at the Alexander Avenue site averaged greater than 1 $\mu g/m^3$ with an associated uncertainty around 15 percent. These samples were associated with light southeast winds or stagnant air conditions. The Kaiser aluminum plant is 1 km southeast of the Alexander Avenue sampling site. Fine-particle aluminum concentrations were not similarly high at the Morse Industrial Supply sampling site on those or any sampling intervals. Conversely, coarse-particle aluminum concentrations on many sampling days were much higher and measured with lower uncertainty at the Morse Supply site than at the Alexander Avenue site. Because aluminum is the most abundant metal found in the earth's crust in addition to being an aluminum smelter product, the high coarse-particle aluminum concentrations (and high total coarse-particle mass) at the Morse Supply site may indicate more resuspended soil dust at that site. Samplers were set up on a platform at this site, and thus were closer to the ground than the Alexander Avenue site samplers, which were located on the rooftop of a one-story building.

VOC data are summarized in Tables 6-3 (a) and (b) for those species where no more than 30 percent of the samples were below the detection limit. In cases where VOC data were below the detection limit, the concentration was set equal to zero (plus or minus the detection limit) for the averaging process. VOC data for all samples are tabulated in Appendix E-4.

Tables 6-1 to 6-3 show that the Morse Supply site tended to have somewhat higher concentrations of most fine- and coarse-particle constituents and VOCs. One reason for this is that there may be more vehicle traffic to resuspend dust near the Morse Supply site, because it is closer to arterial grids that have higher traffic usage than the Alexander Avenue site. Exceptions to the higher concentration at Morse Supply include fine-particle copper concentrations, which were nearly four times higher at the Alexander Avenue site than at the Morse Supply site. Coarse-particle copper was also higher at the Alexander Avenue site. The elevated copper concentrations are most likely an artifact resulting from the operation of an adjacent sampler with a type of motor containing copper wire brushes. These motors are known to eject copper particles during their operation. A similar sampler was operated at the Morse Supply site, but it was not immediately adjacent to the PM_{10} samplers.

Coarse-particle iron concentrations were twice as high at the Alexander Avenue site as at the Morse Supply site, while fine-particle iron was about 50 percent higher at the Morse Supply site. Coarse-particle chromium was about three times higher at the Morse Supply site than at the Alexander Avenue site. Given the relatively close proximity of the two sampling sites, these observations indicate that there were local activities contributing to some of the differences seen in the specific composition of ambient air measured at each of the sites.

At both sites, the most outstanding feature of the data is the amount of fine-particulate organic carbon compared with the total fine particles. Figures 6-1 and 6-2 show the relative contributions of the major constituents of the fine-particle mass at the Alexander Avenue and Morse Supply sampling sites. Organic carbon concentrations were multiplied by 1.4 to account for the hydrogen and oxygen which, together with organic carbon, constitute the average organic compounds in the ambient air (Countess et al., 1980; Shah et al., 1984). The average composition was about the same at each site, with organic compounds accounting for over one-half of the fine-particle mass.

Table 6-3(a). Average VOC Concentrations at the Alexander Avenue Site

	Mean Concentration, ppb			Uncertainty
	Day	Night	All	All
Dichlorodifluoromethane	0.72	1.26	0.99	9%
Trichlorofluoromethane	0.74	0.76	0.75	15%
1,1,1-Trichloroethane	0.62	0.51	0.57	3%
Benzene	2.24	2.03	2.14	8%
Carbon Tetrachloride	0.10	0.097	<0.1	14%
2,2,4-Trimethylpentane	0.28	0.21	0.24	7%
Toluene	4.57	3.79	4.18	9%
Ethylbenzene	0.76	0.53	0.65	6%
m,p-Xylene	2.91	2.05	2.48	4%
o-Xylene	1.02	0.74	0.88	5%
4-Ethyltoluene	0.25	0.18	0.22	14%
1,3,5-Trimethylbenzene	0.23	0.19	0.21	11%
1,2,4-Trimethylbenzene	0.77	0.58	0.67	13%

Table 6-3(b). Average VOC Concentrations at the Morse Supply Site

	Mean Concentration, ppb			Uncertainty
	Day	Night	All	All
Dichlorodifluoromethane	2.03	0.62	1.32	15%
Trichlorofluoromethane	0.74	0.68	0.71	8%
1,1,1-Trichloroethane	0.75	0.50	0.62	2%
Benzene	3.30	2.50	2.90	6%
Carbon Tetrachloride	0.11	0.11	0.11	9%
2,2,4-Trimethylpentane	0.41	0.31	0.36	6%
Toluene	6.94	4.80	5.82	6%
Ethylbenzene	1.04	0.69	0.86	3%
m,p-Xylene	3.86	2.56	3.21	2%
o-Xylene	1.36	0.92	1.14	3%
4-Ethyltoluene	0.34	0.23	0.29	14%
1,3,5-Trimethylbenzene	0.33	0.25	0.29	4%
1,2,4-Trimethylbenzene	1.04	0.76	0.90	6%

Figure 6-1. Major Constituents of Fine-Particle Mass at the Alexander Avenue Site
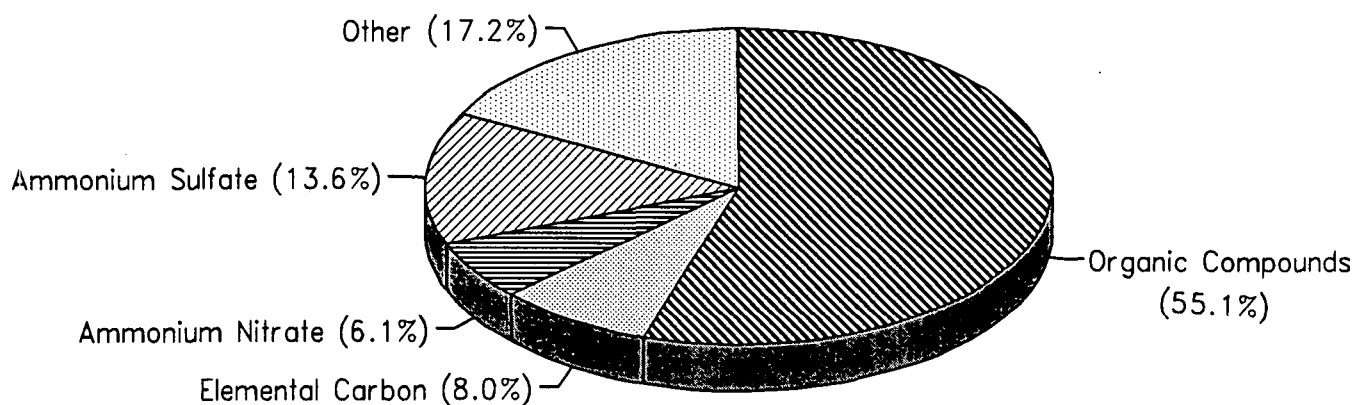
Figure 6-2. Major Constituents of Fine-Particle Mass at the Morse Supply Site
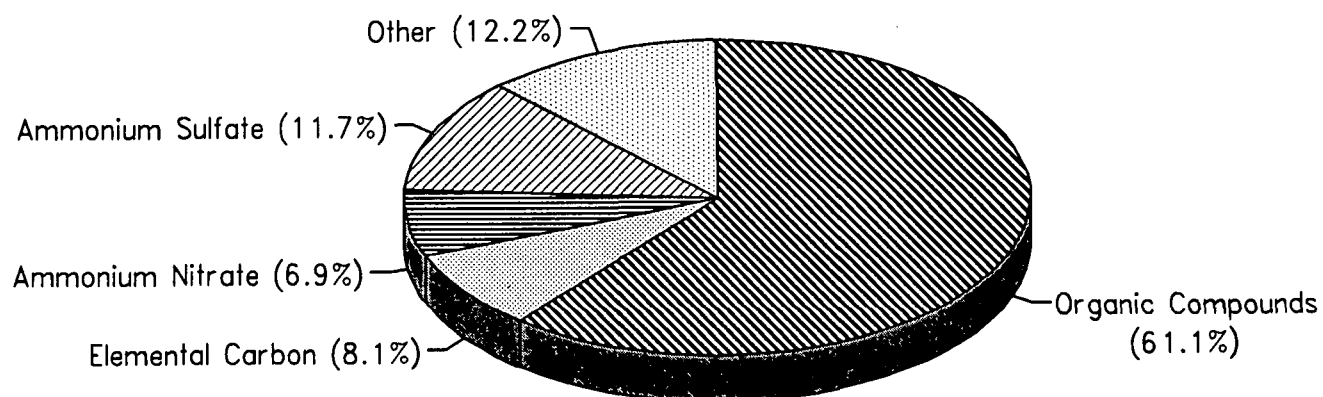
Ion chromatographic data for nitrate and sulfate were corrected to reflect their possible association with the ammonium ion. If sulfate existed as un-neutralized sulfuric acid, its contribution to fine mass would be 25 percent less than the fully neutralized ammonium sulfate. As no precautions were taken to preserve the original acidity of the sample, the maximum neutralization was assumed for the calculations. Even so, sulfate expressed as ammonium sulfate was a distant second in the contribution to fine-particle mass at only 13 percent on average.

On average, 15 percent of the fine-particle mass falls in the "other" category. This category includes metals plus other elements associated with them (such as oxides and anions). It may also include water associated with species in the fine fraction.

Meteorological Conditions

As described in Chapter 3, meteorological data were collected throughout the study from a 10-meter meteorological instrument tower at the Alexander Avenue site. Average conditions for each 12-hour sampling period are presented in Appendix E-5. During the December 5 to 15 and January 2 to 8 sampling intervals, very different meteorological conditions prevailed. The December sampling days were, with few exceptions, under fairly stagnant conditions with little or no precipitation. Fine-particle concentrations averaged 30.3 ± 0.6 $\mu g/m^3$ during this period. By contrast, the January sampling days were associated with higher wind speeds, more precipitation, and lower fine-particle loadings (10.2 ± 0.2 $\mu g/m^3$). Winds during the entire study were most often from the southeast or the south. There were some important exceptions which had a considerable influence on the mass loadings observed. A more thorough analysis is given in the following sections.

Temporal Variations of Key Parameters and Correlations Between Sites

Figures 6-3 to 6-7 show the temporal variation of some of the chemical species measured in this study. The total fine particle mass at each site tracked one another quite well. This is not unreasonable because of the close proximity (3.5 km) of the two sampling sites. Organic carbon and fine-particle mass data correlated quite well [correlation coefficient (r) = 0.96 in a linear regression comparison]. This is a consequence of the fact that an average of 58 percent of the fine-particle mass was composed of organic carbon compounds. The similarity of these two parameters also serves a quality assurance role because the underlying analytical procedures (gravimetric and thermal-optical) are fundamentally different. The similar temporal patterns of all of the fine-particle species shown indicate the overriding influence of meteorology on fine-particle concentrations. As discussed earlier, coarse particles exhibited more distinct differences between the sites, which may be a reflection of both local emission sources and differences in height of the samplers.

The highest concentrations of fine mass (42 $\mu g/m^3$) and organic carbon (18 $\mu g/m^3$) found during the 18-day study occurred between December 9 (p.m.) and 15 (a.m.). This approximately corresponds to the time period (December 9 to 13) when the hogged-fuel boiler and most other components of the Simpson Tacoma Kraft plant were not operating (see Figure 2-2 for location of Simpson point source.) This is also a time period associated with the most stagnant air conditions of the study. The winds were mostly from the southeast, following the flow through the valley toward the bay. During this time period, the organic carbon concentration dropped from its otherwise high levels twice (see Figure 6-7.) These lower concentrations (though not as low as the average for the study) occurred on days when the winds had a northerly or northeasterly component.

Figure 6-3. Fine-Particle Mass Comparison of Alexander Avenue and Morse Supply Sites versus Sampling Interval
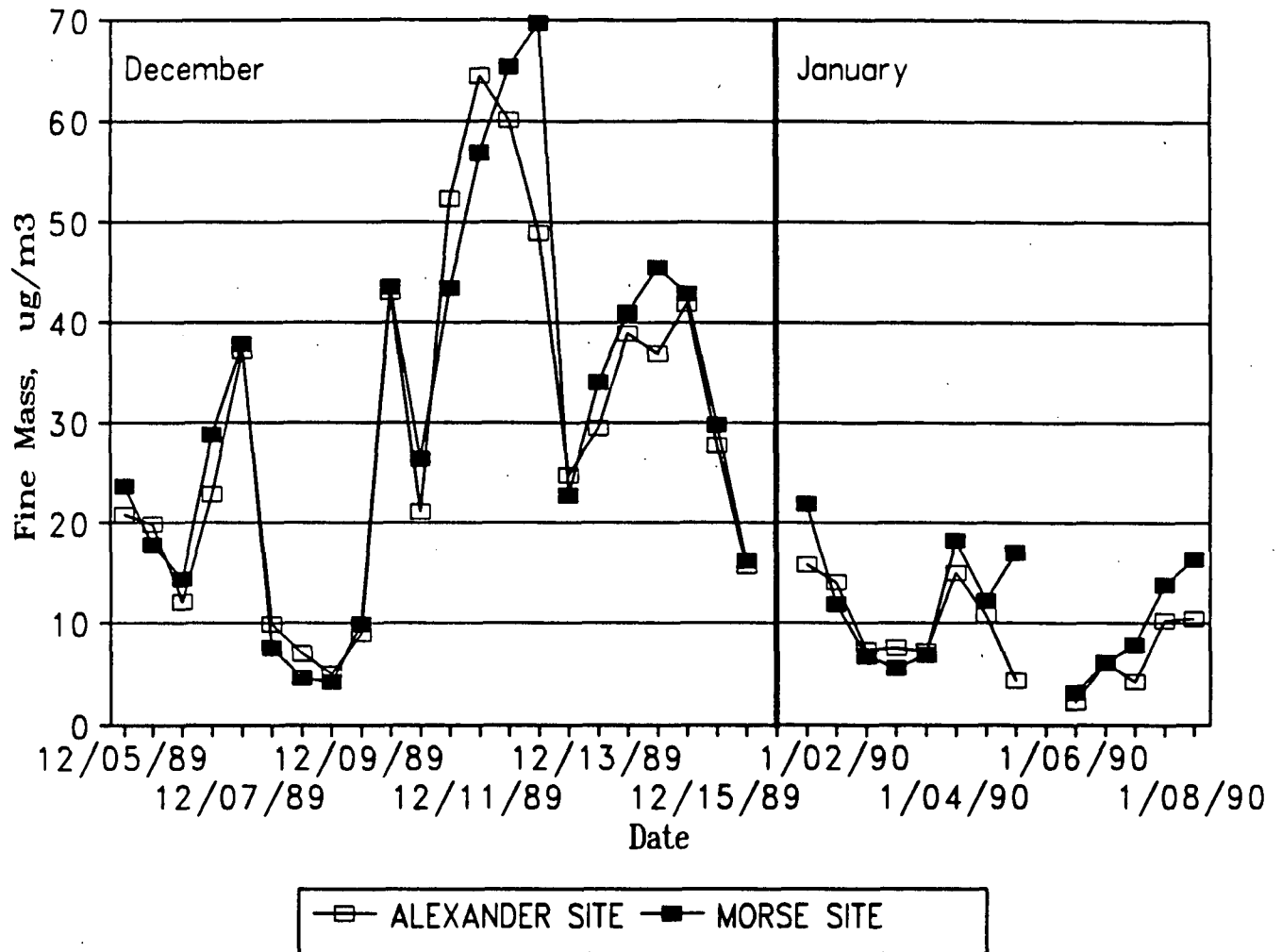
Figure 6-4. Coarse-Particle Mass Comparison of Alexander Avenue and Morse Supply Sites versus Sampling Interval
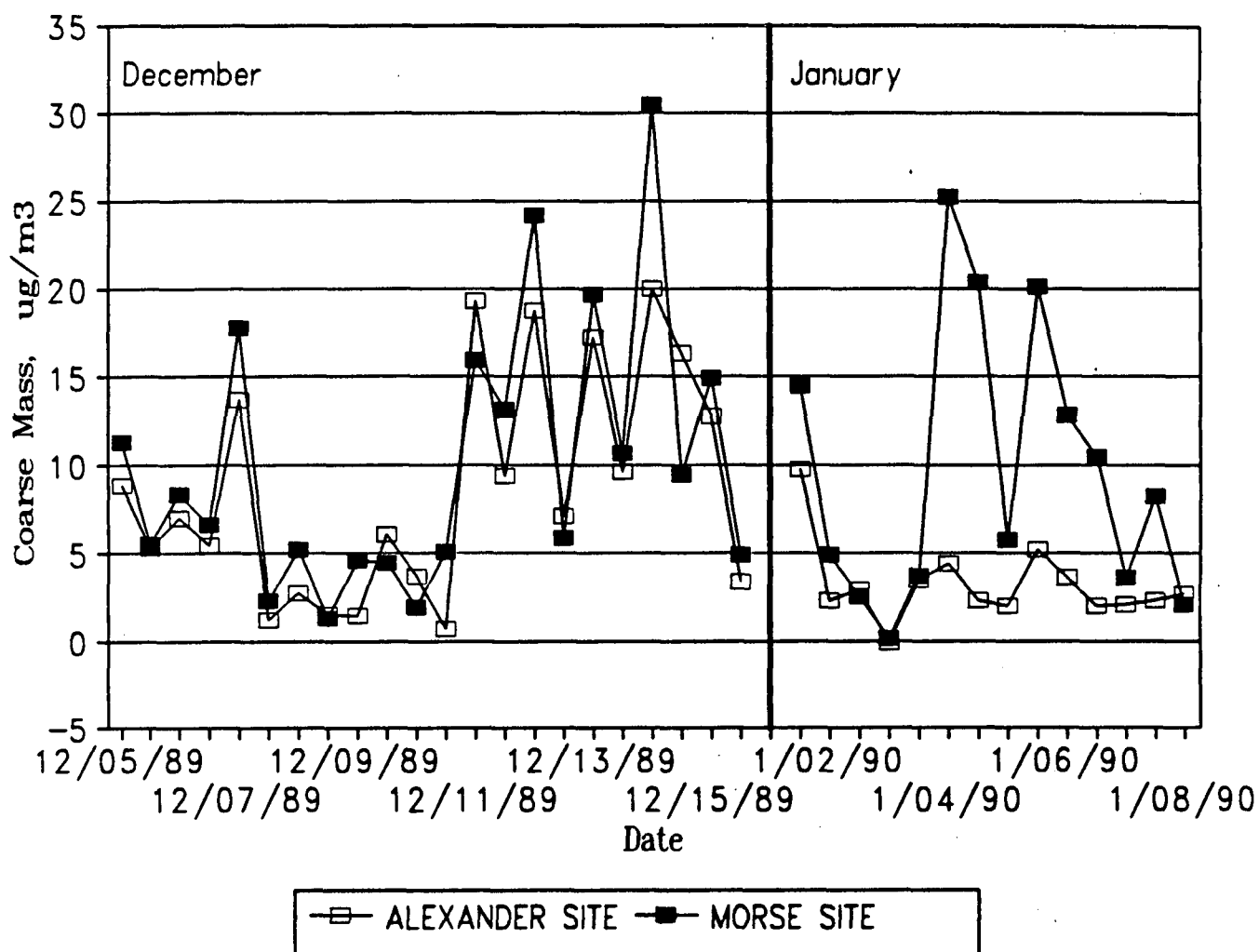
Figure 6-5. Fine-Particle Elemental Carbon Comparison of Alexander Avenue and Morse Supply Sites versus Sampling Interval
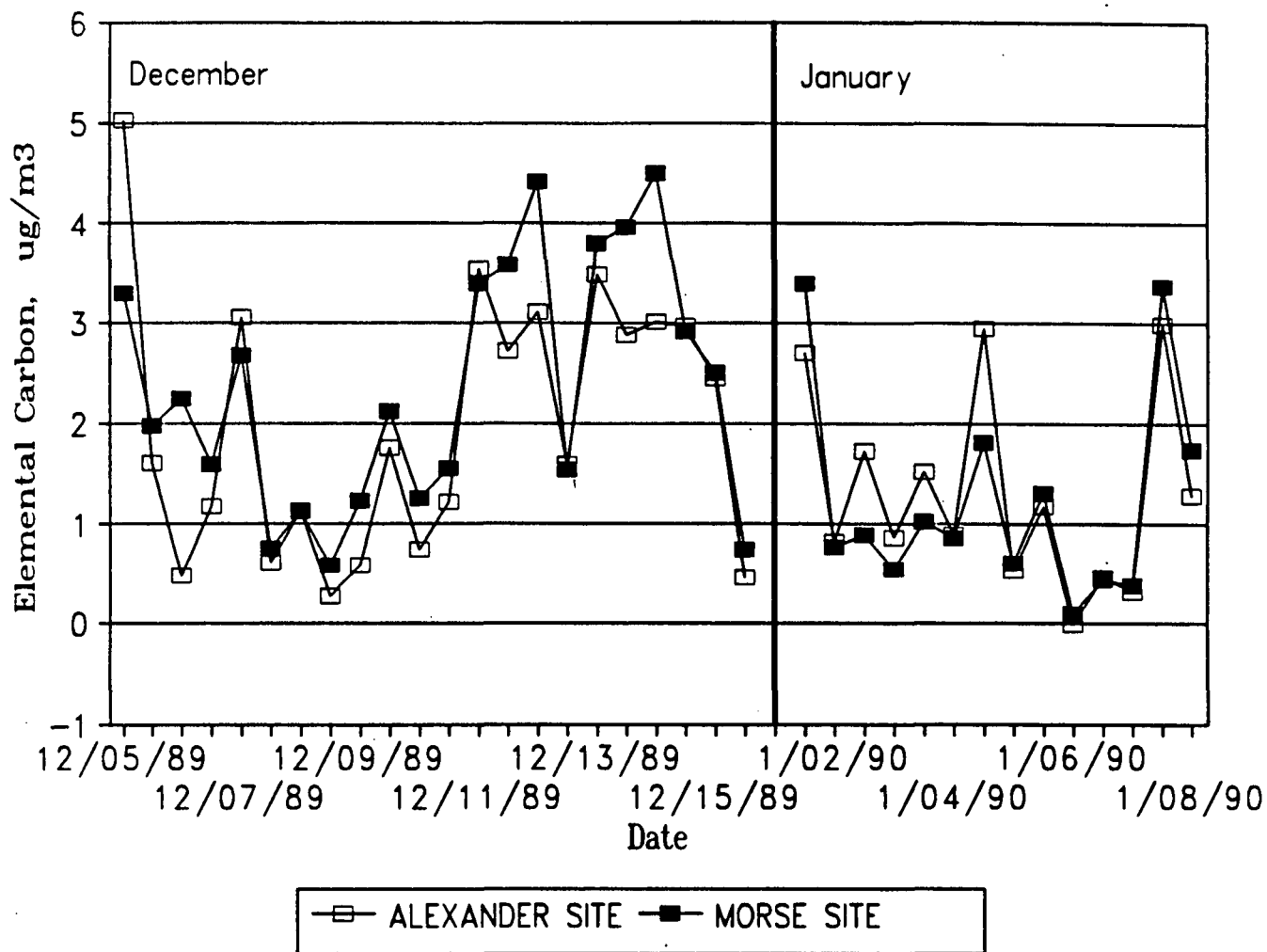
Figure 6-6. Fine-Particle Sulfate (by Ion Chromatography) Comparison of Alexander Avenue and Morse Supply Sites versus Sampling Interval
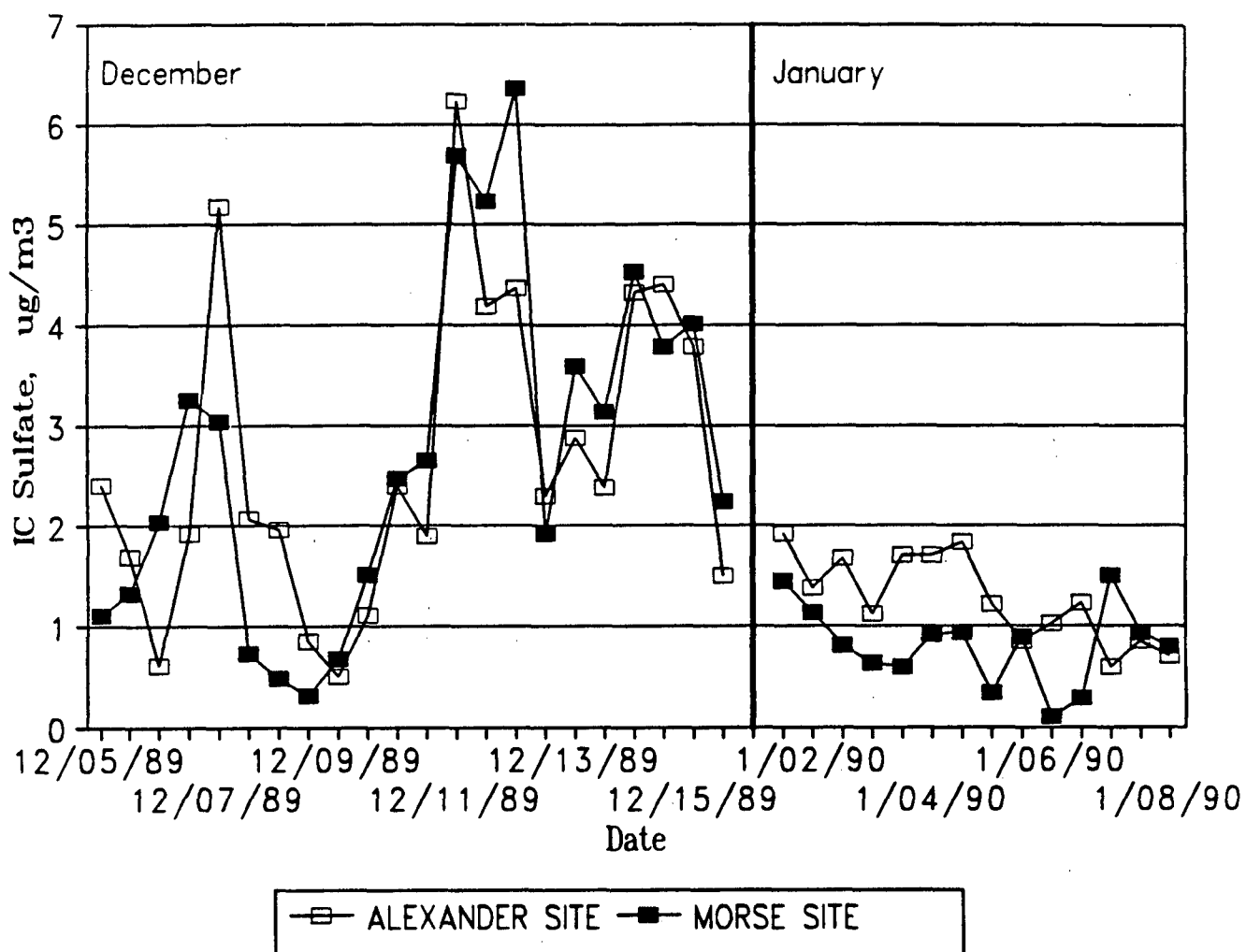
Figure 6-7. Fine-Particle Organic Carbon Comparison of Alexander Avenue and Morse Supply Sites versus Sampling Interval
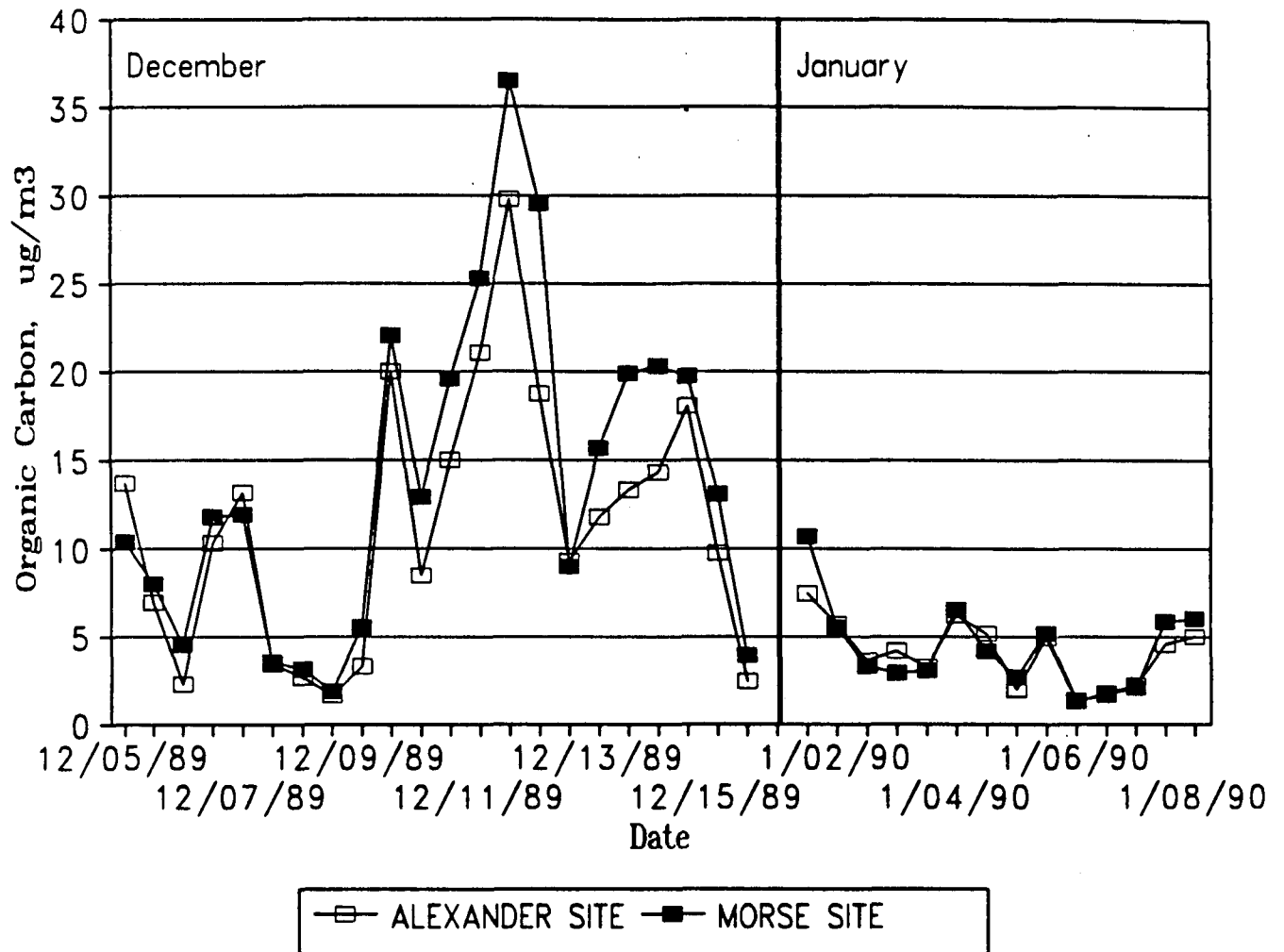
In December, a period of very low fine mass and organic carbon concentrations occurred from December 7 (nighttime) to December 9 (daytime). This period was associated with precipitation and with higher wind speeds with a southerly or southwesterly component. The January sampling days were associated with precipitation, higher winds, and much lower filter loadings of fine particles. Coarse-particle concentrations at the Morse Supply site were generally higher than at the Alexander Avenue site, especially during the January sampling period.

Appendix E-6 contains figures with concentrations measured at the Morse Supply site plotted versus concentrations measured at the Alexander Avenue site. All figures show very good correlations between the two sites [correlation coefficient (r) = 0.92 or greater], with somewhat higher concentrations measured at the Morse Supply site.

PAH Results

Total ion chromatograms and peak identifications for PAHs appear in Appendix E-7. All identifications are based on automated searches of mass spectral libraries and should be considered tentative. Tentative identifications were confirmed with selected ion monitoring (SIM). The results of this analysis are also in Appendix E-7. Analyses were difficult because PAH levels were near the detection limits of the instruments. The quantitative results should be considered as not better than ±50 percent. The qualitative identifications are somewhat uncertain due to the constant loss of chromatographic performance caused by the high levels of nonvolatile material in the extracts. PAHs may also have been missed due to interferences or shifting retention times. Data with less uncertainty are required for receptor modeling applications, therefore the PAH data acquired in this study were not used further.

Motor Vehicle Tracers - Lead

Lead and/or bromine have traditionally been used as tracers for motor vehicles. The correlation between fine lead and bromine at the two sampling sites was generally good (r = 0.88), though not as good as in past studies (Lewis et al., 1988a). As indicated in Tables 6-1 (a) and (b), lead concentrations followed a weak diurnal pattern, with the higher concentrations mostly occurring during the day when total motor vehicle use is at the highest. Elemental carbon followed a similarly strong diurnal pattern, while total fine particles did not. Elemental carbon could be a component of automobile emissions, especially for diesel powered vehicles. A bromine-to-lead ratio in the range of 0.3 to 0.4 in urban areas (Lewis et al., 1986; Koutrakis and Spengler, 1987) is consistent with concentrations of lead and bromine originating from motor vehicles (this ratio is not expected to change as the total amount of lead is reduced in the fuel supply). During this study, the ratio averaged 0.24 ± 0.07, which is somewhat low, but still within range to be representative of motor vehicles. These findings, coupled with sufficient loadings of lead, indicate that lead may be used as a tracer for motor vehicles in this study. The low bromine-to-lead ratio indicates there may be a source of lead other than automobiles.

Motor Vehicle Tracers - Volatile Organic Compounds (VOCs)

Several VOCs were identified as candidates for tracers of fine-particle carbon and extractable organic matter (EOM) from mobile sources as part of a wintertime air pollution study in Boise, Idaho in 1986 and 1987 (Stevens et al., 1989; Zweidinger et al., 1990). Two of those candidate tracers, which were also measured in this study, are o-xylene and 2,2,4-trimethylpentane. In the Boise study, ambient concentrations of a candidate VOC were required to have a high correlation with ambient concentrations of fine-particle lead. Furthermore, the VOCs had to have a low correlation with soil-corrected fine-particle potassium, which has been shown to be a tracer of woodsmoke (Lewis and Einfeld, 1985). The latter requirement is necessary to exclude VOCs highly correlated with combustion sources other than motor

vehicles. Assuming lead is still a reasonable tracer for motor vehicles, this same approach can be used for the Tacoma Tideflats data.

Calloway et al. (1989) showed that water-soluble potassium represents the nonsoil derived potassium in the fine fraction. It is likely that potassium is formed in water-soluble form by all combustion sources that produce potassium. Usually the amount of potassium from windblown soil is greater than potassium from other sources. Furthermore, windblown soil is concentrated in the coarse-particle fraction, with some contamination in the fine fraction, so the coarse-particle potassium concentration should be higher than the fine-particle potassium concentration if soil is the dominant source of potassium. Tables 6-1 (a) and (b) and 6-2 (a) and (b) show that the fine-particle potassium concentration was more than twice the coarse-particle potassium concentration, suggesting that soil was not the dominant source of potassium. Therefore, the correction for potassium originating from soil should be small.

The correction is made using the ambient coarse-particle potassium-to-iron (K:Fe) ratio as the best estimate of the ratio in local soil. In this data set, that ratio was quite variable (± 120 percent), indicating that there may have been a nonsoil component in either the coarse potassium or coarse iron. This is entirely possible in such an industrial area. If this nonsoil, nonwoodsmoke, coarse-particle K:Fe ratio is the same as in the fine fraction, the correction is still valid. There is no way to check that assumption with this data base.

Soil-corrected potassium, represented by K', is calculated using the method described by Lewis and Einfeld (1985):

$$[K'] = [K]_{fine} - [K:Fe]_{coarse} \cdot [Fe]_{fine}$$

where [K] and [Fe] are the ambient fine or coarse-particle potassium and iron concentrations. Because of the large coarse K:Fe variation, individual sample ratios were applied to corresponding fine-particle data.

In the Tacoma Tideflats airshed, both residential and industrial woodsmoke, as well as other nonmotor vehicle combustion sources, may contribute to the nonsoil potassium in the fine-particle fraction. Motor vehicles have a negligible contribution to fine-particle potassium. Unfortunately, there are no data that show the water-soluble potassium content of other major sources in the airshed. Table 6-4 indicates that K' varied diurnally, with higher concentrations occurring at night. This may indicate a significant residential woodsmoke source contribution.

Table 6-4. Average Concentrations of Soil-Corrected Potassium, K'

	Alexander (AS) Avg. K', ng/m³	Morse (MS) Avg. K', ng/m³
Day	78 ± 11	109 ± 16
Night	108 ± 12	148 ± 17
All	93 ± 11	128 ± 16

The correlation between the VOCs and fine-particle lead and K' is presented in Table 6-5. The VOCs measured in this study (with less than 30 percent of the measurements below detection) are listed in descending order of their squared correlation coefficients with lead. Benzene tops the list, but benzene also has the highest correlations with K' and is not expected to be a reliable mobile source tracer. The Boise study indicates that woodsmoke may have significant benzene and toluene components. O-xylene was ranked third in correlation with lead and had a reasonably low correlation with K'. It is thus confirmed as a possible mobile source tracer.

The other promising mobile source tracer identified from the Boise data, 2,2,4-trimethylpentane, was measured at low levels in this study and had a fairly high correlation with K'. Both o-xylene and 2,2,4-trimethylpentane were mildly diurnal, with higher concentrations occurring during the day.

Table 6-5. Correlations of VOCs with Lead and K'(N=71)

VOC	Pb (r^2)	K' (r^2)	VOC avg. ppb
Benzene	0.819	0.455	2.52
Toluene	0.799	0.386	5.00
o-Xylene	0.779	0.334	1.01
1,2,3-Trimethylbenzene	0.770	0.366	0.79
2,2,4-Trimethylpentane	0.758	0.437	0.30
m,p-Xylene	0.757	0.303	2.84
4-Ethyltoluene	0.752	0.349	0.25
Ethylbenzene	0.751	0.311	0.76
1,3,5-Trimethylbenzene	0.699	0.334	0.25
1,1,1-Trichloroethane	0.565	0.268	0.60
Trichlorofluoromethane	0.414	0.326	0.73
Dichlorodifluoromethane	0.016	0.009	1.16
Carbon tetrachloride	0.0017	0.0002	0.10

RECEPTOR MODELING RESULTS

Source Apportionment by Chemical Mass Balance

EPA's CMB model, version 7 (Watson et al., 1990), was used to apportion fine-particle chemical species measured at the sampling sites to sources which may have been impacting those sites. The CMB model consists of a least squares solution to a set of linear equations which expresses each measured concentration of a chemical species i (C_i) as a linear sum of products of the abundance of i as emitted by source j (A_{ij}) and the total mass concentration due to source j (M_j):

$$C_i = \Sigma \ A_{ij}M_j + e_i,$$

where e_i is the residual that represents the difference between the measured and calculated concentrations. This equation is solved for M_j by minimizing Chi^2 in the expression:

$$Chi^2 = \Sigma \ e_i^2/E_i^2,$$

where E_i is the effective variance, which represents uncertainty in both A_{ij} and C_i. The set of abundances of all species (i) as emitted by source (j) represents the "source profile" of source (j).

In performing a CMB, it is assumed that: (1) the abundance of a species (i) used in the fitting procedure is known for each source type; and (2) all major sources of each species (i) must be included in the CMB. Usually, there are more species (i) fitting the above criteria than there are sources.

Based on 1988 PM_{10} emissions data for the Tacoma Tideflats, the Simpson Tacoma Kraft Company and the Kaiser Aluminum and Chemical Corporation are by far the largest point sources in the area. It is presumed that a large fraction of the PM_{10} emissions, which are from combustion sources, are in the fine-particle (<2.5 μm) mode. Simpson operates a hogged fuel boiler which is responsible for much of the Simpson PM_{10} emissions. Kaiser emits particles through the roof monitors and baghouses. However, less than 30 percent of the Kaiser emissions are less than 10 μm in diameter (see Chapter 5). Other major point sources include two veneer and plywood manufacturers and a petroleum refinery.

Major area sources are expected to be residential woodsmoke and motor vehicle exhaust. Motor vehicle exhaust is a mix of emissions from leaded-fuel vehicles, unleaded-fuel vehicles, and diesel-operated equipment.

Most of the major area and point sources in the Tacoma Tideflats airshed emit nonnegligible amounts of fine-particle organic carbon (e.g., motor vehicles, woodstoves, residual oil burning, aluminum production, and veneer dryers), and there are multiple sources of potassium (hogged fuel boilers and woodstoves) and elemental carbon (diesel vehicles, woodstoves, and residual oil). Species such as chlorine and bromine should only be used as fitting species if absolutely necessary, as they may not be stable on particles. Thus, resolving individual source types in the Tideflats airshed presented a considerable challenge. In terms of the chemical mass balance equation, the problem was underdetermined, so the fine-particle mass apportionment could not be accomplished by CMB alone. Other indirect methods of apportioning some of the sources were implemented. Motor vehicle sources were apportioned by alternate methods in addition to CMB because the source profile of the average vehicle mix is not well known.

Description of Sources

The following components were included in the CMB calculations for fine particles: residential woodstoves, hogged fuel boilers, aluminum production (one site only), residual oil boilers, scrap metal fugitives, and motor vehicle exhaust. For the Alexander Avenue site, all source types listed were included in the CMB calculation. The species used in the Chi^2 minimization were either Al, Cl, K, Zn, and Pb or VOCs, OC, and SO_4^-. For the Morse Supply site samples, the aluminum production source was not included because it produced a poor fit, and because fine aluminum was near detection limits and thus had high uncertainties. The Morse Supply site is farther from the Kaiser aluminum plant than the Alexander Avenue site and was not downwind as often. In this case, the species used in the Chi^2 minimization were Cl, K, Zn, and Pb or VOCs, OC, and SO_4^-. Attempts were made to include an urban dust (or crustal dust) source category, but it contributed insignificantly to fine mass. Its major chemical element, silicon, was measured at levels too low to yield consistently good data. Similarly, attempts were made to include veneer dryers but this resulted in collinearities with other sources and an insignificant contribution to fine mass in the CMB.

Two alternative CMB/source apportionment calculations were performed for each sampling site. The first (Vehicle Exhaust I) used a leaded-gas vehicle signature to calculate the contribution from leaded-gas vehicles. This number was scaled up using emissions and fuel use data to get the total vehicle exhaust contribution. The second CMB/source apportionment (Vehicle Exhaust II) used a VOC as the tracer for total vehicle exhaust. This apportionment method was attempted with o-xylene and 2,2,4-trimethylpentane as VOC vehicle exhaust tracers.

<u>Residential Woodsmoke</u>

In this study, over one-half of the fine-particle mass was comprised of organic compounds. A potentially significant source of organic carbon is woodsmoke. In previous studies in western

states (Lewis et al., 1988a, 1988b) residential woodsmoke was shown to be a significant source of fine particles. Other residential burning may include the burning of grass, trees, brush, yard and garden waste, and household waste. A survey conducted by the PSAPCA indicates the use of woodstoves dominates the residential burning activities in Pierce County, which incorporates the Tideflats and surrounding area. The highest fine-particle mass and organic carbon concentration measured during the 18-day study occurred when the Simpson Tacoma Kraft plant, a major industrial wood fuel source, was not operating. In order to draw definitive conclusions about the dominant sources for all stagnation conditions, it would be necessary to compare CMB results for a similar set of meteorological conditions when the Simpson plant was operating. In this CMB application, the source signature for woodsmoke used was Profile Number 42106 for residential woodstove emissions from the Pacific Northwest Source Profile Library (PNSPL). This profile represents laboratory data using a typical Portland/Seattle wood mix. The abundances of organic carbon and potassium in this profile were 47 percent and .25 percent, respectively.

Vehicle Exhaust I

A fraction of the total vehicle fleet in the Tideflats area is comprised of vehicles that burn leaded gasoline. While the number of leaded fuel vehicles on the road is continually decreasing, leaded fuel combustion is still expected to make a significant contribution to fine-particle lead. A source profile for leaded fuel exhaust was used to estimate the contribution of leaded fuel exhaust to the total fine-particle mass. The leaded vehicle source signature used was Profile Number 31103 from the PNSPL. Including a diesel vehicle source in the CMB was also attempted (using Profile Number 32203 from the PNSPL and elemental carbon as the fitting species), but this resulted in collinearity between diesels and woodsmoke, forcing this approach to be abandoned.

Vehicle Exhaust II

A second apportionment of the motor vehicle exhaust was performed using VOCs as the tracer for the total vehicle fleet. Zweidinger et al. (1990) identified several VOCs as contaminants of fine-particulate carbon and extractable organic matter (EOM) from mobile sources in Boise. Two of those candidate contaminants which were measured in this study are o-xylene and 2,2,4-trimethylpentane. These were confirmed as possible mobile source contaminants in this study, although 2,2,4-trimethylpentane is the weaker candidate and was measured at low levels. Concentrations of o-xylene and 2,2,4-trimethylpentane were comparable to concentrations of these two compounds measured in the Boise study. EOM was regressed against each VOC (in separate regressions) and a woodsmoke tracer K' in the Boise study. The inverse of the EOM coefficients for motor vehicles represents the abundance of each VOC with respect to EOM. This abundance was multiplied by 78 percent to get the abundance with respect to total fine particles. The 78 percent was derived from Lewis et al. (1986) using their calculated motor vehicle source profile. The calculated volatile carbon abundance (65 percent) was multiplied by 1.2 to estimate the total EOM abundance in the fine-particle fraction for motor vehicles.

Aluminum Production

A major point source in the Tideflats area is the Kaiser Aluminum and Chemical Corporation. This source is located just 1 km southeast of the Alexander Avenue sampling site, and therefore was upwind of the site for most of the study. The source profile for an aluminum reduction potline (Profile Number 29102 from the U.S. EPA Receptor Model Source Composition Library, EPA-450/4-85-002) was used to represent the Kaiser aluminum plant in the CMB. The organic carbon abundance is 28.2 percent in this profile; the aluminum abundance is 15.2 percent.

Hogged Fuel Boiler

Another major point source in the Tideflats area is the Simpson Tacoma Kraft Company. Among its emitting sources is a hogged fuel boiler, which is suspected to be a major contributor to the fine-particle mass in the Tideflats airshed. This source is located north of the Morse Supply sampling site and is closer to this site than to the Alexander Avenue site, which is east of Simpson Tacoma Kraft and the Morse Supply site (Figure 2-2). Several other point sources in the area operate hogged fuel boilers, though they are much smaller than the Simpson boiler. These other sources include Buffelen Woodworking, Puget Sound Plywood, and West Coast Door. Data collected during the source test at the Simpson hogged fuel boiler (Chapter 5) were used in the CMB source profile for hogged fuel boilers. The abundances of organic carbon and potassium in this profile are 2.3 and 12.7 percent, respectively (compared with 47 percent organic carbon and 0.25 percent potassium for woodstove emissions). While both residential woodstoves and hogged fuel boilers burn wood or wood products, the chemical profiles of those two sources are sufficiently different that the two sources can be resolved in the CMB.

Residual Oil Boiler

U.S. Oil and Refining operates a residual oil-fired boiler in the center of the Tideflats. Oil-fired boilers could be a major source of fine-particle sulfur in the Tideflats. Sulfates comprised about 13 percent of the fine-particle mass as calculated if they existed as ammonium sulfate. Profile Number 13502 from the PNSPL was used for the residual oil boiler signature in the CMB. This profile was produced from several samples taken at the U.S. Oil and Refining residual oil boiler in Tacoma, Washington, in 1988.

Scrap Metal Fugitives

Lead was used as a fitting species (for leaded fuel exhaust) in one version of the CMB for this study. CMB requires that all significant sources of a fitting species be included in the calculation. General Metals of Tacoma engages in scrap-metal handling activities that can contribute to the toxic metal loading, including lead, in the Tideflats. Most of the aforementioned source types do not contribute significant quantities of zinc, and there are likely no other significant sources of zinc other than scrap metals. Therefore, zinc could be used as a fitting species for metals. The PACS Profile Number 3193 was used in the CMB to represent many sources of metals, such as scrap-metal handling, car shredding, and boat building. Ore off-loading is another industrial activity in the Tideflats area, however there was no source profile to represent this activity. It was assumed that the ore off-loading contribution is primarily in the coarse particle fraction, so it was not used in the CMB.

Results and Discussion

Each CMB calculation was applied separately to data for the average of all samples from the Alexander Avenue site, for the average of all data from the Morse Supply site, and for the average daytime and nighttime samples for each site.

Two CMB/source apportionment calculations were performed for each sampling site. The first used a leaded-gas vehicle signature to calculate the contribution to fine mass from leaded gas vehicles, which turned out to be less than 1 percent. Fuel consumption data for 1988 from Chevron, a major distributor in the area, indicates that leaded fuels comprised 25 percent of the total gasoline sales, while unleaded fuels comprised the remaining 75 percent in the Seattle-Tacoma area (Pade, 1990). The numbers for 1989 are not expected to be significantly different. The contribution of leaded fuel exhaust to the fine-mass was multiplied by four to calculate the total gasoline (leaded plus unleaded) exhaust contribution. If leaded vehicles emit more fine-

particulate matter per gallon than unleaded vehicles, which is likely due to the age of leaded fuel vehicles, then this calculation is an upper estimate for gasoline-powered vehicles. According to a survey conducted by the PSAPCA (Pade, 1990), all nondiesel vehicles account for 16 percent of the total grams per vehicle mile of motor vehicle emissions. Therefore, dividing the mass estimate for all gasoline-powered vehicles by 0.16 yields the total contribution to fine mass for all motor vehicles, diesel and nondiesel. This estimate is highly uncertain because of the high uncertainty in the CMB estimate for leaded fuel exhaust (> ± 50 percent) and uncertainties in the fuel use data and vehicle emission inventory.

Results of the CMB/source apportionment using leaded fuel as the tracer for motor vehicles are depicted in Figures 6-8 and 6-9 for the Alexander Avenue and Morse Supply sampling sites, respectively. Motor vehicle exhaust contributed only seven to 10 percent of the fine-particle mass, according to the estimate scaling up the contribution of leaded fuel exhaust. Fine-particle mass was over-predicted by 16 to 24 percent. Contribution of a source type to fine-particle mass is normalized by expressing it as the percentage of calculated mass rather than measured mass, thus simplifying the graphical presentation of the data. Uncertainties in the source estimates range from 10 to 30 percent, except for the motor vehicle uncertainty, which was at least 50 percent.

At both sampling sites, the largest fine-particle mass component was residential woodsmoke, accounting for 62 to 72 percent of the fine-particle mass. By contrast, the industrial woodsmoke component (hogged fuel emissions) accounted for only two to three percent of the fine-particle mass. These results are consistent with the prevailing meteorology during the study in which winds were infrequently from the direction of the Simpson Tacoma Kraft plant. Furthermore, Simpson shut down its operations during part of the December sampling period. However, levels of hogged fuel emissions identified by the CMB were similar during operation and shut-down. These results indicate a small impact of other hogged fuel boilers on the sampling sites during the study. The Kaiser aluminum production appears to have made a significant impact on the Alexander Avenue site, which was about 1 km distant and downwind for most of the study. This source did not make a significant impact on the Morse Supply site, which was more distant and not frequently downwind. There were several Alexander Avenue site samples with aluminum loadings from about 1 to 8 $\mu g/m^3$, all collected at night.

The U.S. Oil and Refining residual oil boiler was apportioned assuming that the sulfate was primary [i.e., no sulfur dioxide (SO_2) from the boiler (or any other source) was converted to sulfate before arriving at the sampling sites]. This assumption yields an upper estimate of the contribution of the residual oil boiler to fine mass.

Including veneer dryers in the CMB resulted in many collinearities, because the most abundant species in the veneer dryer profile by far is organic carbon, which is emitted in significant amounts by woodsmoke and other sources. An upper-limit estimate of veneer dryers' contribution to fine-particle mass was made by comparing annual PM_{10} emissions of sources operating veneer dryers with emissions from Kaiser Aluminum, whose fine-particle mass contribution was estimated successfully. At the Alexander Avenue site, Kaiser contributed about 12 percent of the fine-particle mass, and, based on meteorology and proximity, probably had the largest impact on that site of any of the major point sources. Kaiser Aluminum plant's annual PM_{10} emissions are about 330 tons/year. Puget Sound Plywood and Buffelen Woodworking each had annual PM_{10} emissions of about 44 tons/year. Both of these sources operate veneer dryers. If their impact on the Alexander Avenue site was the same as Kaiser's, then they would each contribute 44/330 • 12 percent = 1.6 percent of the total fine-particle mass. Buffelen Woodworking is located to the northwest of the Alexander Avenue sampling site. Puget Sound Plywood is located in Tacoma, but not in the Tideflats area. It is unlikely that these point sources had the same potential to affect the Alexander Avenue site as did

Figure 6-8. Fine-Particle Receptor Modeling Results at the Alexander Avenue Site Using Lead (Pb) as the Leaded-Fuel Vehicle Tracer, Total Motor Vehicle Exhaust is Reported*

Aluminum Production (12.0%)

Vehicle Exhaust (7.0%)

Residual Oil (10.0%)

Scrap Metal (7.0%)

Hogged Fuel (2.0%)

Residential Woodsmoke (62.0%)
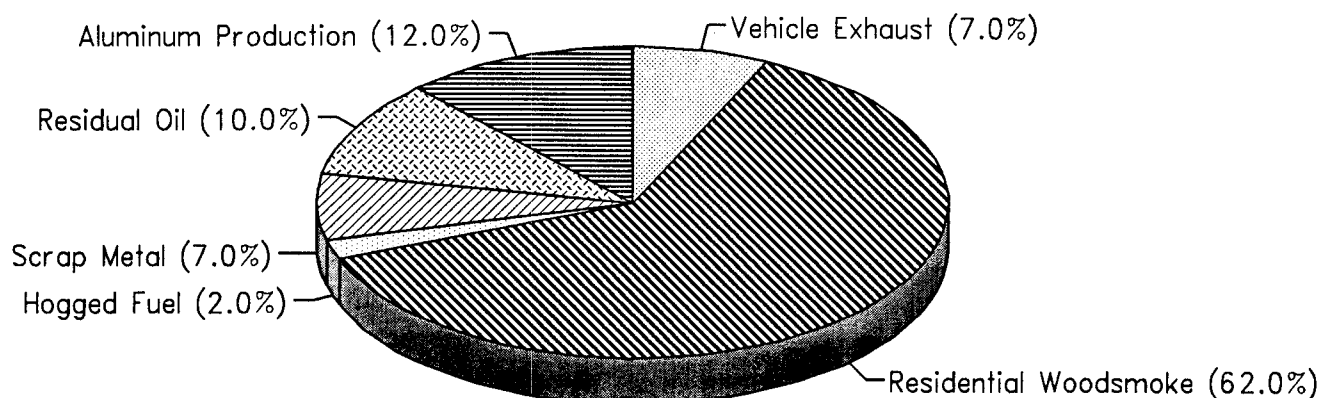
* Fine mass was overpredicted by 16%; values shown are normalized so that the sum is 100%.

Figure 6-9. Fine-Particle Receptor Modeling Results at the Morse Supply Site Using Lead (Pb) as the Leaded-Fuel Vehicle Tracer, Total Motor Vehicle Exhaust is Reported*

Residual Oil (10.0%)

Vehicle Exhaust (10.0%)

Scrap Metal (5.0%)

Hogged Fuel (3.0%)

Residential Woodsmoke (72.0%)
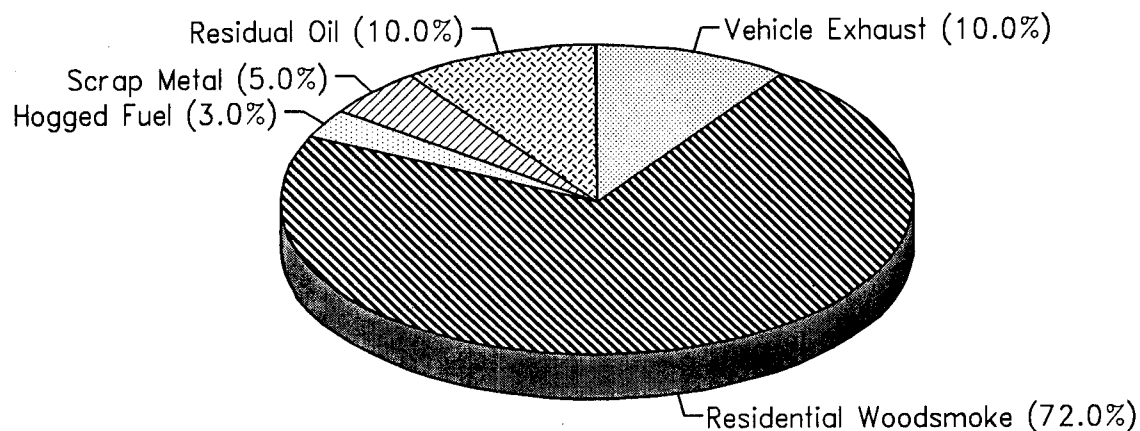
* Fine mass was overpredicted by 16%; values shown are normalized so that the sum is 100%.

Kaiser, given the location of those sources and the prevailing meteorology (mostly south to southeast winds). Furthermore, only a portion of the total PM_{10} output of those sources would be due to veneer dryers. It is therefore concluded that the veneer dryers can be regarded as insignificant in the CMB and the source apportionment.

The second CMB/source apportionment used the VOCs o-xylene and 2,2,4-trimethylpentane as tracers for total vehicle exhaust. The abundance of each of these VOCs with respect to fine-particle mass was used as the motor vehicle source profile in separate CMB calculations to estimate the motor vehicle contribution to fine particles. Results using o-xylene as a motor vehicle tracer indicate that motor vehicles contribute 18 to 20 percent to the calculated fine particles (Figures 6-10 and 6-11). Results using 2,2,4-trimethylpentane as a motor vehicle tracer indicate that motor vehicles contribute three to four percent of the calculated fine-particle mass (Figures 6-12 and 6-13). These results compare well with the seven to 10 percent estimate from the other motor vehicle apportionment described above, considering the uncertainty of the estimates. There is little difference between the fine mass contribution of the sources other than vehicle exhaust calculated by the two CMB/source apportionment methods.

Collinearity Assessment in the CMB Calculation

The CMB program contains diagnostic procedures to identify collinearity among the source profiles or high uncertainties in the individual profiles. For the most part, no collinearities were detected by the CMB program's diagnostic procedure for the samples presented in this report, with the exception of average nighttime samples collected at the Alexander Avenue site (Table 6-6).

The CMB values indicate that woodstoves were by far the dominant source of fine-particle mass during the study. The magnitude of the woodstove contribution was verified by performing the CMB calculations without the woodstove source profile. Organic carbon and potassium have significant contributions from residential woodsmoke, but they are not unique tracers of residential woodsmoke in this airshed. Leaving these species in the CMB without the woodstove source profile violates one of the fundamental assumptions of the CMB calculations. Therefore, CMBs without woodstoves were calculated first excluding and then including organic carbon and potassium as fitting species. Leaded-fuel vehicle contributions were scaled up to estimate total motor vehicle exhaust, as detailed above (Vehicle Exhaust I).

The sum of individual source contributions was 44 ± 7 percent of the measured fine particles for the Alexander Avenue site and 36 ± 7 percent for the Morse Supply site for the source apportionment without the woodstove source profile and without organic carbon and potassium as fitting species. In comparison, source contributions summed to 57 ± 7 percent (Alexander Avenue) and 39 ± 7 percent (Morse Supply) when organic carbon and elemental carbon are included as fitting species while still excluding woodstoves. The source apportionment including the woodstove source profile (and organic carbon and potassium) estimated that the sum of non-woodsmoke sources accounted for 44 ± 6 percent of the measured fine-particle mass at the Alexander Avenue site and 34 ± 6 percent at the Morse Supply site.

There is little difference between the CMBs including and excluding the woodstove profile. The small increase in the non-woodstove estimate when organic carbon and potassium are included as fitting species in the absence of a woodstove profile indicates the CMB is fairly insensitive to collinearities between woodstove and non-woodstove signatures.

Figure 6-10. Fine-Particle Receptor Modeling Results at the Alexander Avenue Site Using o-xylene as the Motor Vehicle Tracer*

Aluminum Production (10.7%)
Residual Oil (8.9%)
Scrap Metal (6.3%)
Hogged Fuel (1.6%)
Vehicle Exhaust (17.6%)
Residential Woodsmoke (54.9%)
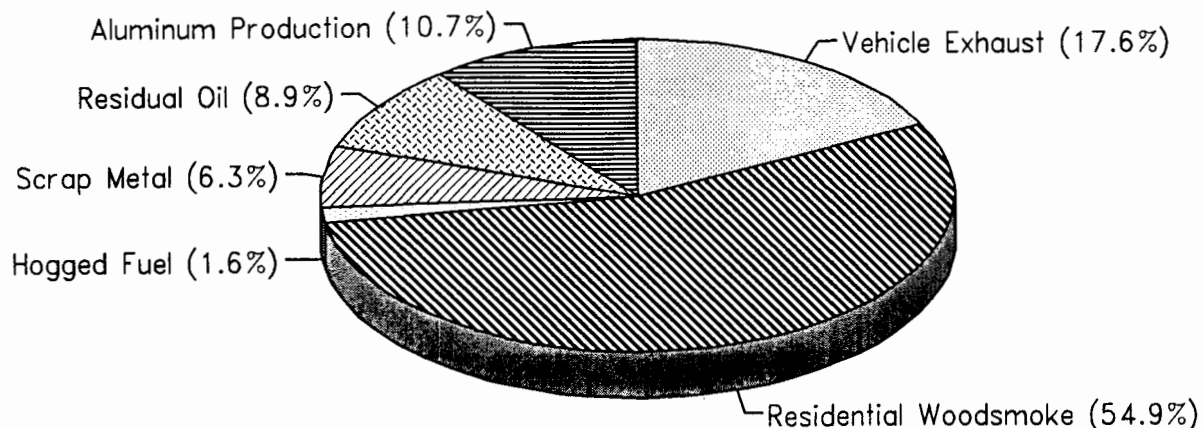
* Fine mass was overpredicted by 31%; values shown are normalized so that the sum is 100%.

Figure 6-11. Fine-Particle Receptor Modeling Results at the Morse Supply Site Using o-xylene as the Motor Vehicle Tracer*

Residual Oil (9.0%)
Scrap Metal (5.0%)
Hogged Fuel (2.4%)
Vehicle Exhaust (19.6%)
Residential Woodsmoke (64.0%)
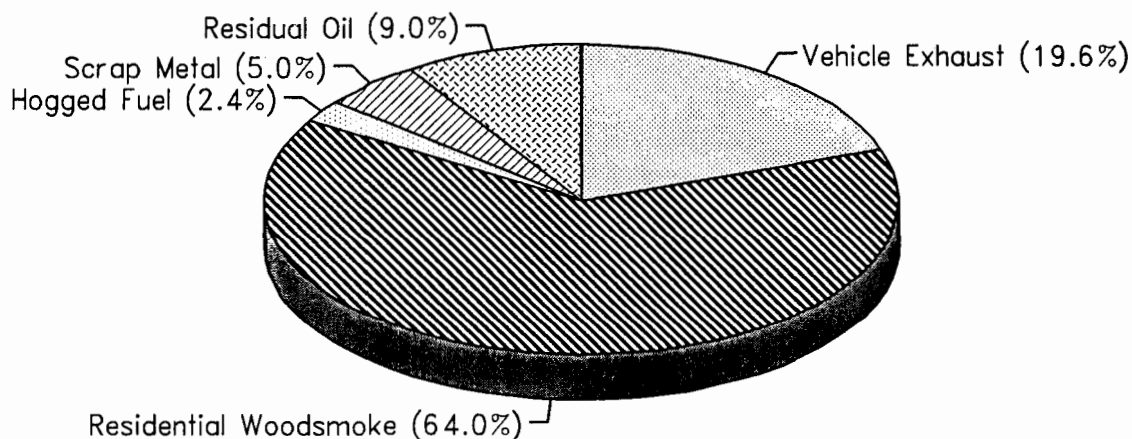
* Fine mass was overpredicted by 39%; values shown are normalized so that the sum is 100%.

Figure 6-12. Fine-Particle Receptor Modeling Results at the Alexander Avenue Site Using 2,2,4-trimethylpentane as the Motor Vehicle Tracer*

Aluminum Production (12.6%)

Residual Oil (10.4%)

Scrap Metal (7.4%)

Hogged Fuel (1.9%)

Vehicle Exhaust (3.4%)

Residential Woodsmoke (64.3%)
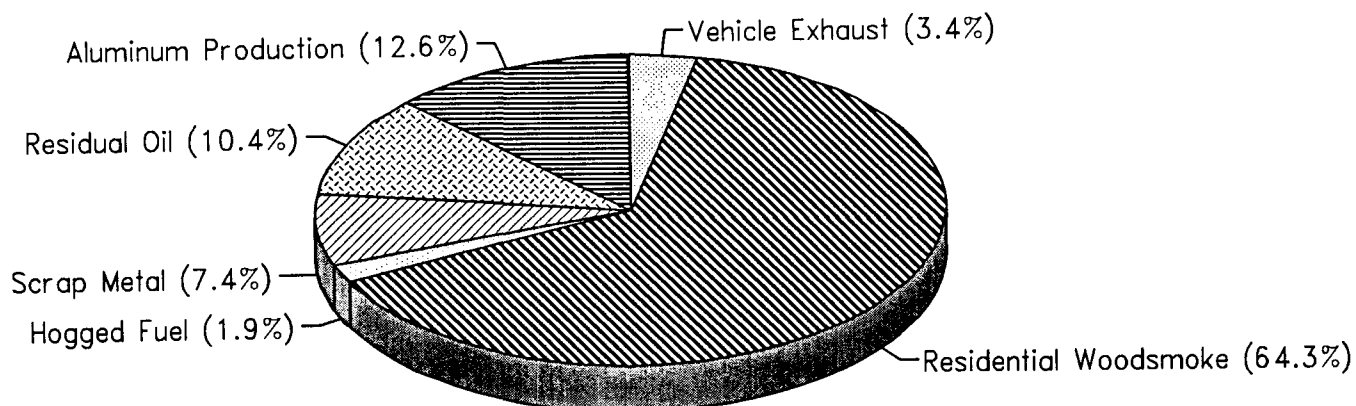
* Fine mass was overpredicted by 12%; values shown are normalized so that the sum is 100%.

Figure 6-13. Fine-Particle Receptor Modeling Results at the Morse Supply Site Using 2,2,4-trimethylpentane as the Motor Vehicle Tracer*

Residual Oil (10.7%)

Scrap Metal (5.9%)

Hogged Fuel (2.8%)

Vehicle Exhaust (4.5%)

Residential Woodsmoke (76.1%)
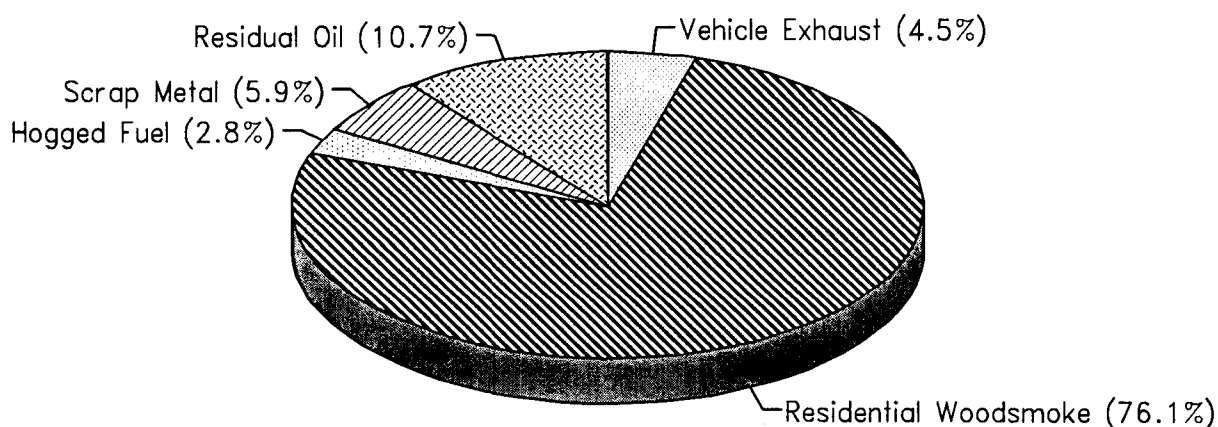
* Fine mass was overpredicted by 17%; values shown are normalized so that the sum is 100%.

Table 6-6. Percent Contribution of Major Sources to Calculated Fine-Particle Mass for Daytime, Nighttime, and All Samples - Alexander Avenue Site

Source	Day % of calculated mass	Night % of calculated mass	All % of calculated mass
Residential woodsmoke	63 ± 7	} 87 ± 8	62 ± 7
Aluminum production	3 ± 2		12 ± 3
Residual oil boiler	16 ± 3		10 ± 3
Motor vehicles	8 ± 5	5 ± 3	7 ± 4
Scrap metals	8 ± 1	6 ± 1	7 ± 1
Hogged fuel	2 ± 0.3	2 ± 0.3	2 ± 0.3

Day versus Night

CMB calculations using leaded vehicles to apportion mobile sources were performed for daytime and nighttime averaged samples. Results are presented in Tables 6-6 and 6-7. The errors represent the standard error estimated by the CMB. For the Morse Supply site, there was little difference between the day and night sample source apportionments, considering the limits of the standard errors of the source contributions estimated by the CMB program. Automobile exhaust emission estimates varied little from day to night within the large estimated uncertainties. The scrap metal source was found to have a greater impact during the day than at night, indicating that it is associated with mostly daytime activities. For the Alexander Avenue site, the nighttime average source contributions could not be completely resolved. Woodsmoke, residual oil boilers, and aluminum production were grouped together as one source contribution. However, daytime average source contributions for the Alexander Avenue site were completely resolved, and they indicate that the aluminum production source contributed significantly less to the fine-particle mass for daytime samples (3 ± 2 percent) compared with daytime plus nighttime averaged samples (12 ± 3 percent). It can therefore be inferred that aluminum production activities were, on average, significantly higher at night than during the day. This is consistent with the ambient data in which nighttime average aluminum concentrations were 816 ng/m^3, compared with an average of 143 ng/m^3 aluminum for the daytime samples. The three samples with aluminum concentrations in the 1 to 8 μg/m^3 range were all nighttime samples. The diurnal pattern of aluminum cannot be explained by nighttime stagnation, as other elements measured in the fine-particle fraction showed no such diurnal pattern, (i.e., very high nighttime concentrations; see Tables 6-1 (a) and (b). Auto exhaust and scrap metals at the Alexander Avenue site showed the same diurnal behavior as at the Morse Supply site. The scrap metal handling source type contributed from 20 percent (Morse Supply, nighttime) to 34 percent (Alexander Avenue, daytime) of the fine-particle lead. This makes scrap metal activities competitive with mobile sources as a source of fine-particle lead.

Table 6-7. Percent Contribution of Major Sources to Calculated Fine-Particle Mass for Daytime, Nighttime, and All Samples - Morse Supply Site

	Day	Night	All
	% of calculated mass	% of calculated mass	% of calculated mass
Residential woodsmoke	68 ± 7	76 ± 7	72 ± 7
Residual oil boiler	12 ± 3	10 ± 3	10 ± 3
Motor vehicles	12 ± 6	8 ± 4	10 ± 5
Scrap metals	7 ± 1	4 ± 1	5 ± 1
Hogged fuel	2 ± 0.3	3 ± 0.3	3 ± 0.4

December versus January

Source apportionments were performed separately for the December and January samples because of the differences in meteorology between December (dry, lower wind speeds) and January (wet, higher wind speeds) and the differences in total fine-particle mass (about 30 μg/m^3 in December versus about 10 μg/m^3 in January). Results are presented in Table 6-8. Differences between the December and January source apportionments at either site were small. The hogged fuel boiler source had a greater impact on the Morse Supply site in January (5 ± 0.8 percent) than in December (2 ± 0.2 percent). This is consistent with the shutdown of the Simpson Tacoma Kraft hogged fuel boiler during most of the December sampling period. The aluminum production impact on the Alexander Avenue site in January (17 ± 4 percent) was higher than in December (11 ± 3 percent).

Table 6-8. Percent Contribution of Major Sources to Total Fine-Particle Mass for December and January Samples

	Alexander Site		Morse Site	
	December	January	December	January
Residential woodsmoke	63 ± 7	57 ± 7	72 ± 7	70 ± 7
Aluminum production	11 ± 3	17 ± 4	0	0
Residual oil boiler	10 ± 3	12 ± 4	11 ± 3	9 ± 3
Motor vehicles	7 ± 4	5 ± 3	10 ± 5	11 ± 6
Scrap metal	7 ± 1	6 ± 1	6 ± 1	5 ± 1
Hogged fuel	2 ± 0.3	2 ± 0.3	2 ± 0.2	5 ± 0.8
Measured mass, ng/m^3	29,500	8,910	31,200	11,400
Calculated mass, ng/m^3	33,535	12,345	40,839	12,730
Percent overestimated	14	38	31	12

SUMMARY

Aerosol (PM₁₀)

► The outstanding feature of the data at both sites (Morse and Alexander Avenue) was the high relative amount of fine-particle organic compounds compared with the total mass.

► High fine-particle aluminum concentrations measured at the Alexander site were associated with light southeast winds or stagnant conditions.

► Coarse-particle aluminum concentrations were much higher and measured with lower uncertainty at the Morse site than at the Alexander site.

► The Morse site tended to have somewhat higher concentrations of most fine- and coarse-particle constituents and VOCs. An exception was the copper concentration at the Alexander site, which may be an artifact of sampler operation.

► Coarse particle iron concentrations were twice as high at the Alexander site, while fine-particle iron concentrations were 50 percent higher at the Morse site. Coarse-particle chromium concentrations were three times higher at the Morse site.

► Organic carbon and fine-particle mass data correlated quite well between the two sites. There were similar temporal patterns of all of the fine-particle species.

► The highest concentrations of fine-particle total mass and organic carbon were associated with the most stagnant conditions of the study. The winds were mostly from the southeast. The Simpson Tacoma Kraft hogged fuel boiler was not operating during this period.

► Insufficient loadings of PAHs in the 18-day ambient sampling study precluded their use in the receptor modeling study.

Receptor Modeling of PM₂.₅ Emissions Sources

[It should be kept in mind when evaluating the study results that the measurements were made over a limited time and spatial scale. Meteorology and season can strongly influence the contribution of the various sources of contaminants to particulate mass. This study covers only a subset of conditions which may exist in the area in any one year and from year to year.]

► Residential woodsmoke was found to be by far the dominant source of fine particles, accounting for 62 to 72 percent of the fine-particle mass by one estimation and 55 to 64 percent by the other.

► Residential woodsmoke accounted for a similar percentage of the fine-particle organic carbon.

► Motor vehicle exhaust, residual oil boilers, and aluminum production at the Alexander Avenue site were a distant second, each accounting for around 10 percent of the fine-particle mass. (This estimation used lead as a tracer for leaded fuel vehicles.)

► Using selected VOCs as tracers for motor vehicle exhaust, estimates of this source contribution ranged from three to 20 percent.

► Diesel powered vehicles accounted for most of the motor vehicle emissions.

▶ Scrap metal handling and similar activities contributed five to seven percent of the fine-particle mass and more than 20 percent of the fine-particle lead, making these activities competitive with leaded fuel vehicles as a source of fine-particle lead in the Tideflats airshed.

▶ Industrial woodsmoke from hogged fuel boilers was estimated to contribute three percent or less of the fine-particle mass. (Note: Winds were infrequently from the direction of the Simpson Tacoma Kraft plant during the study. Also, the plant shut down operations during part of the December sampling period.)

▶ No significant differences were observed between the averaged daytime and nighttime samples, with the exception of aluminum production, which contributed significantly less fine-particle mass during the day, and by inference, significantly more at night.

▶ Any differences between daytime and nighttime for motor vehicles were overshadowed by the large uncertainty in their estimates.

▶ The percentage that woodsmoke contributed to total fine-particle mass did not vary diurnally.

Chapter 7. Diffusion/Transport Modeling

OBJECTIVES

▶ Develop a customized, state-of-the-art diffusion model to predict the aerosol and deposition concentrations of contaminants in the Tacoma Tideflats area.

▶ Develop a model to estimate the fractions of contaminants entering the Commencement Bay stormwater runoff following deposition on the watershed.

▶ Run these models for the entire field sampling period, using the meteorological and emissions data to drive the daily simulations for transport and deposition.

The analysis of ambient aerosol and deposition samples is a labor- and resource-intensive method to assess atmospheric contributions of contaminants. As a consequence the number of possible samples and sampling sites is limited. A numerical model provides an alternative approach to the problem: it can be an efficient tool for processing emissions source and wind data into predictions of contaminant concentrations and fluxes as functions of time and space.

WV3 EULERIAN GRID DISPERSION MODEL

A mathematical model was developed to simulate the emission, dispersion, and deposition of toxic contaminants, through the atmosphere and into the watershed of Commencement Bay. WYNDvalley, version 3.01 (hereafter WV3), is a time-dependent Eulerian grid simulation that integrates dispersion and deposition equations in three dimensions with arbitrarily varying emissions, both in time and space. The model permits flexible boundary conditions and the separation of the deposition velocity, Vs, into steady and time-varying components, such as rain-modulated removal of soluble contaminants. Appendix F-1 contains a discussion of the model equations.

WV3 (and earlier versions of the model) have been compared with observations and with predictions from RAM, a standard Gaussian Plume model, for PM_{10} at six sites in the Pacific Northwest, including data from 1985 and 1986 at Fire Station No. 12 in the Tacoma Tideflats. The earlier version of WV3 proved superior to RAM in five out of six scoring criteria, which depend on matching observations with simulations, both in time and space. For the sixth, neither model was superior to the other (Harrison et al., 1990).

The modeling domain for the present study is an irregular area comprising 91.5 km² in the Tacoma Tideflats. WV3 is implemented in three vertical layers of 356 cells, each one being 500 x 500 meters wide and 67 meters high. Time-varying source intensities (in this case, PM_{10} emissions) are specified for each cell in the surface layer and for cells in the middle layer that are associated with stacks emitting contaminants at heights between 67 and 133 meters. The PM_{10} size fraction was used in the diffusion modeling. The aerosol sampler used for the aerosol and deposition studies collected aerosol particles up to a cutpoint between 25 and 50 μm, therefore the modeled concentrations are expected to be underestimates of the measured values.

Emissions are modulated as one of four daily schedules (industrial, woodstoves, automotive or dayshift), and by workday/weekend. Figure 7-1 shows the modulation functions used to simulate automotive and woodsmoke emissions over a 24-hour period. Measured wind directions are rounded into one of eight primary octants (n, ne, e, etc.) and time steps are computed as functions of wind velocity to minimize numerical diffusion. Sub-scale eddy diffusion (Kx, Ky, Kz) is added from measurements. Depositions are separated into wet and dry components, the former proportional to rain rates through a washout coefficient, Wr, and the latter as a constant dry deposition velocity, Vd.

Model output is copious, with records of 24-hour averages of the contaminant concentrations and depositions in every surface cell, and hourly averages at seven receptor sites that were placed on the grid at locations representing Brown's Point, Tyee Marina, Morse Industrial Supply, Fire Station No. 12, Sea-Land, Alexander Avenue, and Riverside School (Figures 2-2 and 7-2). Hourly concentrations simulated at the seven receptor sites were averaged over three- to four-day intervals, as appropriate, to coincide with those of the field aerosol measurements.

MODEL INPUT

The model is used to simulate the distribution of the concentrations of atmospheric contaminants and their fluxes to the surface. Required inputs to the model include the spatial and temporal distributions of the sources of emissions, the dispersing winds, and the wet and dry processes that remove the contaminants from the modeled domain.

Point source PM_{10} emission information was taken from the PSAPCA registration files, the source profile library, and relevant source tests as described in Chapter 5. The actual input data used by the model appear in Appendix F-2. Emission estimates were included for all sources exceeding 1 kg/day of PM_{10} emissions, and located within 10 km of the Alexander Avenue site. The source profiles estimate the weight fractions of the various tracers compiled from source tests. Appendix F-2 (c) contains profiles for Cu, Zn, As, and Pb, and Appendix F-2 (d) contains profiles for several PAHs. Emissions from the Kaiser aluminum smelter (Table 7-1) are a special case. These were measured directly (AMTEST, 1988). It should be noted, however, that the uncertainties in these numbers may exceed 40 percent (based on a comparison with previous test results).

The total estimated PM_{10} emitted in the modeled area was 5,692 kg/day. There are 59 point sources, with emissions totaling 4286 kg/day, of which 1014 kg are vented below 67 meters and the remainder above. Emissions from area sources (vehicle exhaust, road dust, railroads, ships, woodstoves) account for the remainder. Table 7-2 shows the total estimated emissions used in the diffusion/transport modeling. Estimates are listed for PM_{10}, Cu, Zn, As, Pb, the sum of the four metals, several PAHs, and the sum of the PAHs. Note that 98 percent of the modeled PAH emissions were from Kaiser.

Figures 7-3 and 7-4 are block contour maps showing estimated PM_{10} emissions at the surface (level 1) and from elevated stacks (level 2, or mid-level).

Figure 7-1. Modulation Function for Cars and Woodsmoke
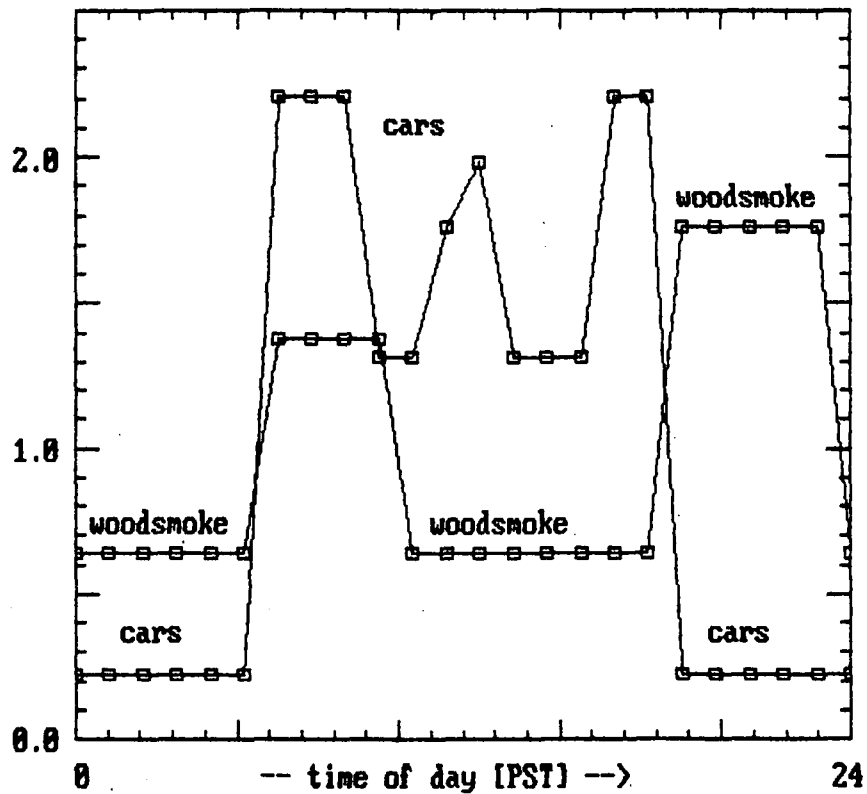
Figure 7-2. Map of Sampling Sites Used for Modeling
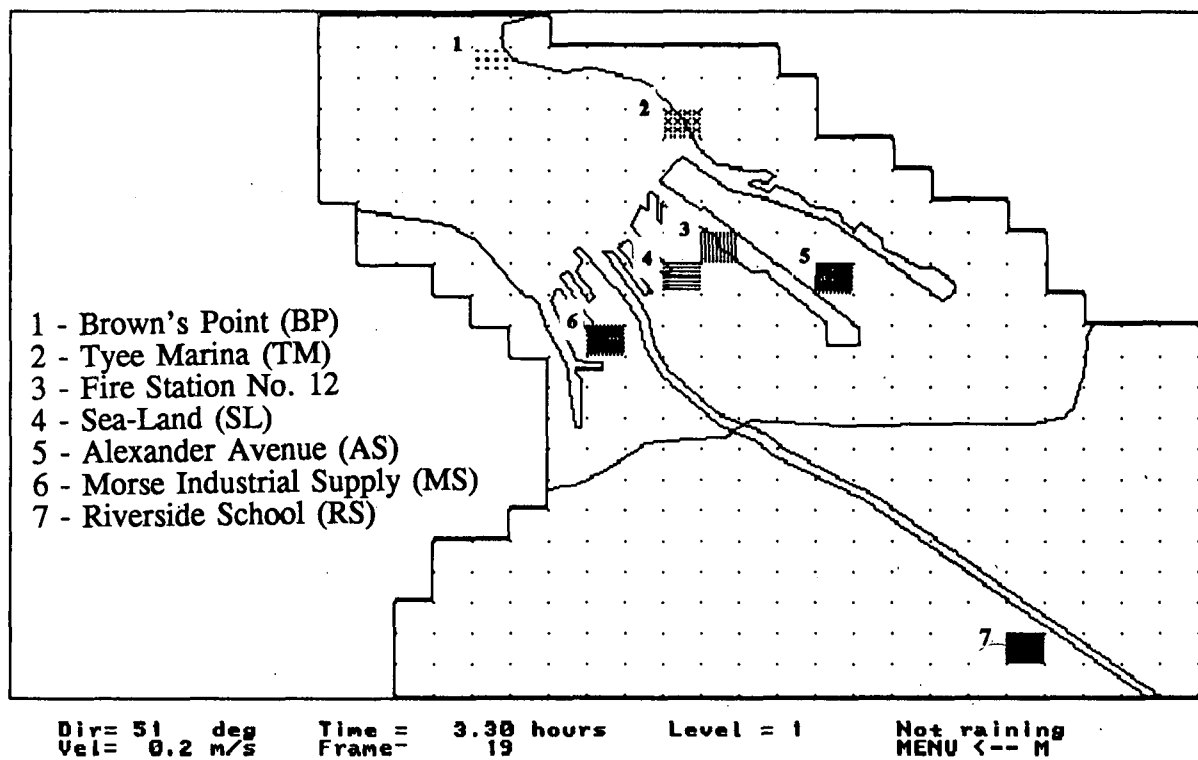
1 - Brown's Point (BP)
2 - Tyee Marina (TM)
3 - Fire Station No. 12
4 - Sea-Land (SL)
5 - Alexander Avenue (AS)
6 - Morse Industrial Supply (MS)
7 - Riverside School (RS)

Table 7-1. PAH Emissions from the Kaiser Aluminum Smelter

kg/day	Code	Comment
204.0	NAPH	naphthalene
2.4	ACNY	acenaphthylene
46.6	ACNE	acenaphthene
30.1	FLOR	fluorene
190.0	PHEN	phenanthrene
13.1	ANTH	anthracene
31.1	FLUO	fluoranthene
20.4	PYRE	pyrene
1.27	BAA	benzo(a)anthracene
3.43	CHRY	chrysene
1.39	BBF	benzo(b)fluoranthene
0.72	BKF	benzo(k)fluoranthene
0.34	BAP	benzo(a)pyrene
0.24	INDP	indeno(1,2,3-)pyrene
0.12	DBA	dibenzo(a,h)anthracene
0.24	BZP	benzo(g,h,i)perylene
0.72	BEP	benzo(e)pyrene

Total   546.2

Table 7-2. Total Estimated Emissions of PM_{10} for Diffusion/Transport Model

	kg/day
PM_{10} (excluding PAH)	5692
Copper	3.85
Zinc	9.88
Arsenic	0.74
Lead	7.07
Cu+Zn+As+Pb	21.54
Fluorene	30
Phenanthrene	190
Anthracene	13
Fluoranthracene	41
Pyrene	20
Chrysene	4
Benzo(a)pyrene	0.3
Retene	0.1
All other Kaiser PAHs	261
All PAHs	560
All Kaiser PAHs	546
Non-Kaiser PAHs	14

NOTE: 1. 98% of all PAHs are from Kaiser.
      2. PAHs comprise 10% of PM_{10}.

Figure 7-3. Distribution of Surface Emissions of PM$_{10}$

Dir=294 deg Time = 0.61 hours Level = 1 Not raining
Vel= 1.9 m/s Frame= 10 MENU <-- M
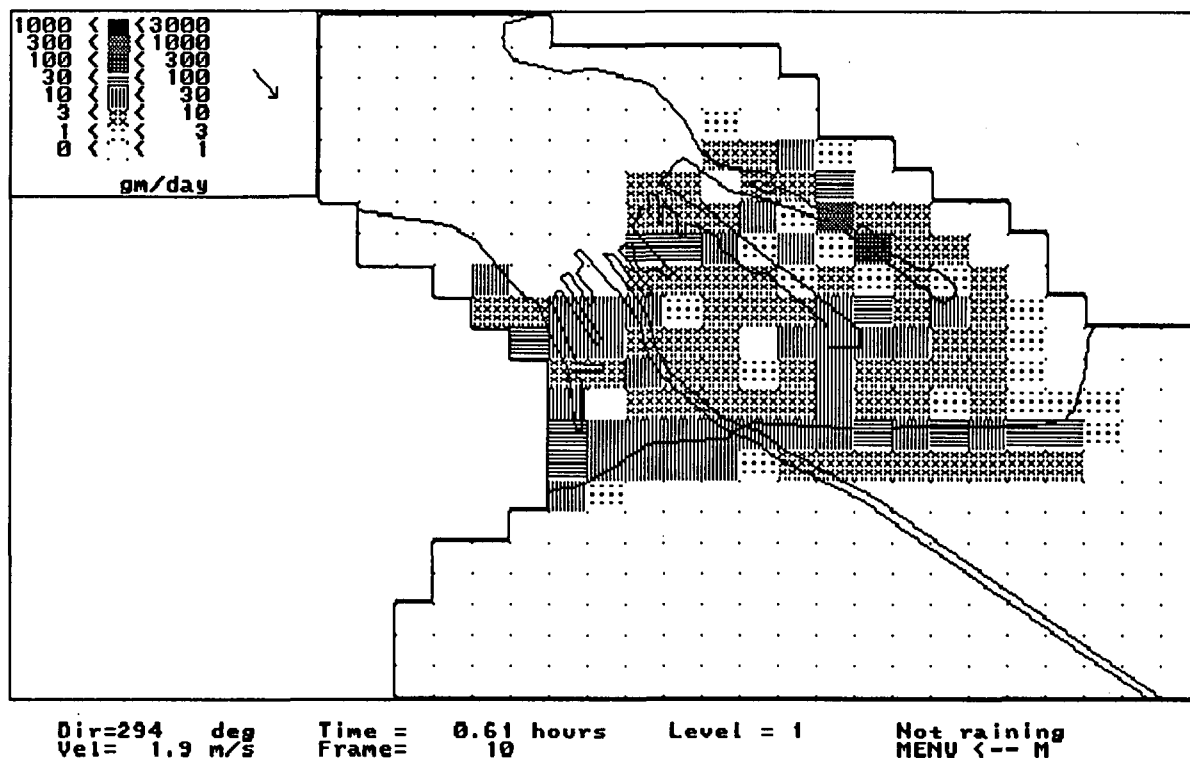
Figure 7-4. Distribution of Mid-Level Emissions of PM$_{10}$

Dir=105 deg Time = 6.25 hours Level = 2 Not raining
Vel= 1.3 m/s Frame= 34 MENU <-- M

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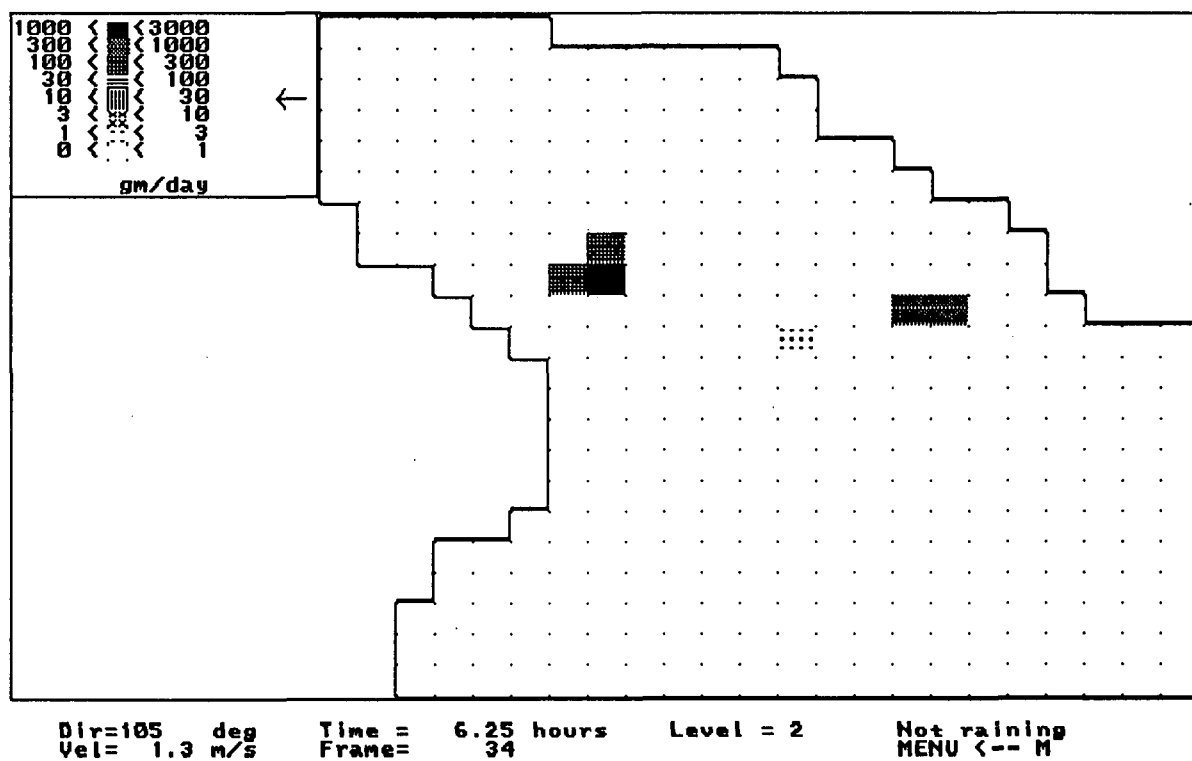
WINDS AND TRANSPORT COEFFICIENTS

The meteorological data gathered at the Alexander Avenue site were processed into daily summaries beginning at noon on July 7, 1989, and ending at noon on January 7, 1990. The velocities and directions were combined as vector averages, the insolation as scalar averages, and the precipitation as simple sums. For each 24-hour period percentages were computed when the winds were within 22.5° of north, north-east, east, etc., and the percentage of five-minute winds less than one meter per second. This summary is presented in Appendix B-2, with dates labeling the first day of each 24-hour period, starting at noon.

Figure 7-5 shows a polar (wind-rose) scattergram of the 24-hour vector winds for all the data, and Figure 7-6 shows a cumulative trajectory for winds at 10 meter height. A similar scattergram to Figure 7-5, which was selected for winds when it is raining, reveals that rainy winds were mostly southerly. Figure 7-6 reveals a dramatic "seasonal corner" on October 5th, when there is a shift from summer winds with a set westerly flow to winter winds with a set southerly flow.

The quality and volume of the meteorological data collected for the present study greatly exceed that which is normally available for atmospheric dispersion studies. In particular, the horizontal variances in wind directions and speeds, combined through Monin-Obhukov similarity theory with the vertical temperature gradients, permit explicit determination of the horizontal and vertical eddy diffusivities.

The vertical eddy diffusivities (Kz) are summarized in Appendix F-3(a) as functions of wind velocity and the vertical temperature gradient between two and 10 meters above the surface.

The ΔT measurement errors affect calculations of Kz, when atmospheric stabilities are near neutral. A +0.1° measurement bias of ΔT (between thermistors separated by eight meters) at a wind speed of 1 m/s would reduce the perceived Kz from 1.66 m^2s^{-1} to 0.67 m^2s^{-1} [see Appendix F-3(a)]. The sensitivity of contaminant concentrations computed by WV3 to estimates of Kz varies markedly with wind speed and direction, but is everywhere else less than 0.3. Thus, a +0.1° bias in ΔT would include positive errors in computed tracer concentrations that should be everywhere less than 45 percent.

Appendix F-3(b) contains two scattergrams, one demonstrates approximate linearity of the horizontal eddy diffusivities with the wind velocities, and the second shows that long-term averages of the transverse and longitudinal horizontal eddies are equal (i.e. that the horizontal turbulence is not dependent on the horizontal direction.

WV3 also requires deposition velocities and washout coefficients to estimate the efficiencies with which suspended particles are deposited on the surface by dry- and rain-modulated processes. For the contaminant tracers of this study, median values for identical or chemically similar tracers, as reported by McMahon et al. (1979), were assumed (see Table 7-3).

Figure 7-5. Wind-Rose Scattergram for 24-Hour Vector Winds

Npts= 186 (Number of Points)
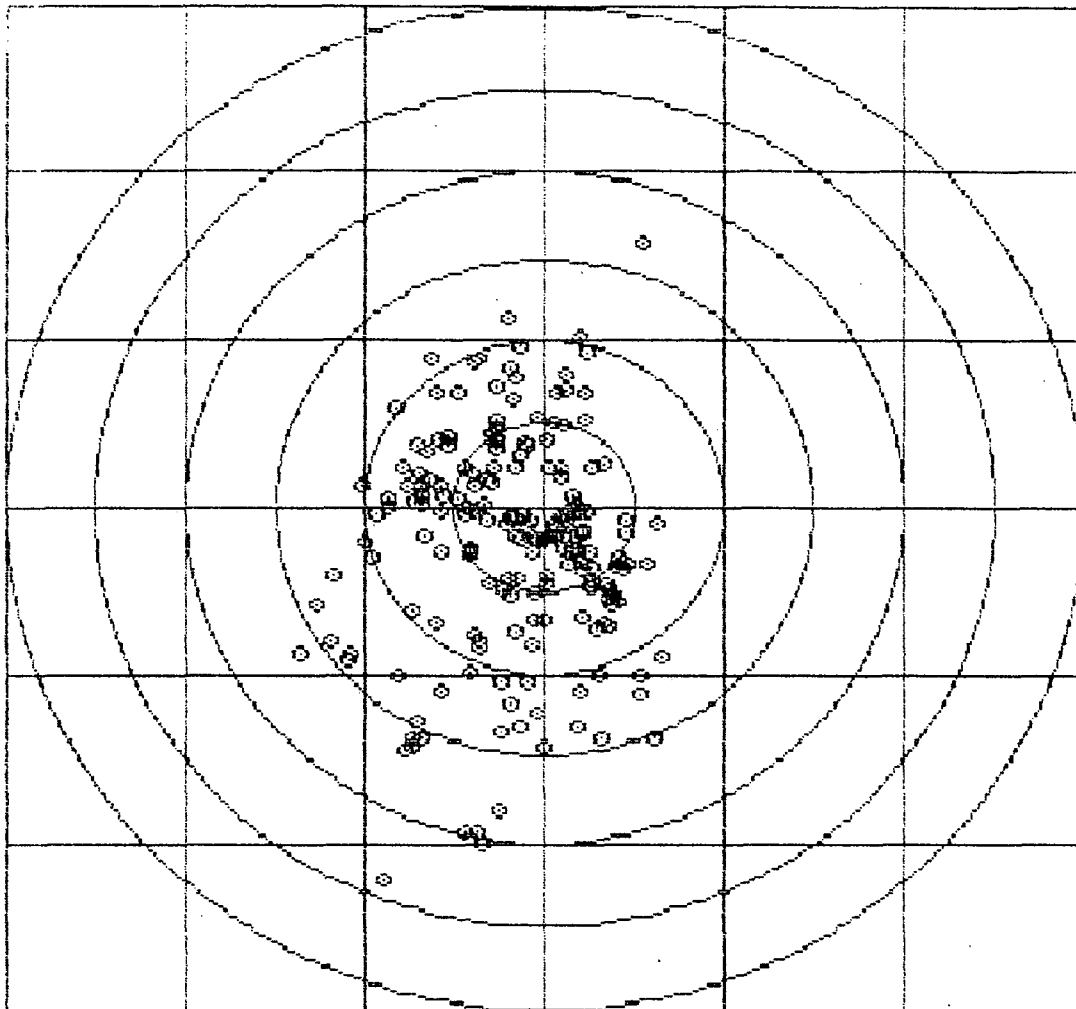
Wind-rose Scattergram for Tacoma Winds. 1 circle = 1 m/s

Figure 7-6. Wind Hodograph for 24-Hour Vector Winds at 10m Height

Npts = 186 (Number of Points)
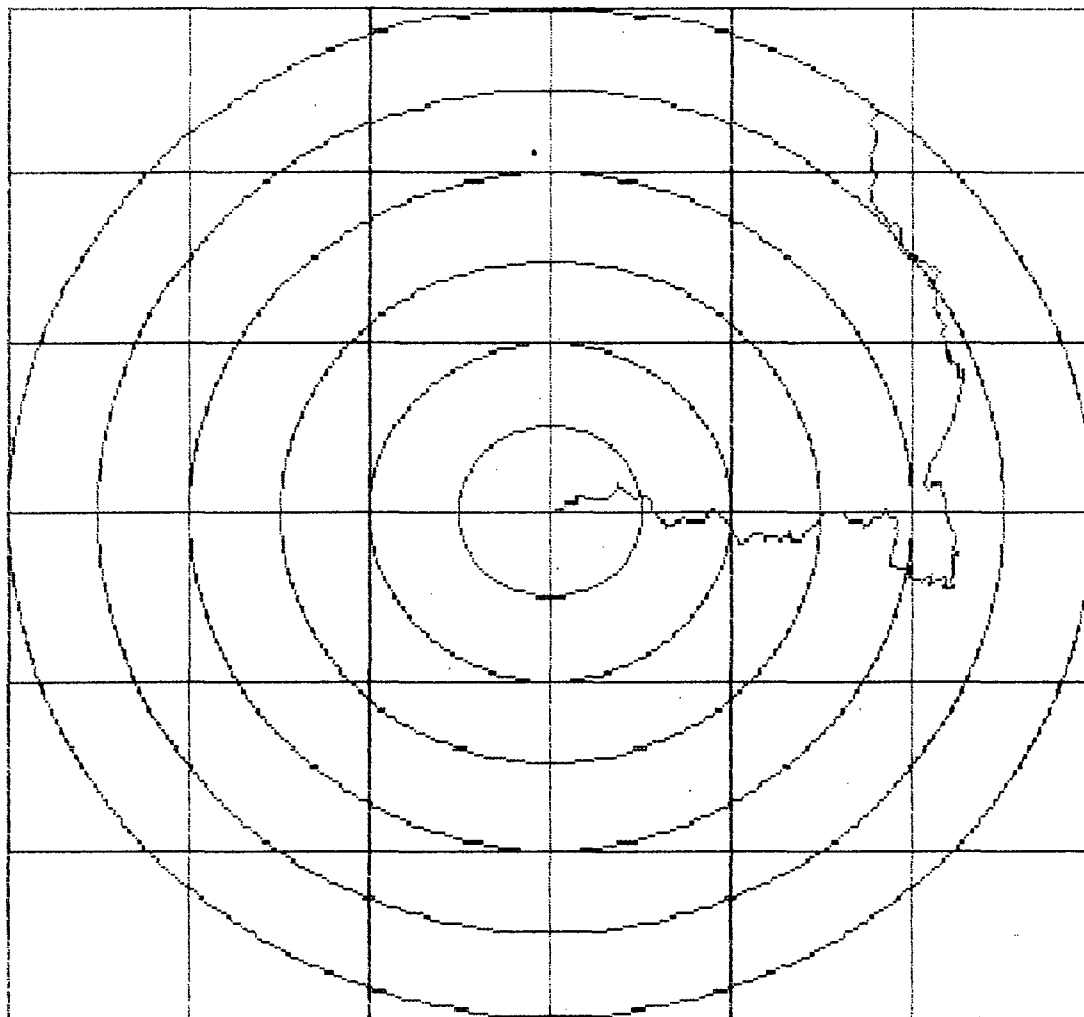
Cumulative Trajectory for Tacoma Winds July 7, 1989 to January 7, 1990

Table 7-3. Empirical Atmospheric Deposition Parameters

Tracer	Vd (cm/sec)[a]	Wr [b]
Arsenic	0.1	1000
Copper	0.1	1000
Lead	0.1	1000
Zinc	0.1	1000
PAH	0.1	300

(a) Vd is defined as the dry deposition velocity.
(b) Wr is defined as (concentration of a tracer in rain)/(concentration of the tracer in air)

RESULTS: SIMULATIONS

The WV3 model was run separately for the inventory emissions of As, Cu, Pb, Zn, and for a generic PAH compound that was assumed from the Kaiser plant only, at a nominal emission rate of 1 kg/day. [Because greater than 90 percent of the PAH compounds that are emitted in the Tacoma Tideflats derive from a single source (the Kaiser aluminum smelter), a useful approximation is to simulate these as if from a single tracer emitted at a standard rate (1 kg/day).] The hourly concentrations from these simulations were averaged over the same three- or four-day intervals as the aerosol sampling at each site (see Appendix F-4).

Simulations of Concentrations and Fluxes

A principal reason for attempting to model the concentrations and fluxes of concentrations through the air and into the watershed of Commencement Bay is to develop both interpolative and extrapolative tools that may be used at other sites within the modeled domain and at different domains entirely. For this purpose, estimates of the spatial distributions of the concentrations and fluxes are crucial.

Estimates using the WV3 model are displayed in Figures 7-7 through 7-11 (each with subscripts a-c). Concentrations and fluxes are estimated for As (Figure 7-7), Cu (Figure 7-8), Pb (Figure 7-9), Zn (Figure 7-10), and a generic PAH tracer (Figure 7-11) that is assumed to have been emitted from Kaiser with a flux of 1 kg/day. (Concentrations and flux values for individual PAHs can be acquired by multiplying by the Kaiser emissions for that PAH; the patterns will remain identical.)

Subscripts in Figures 7-7 through 7-11 represent the following for the pollutant of concern:

(a) The highest 24-hour average concentration;
(b) The 186-day average aerosol concentration; and
(c) The sum of the dry and wet depositions.

Model output simulations for the highest brief episode (five minute), the second-highest 24-hour aerosol concentrations, dry deposition fluxes, and wet deposition rates for each of the five chemical constituents appear in Appendix F-5. Comparisons of modeled concentrations with measured concentrations and an evaluation of model performance are addressed in some detail in Chapter 8, Comparison of Studies.

Figure 7-7(a). Simulated Highest 24-Hour (midnight-to-midnight) Averages for Arsenic (As) Aerosols
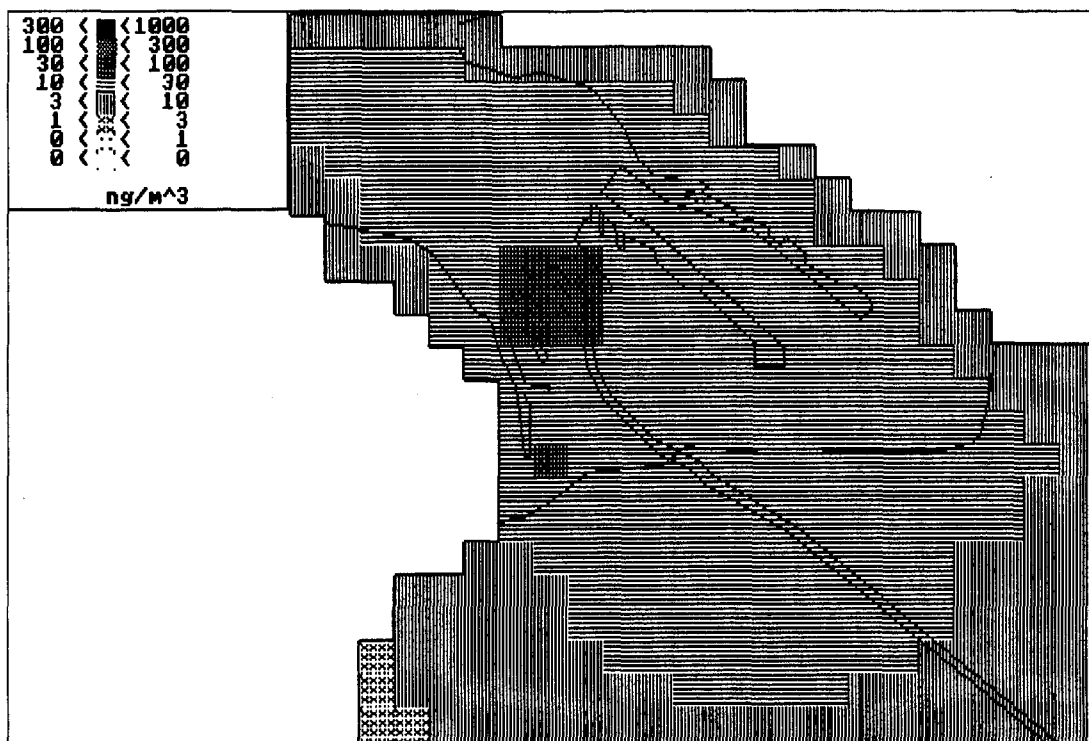
Highest 24-hour average, lower level

Figure 7-7(b). 186-Day Average for Arsenic (As) Aerosols
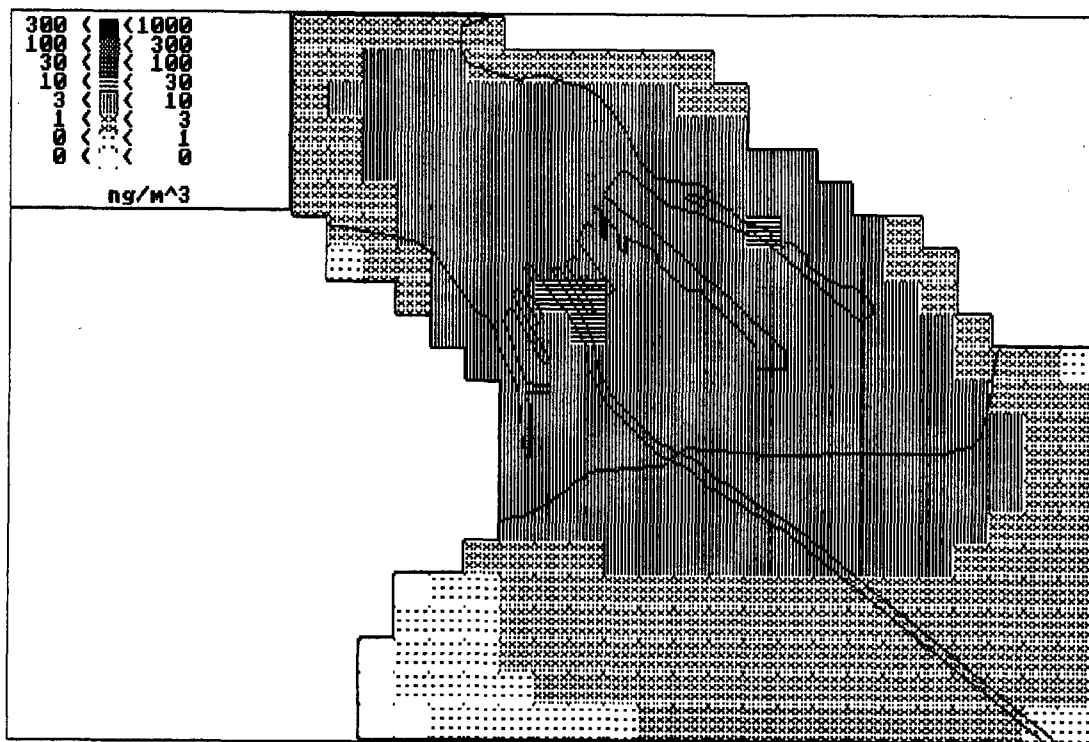
Average Concentration over 186 days

Figure 7-7(c). Sum of Wet and Dry Depositions for Arsenic (As) Aerosols
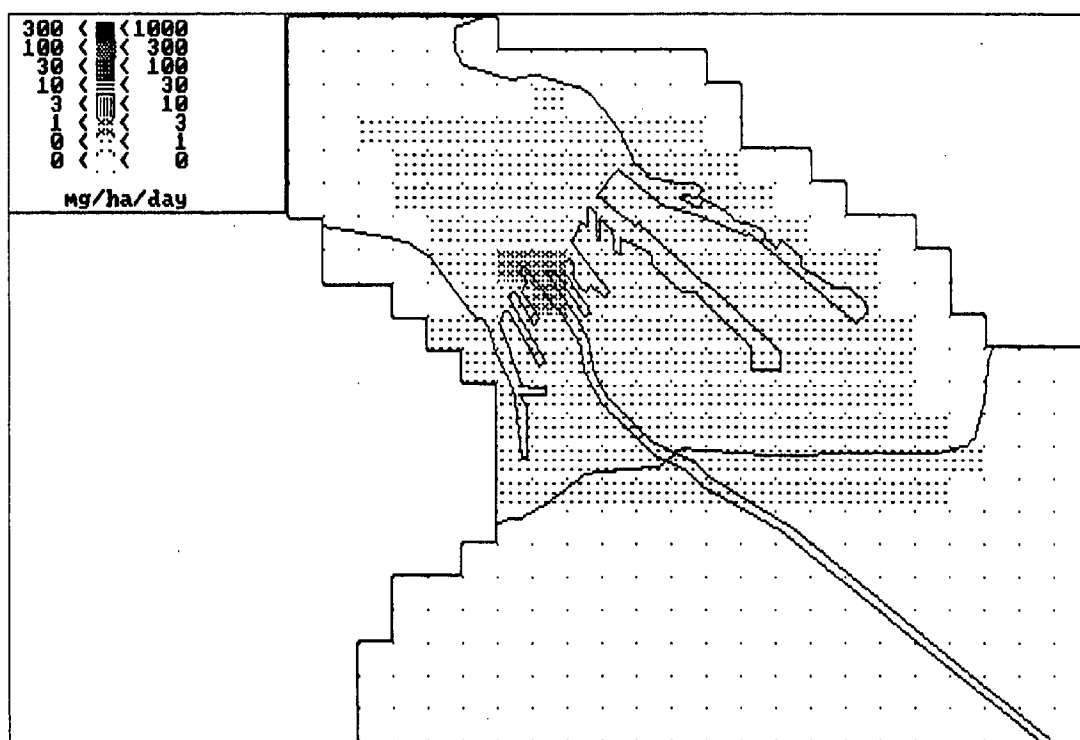
Average Total Deposition Rate: milligrams/hectare/day

Figure 7-8(a). Simulated Highest 24-Hour (midnight-to-midnight) Averages for Copper (Cu) Aerosols
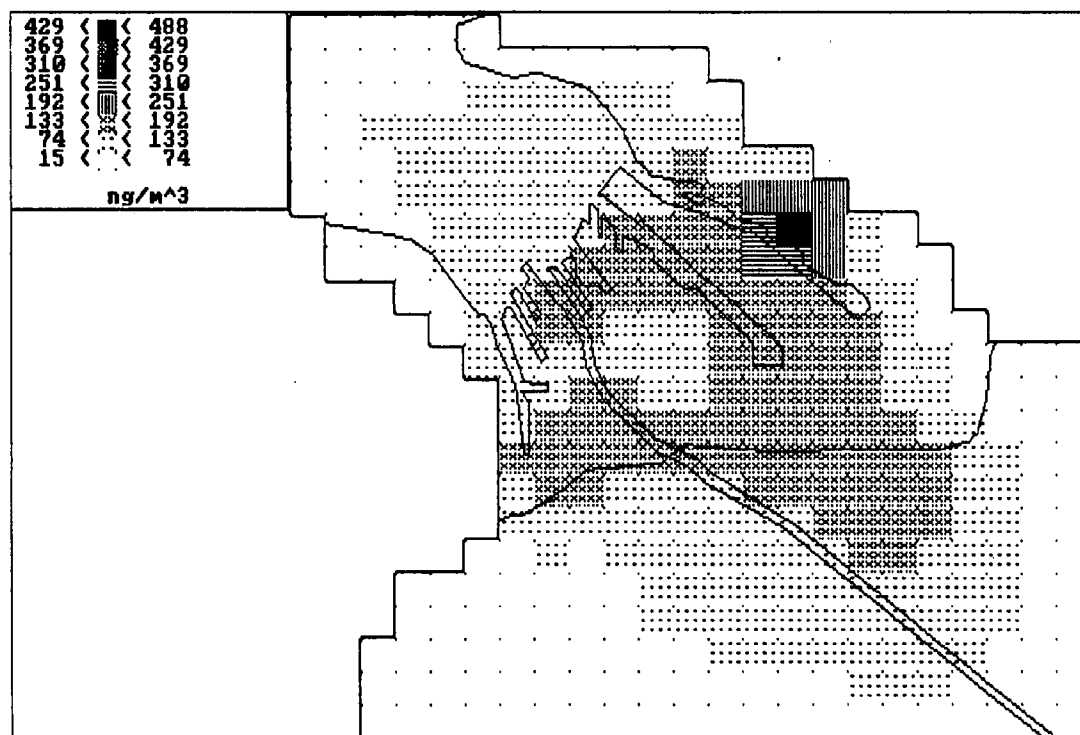
Highest 24-hour average, lower level

Figure 7-8(b). 186-Day Average for Copper (Cu) Aerosols
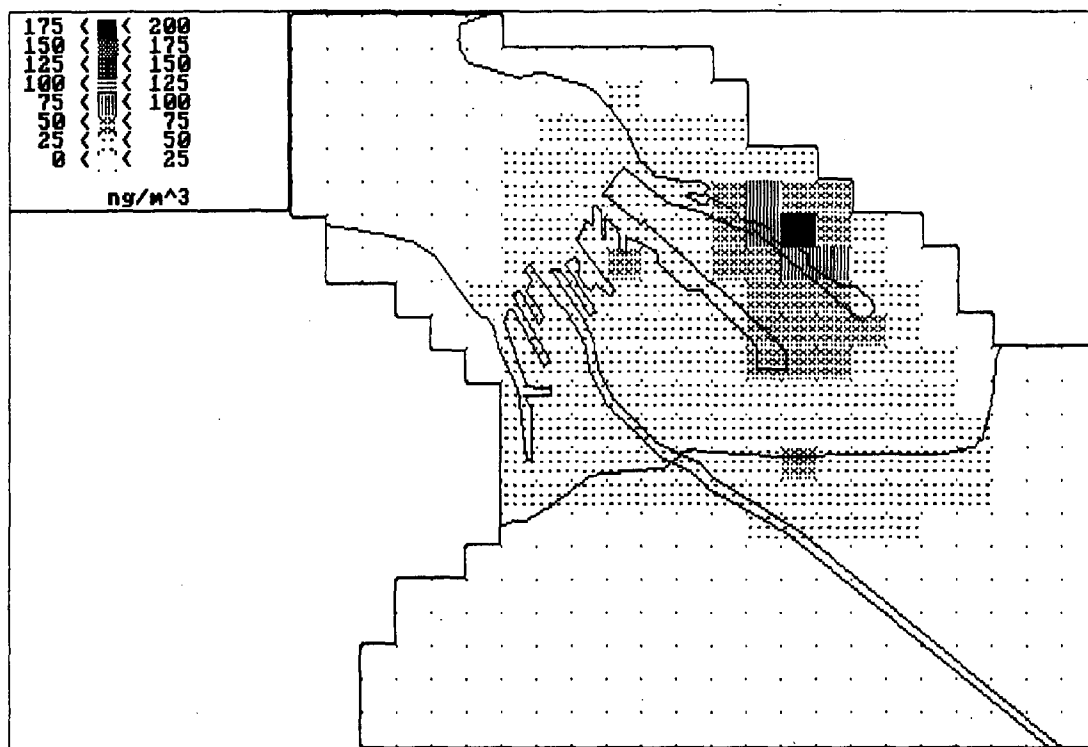
Average Concentration over 186 days

Figure 7-8(c). Sum of Wet and Dry Depositions for Copper (Cu) Aerosols
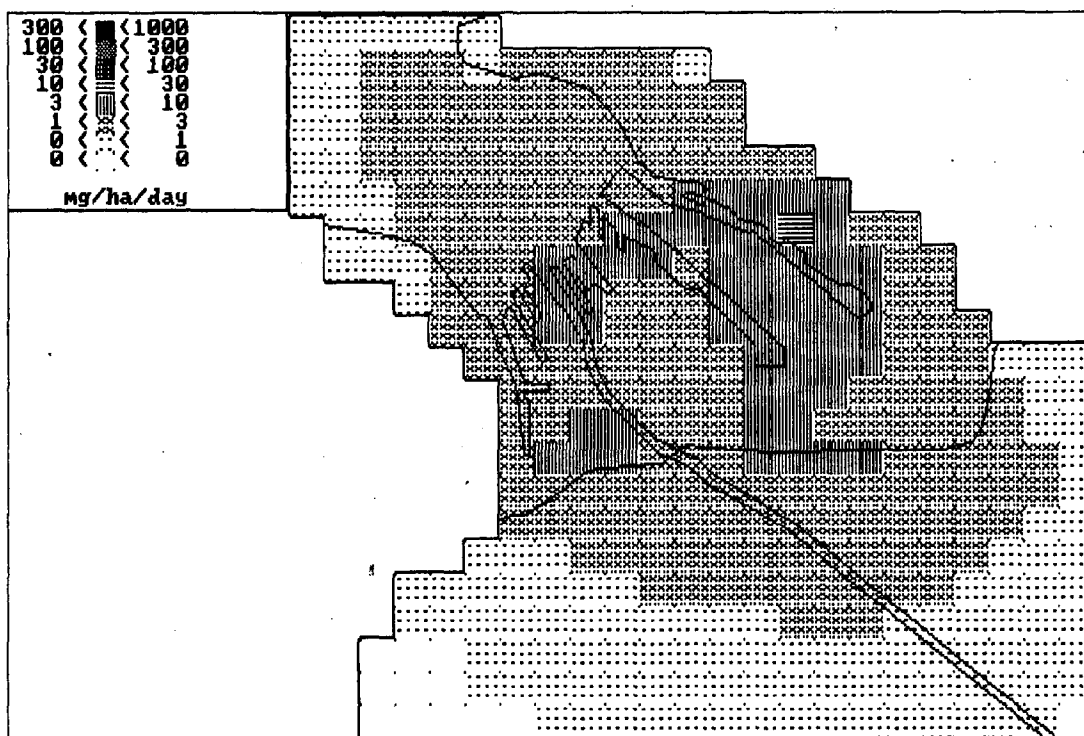
Average Total Deposition Rate: milligrams/hectare/day

Figure 7-9(a). Simulated Highest 24-Hour (midnight-to-midnight) Averages for Lead (Pb) Aerosols
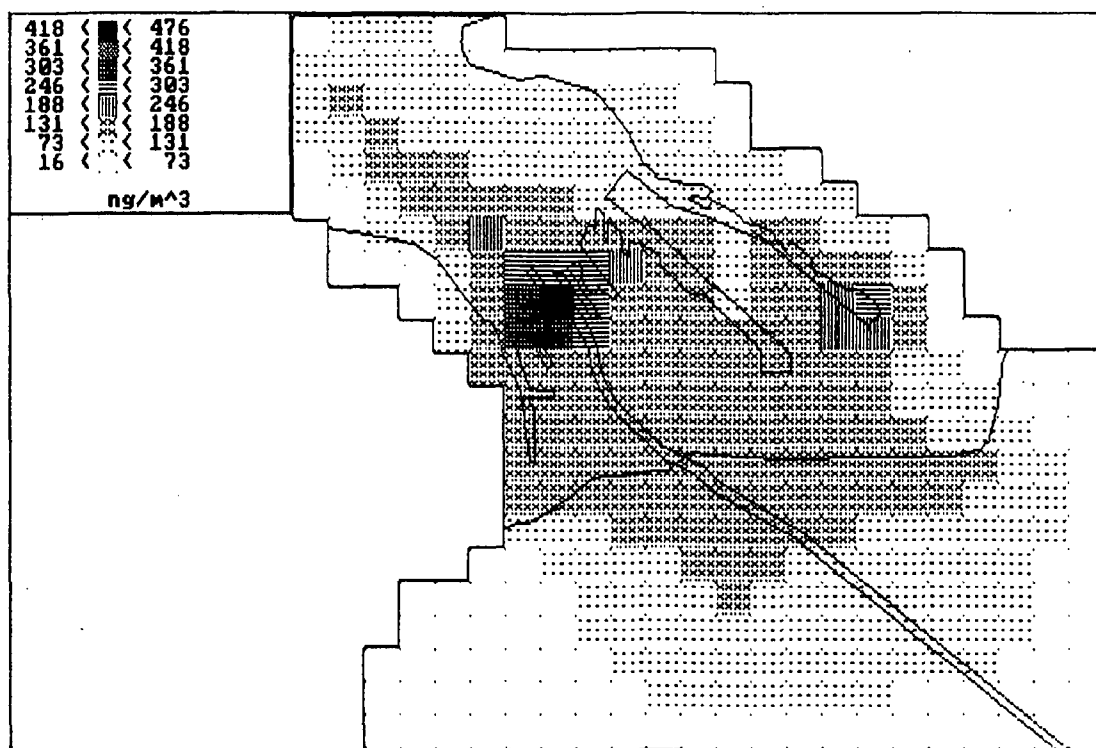
Highest 24-hour average, lower level

Figure 7-9(b). 186-Day Average for Lead (Pb) Aerosols
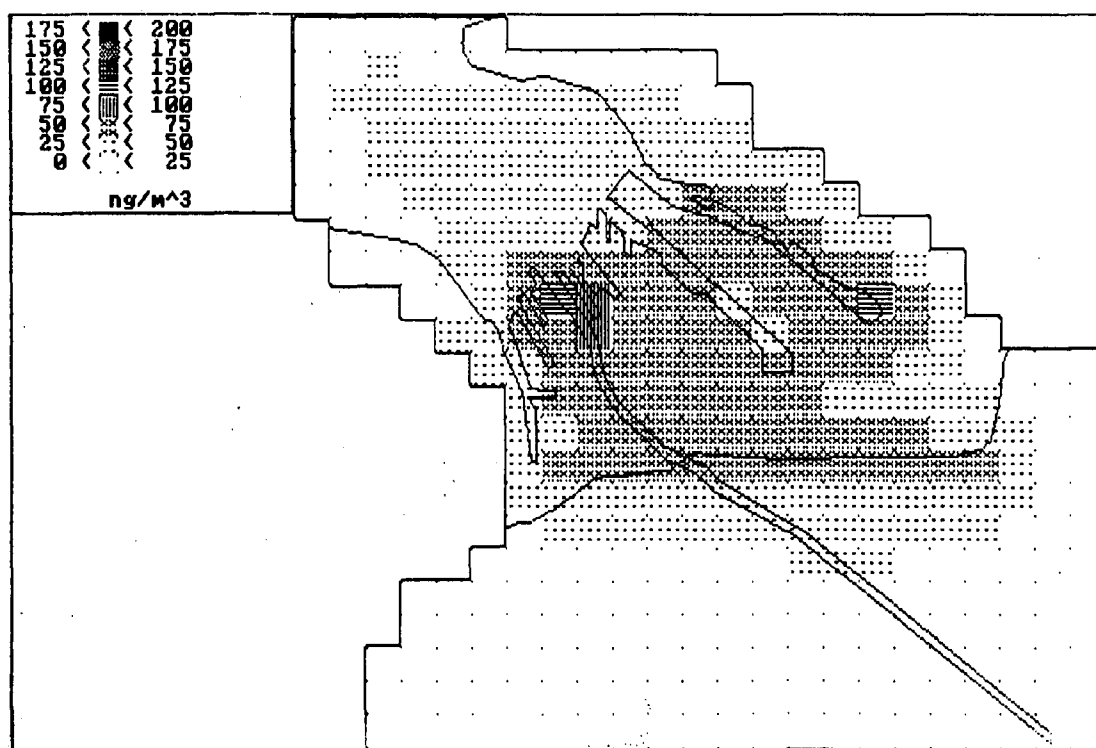
Average Concentration over 186 days

Figure 7-9(c). Sum of Wet and Dry Depositions for Lead (Pb) Aerosols

Average Total Deposition Rate: milligrams/hectare/day
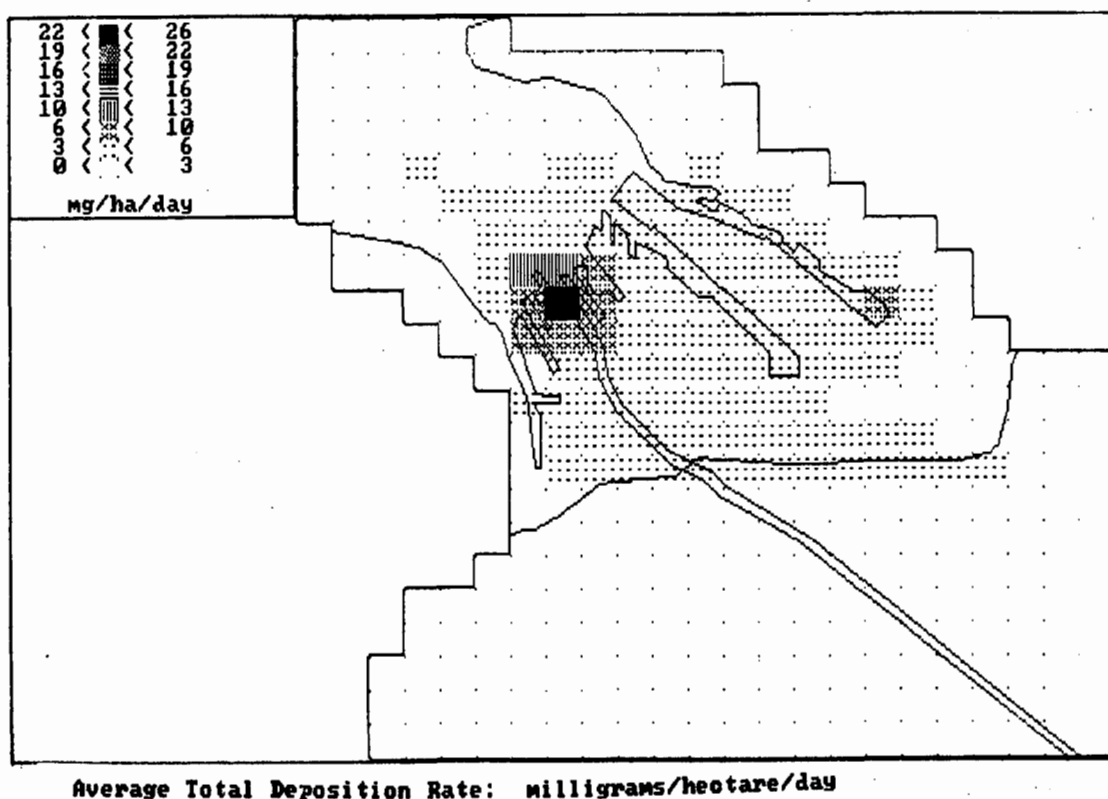
Figure 7-10(a). Simulated Highest 24-Hour (midnight-to-midnight) Averages for Zinc (Zn) Aerosols

Highest 24-hour average, lower level
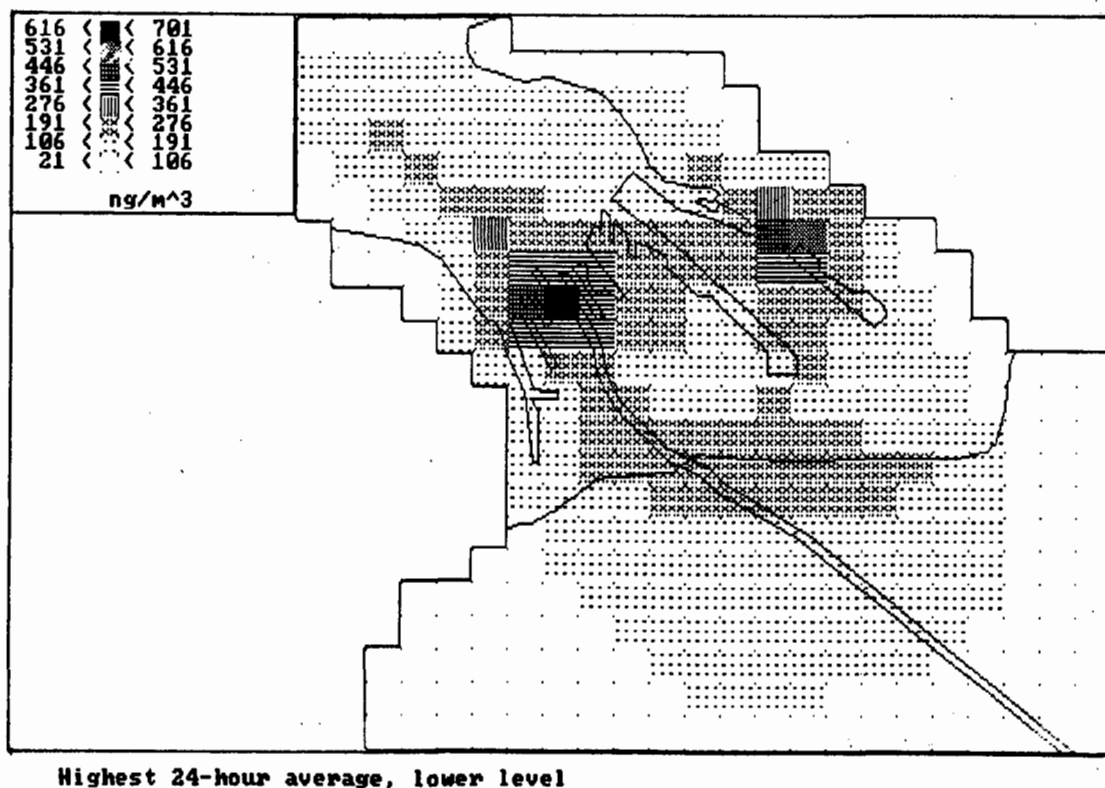
Figure 7-10(b). 186-Day Average for Zinc (Zn) Aerosols
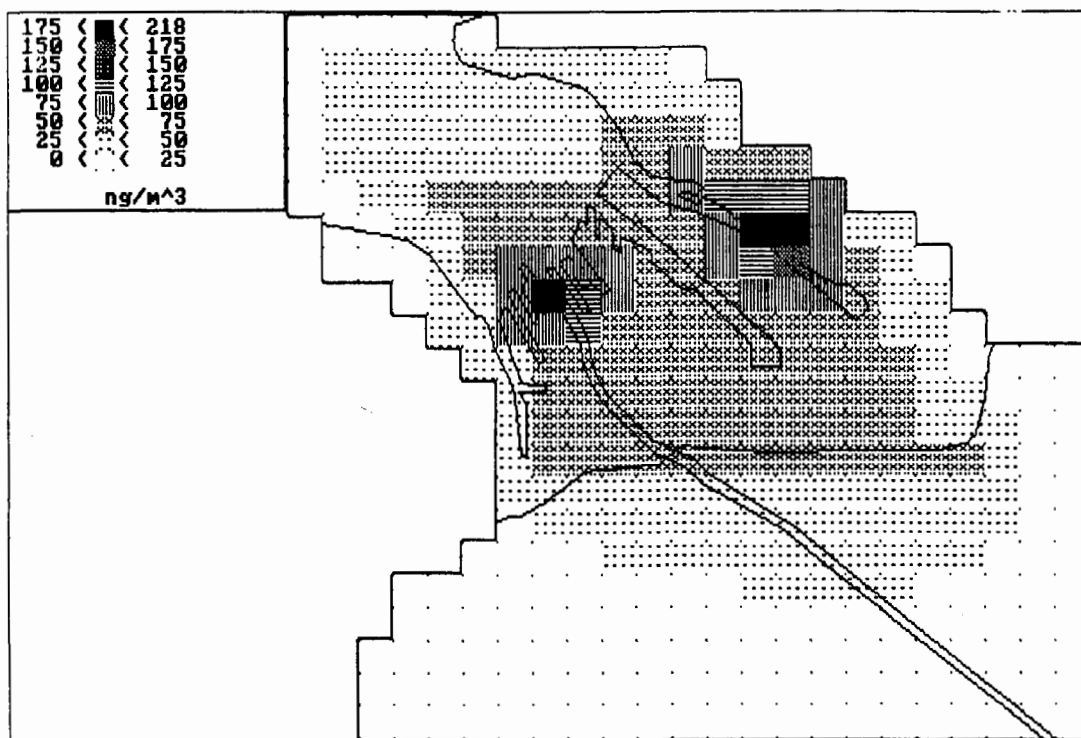
Average Concentration over 186 days

Figure 7-10(c). Average Total Deposition Rate (Wet + Dry) for Zinc (Zn) Aerosols
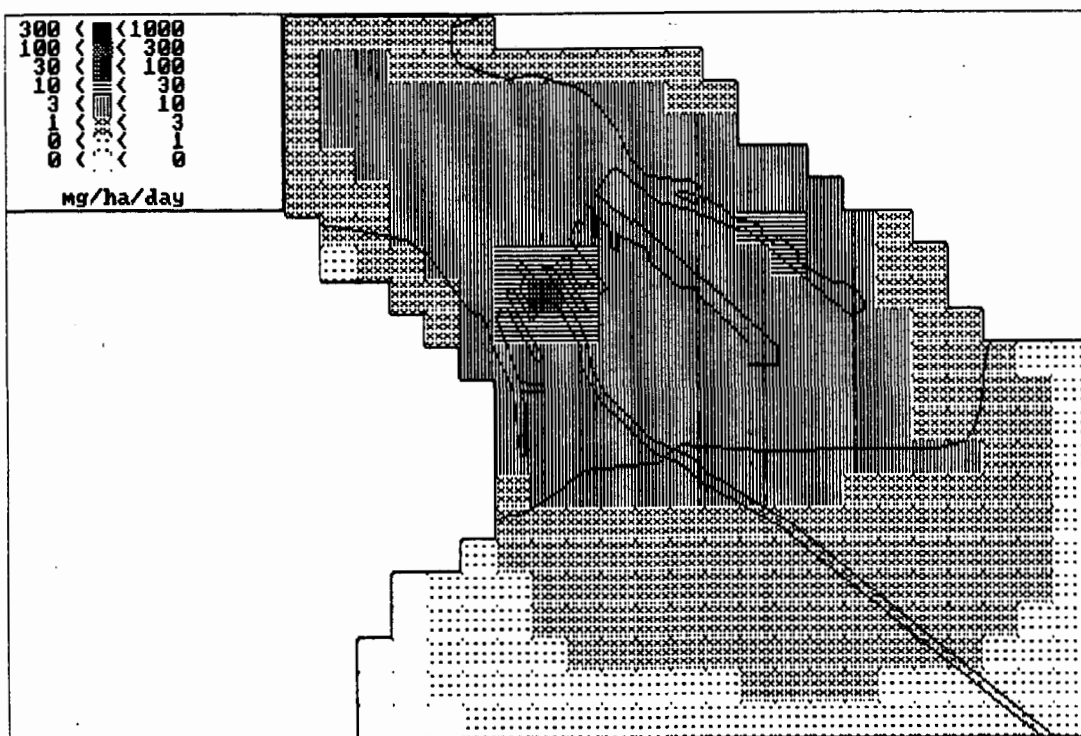
Average Total Deposition Rate: milligrams/hectare/day

Figure 7-11(a). Simulated Highest 24-Hour (midnight-to-midnight) Averages for Vapor + Particulate PAH
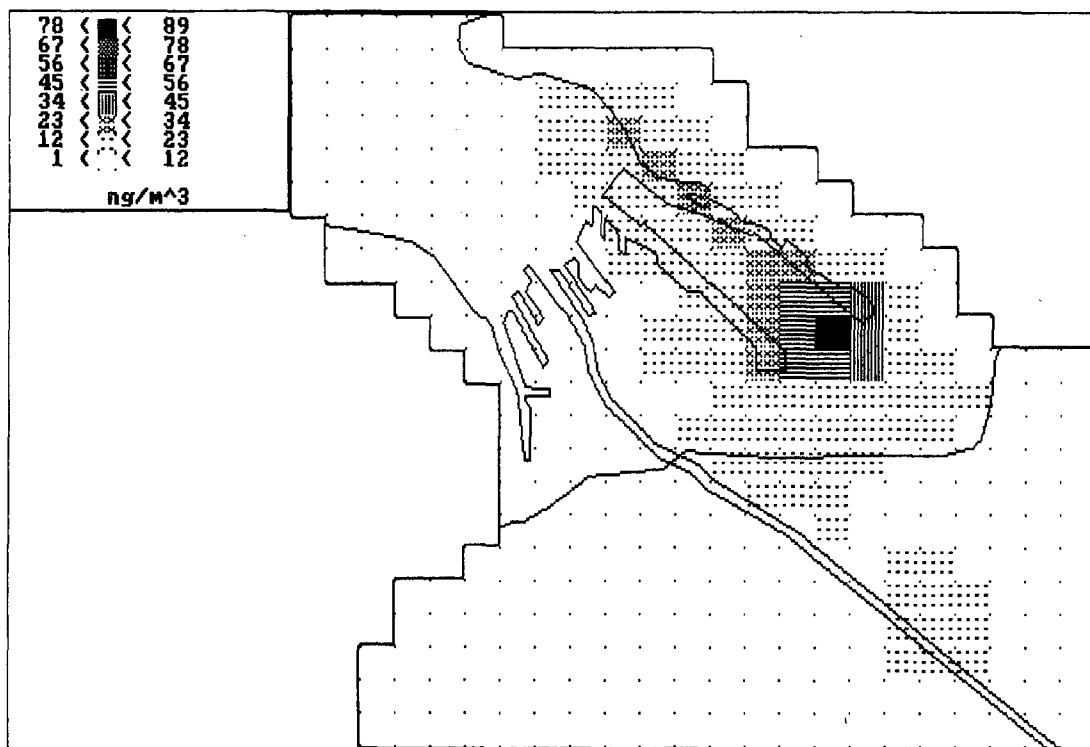
Highest 24-hour average, lower level

Figure 7-11(b). 186-Day Average for Vapor + Particulate PAH
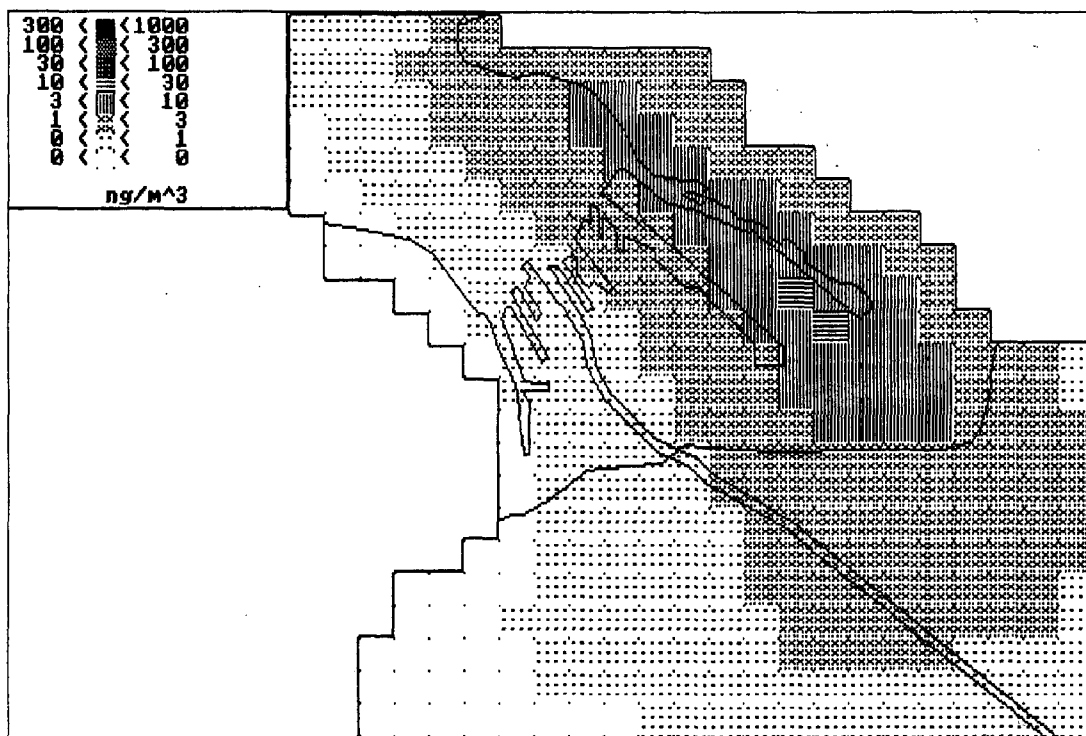
Average Concentration over 186 days

Figure 7-11(c). Sum of Wet and Dry Depositions for Vapor + Particulate PAH

Average Total Deposition Rate: milligrams/hectare/day
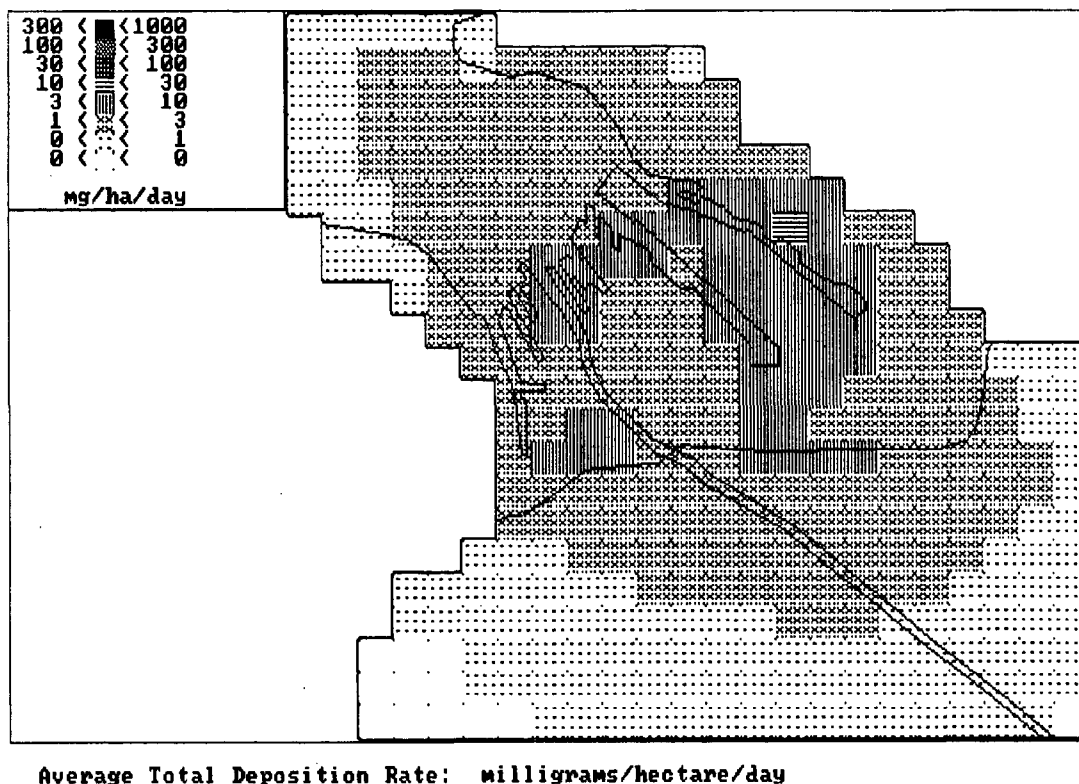
Mobilization into Runoff to Commencement Bay

The "bottom line" for the simulations, and indeed for the study itself, is estimates of the fractions of each contaminant that are deposited onto the watershed and actually reach Commencement Bay. For these estimates, not only are the spatial distributions of the fluxes of each contaminant to the surface needed (Figures 7-7 to 7-11), but also the spatially-dependent efficiencies with which each contaminant in each grid cell is mobilized into the runoff to Commencement Bay (mobilization coefficients). These coefficients have not been experimentally determined for the study area. Instead, annual average mobilization coefficients were estimated with a linear washoff model computed by cell for the area of the Commencement Bay watershed modeled by the diffusion model. Insufficient data were available to allow the calculation of mobilization coefficients for individual metals and PAHs. Therefore, for modeling purposes, both metals and PAHs were assumed to be completely associated with fine sediments, and were considered as a single sediment-bound contaminant.

The development of the Mobilization Coefficient Model is summarized here and the results for the Tacoma Tideflats area are contained in Appendix F-6. A stormwater transport model was developed to serve as the basis of the contaminant transport model. Surface runoff doesn't travel far in the Tacoma Tideflats area before it either enters a drainage pipe or ditch, or infiltrates into the soil. For flow in drainage pipes, bare impervious ditches, and bare pervious ditches that contain water throughout most of the year 100% of the contaminants are assumed to be transported. For ditches that are dry throughout most of the year, but have pervious linings and for ditches that contain substantial vegetation, all metals and PAHs are assumed to be bound to sediment particles and completely removed by filtration and settling. The flatness of the area provides little driving force for overland flow, thereby enhancing stormwater

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infiltration and settling. In the developed industrial area north of Interstate 5 pipe flow is more important than in the rural area south of the Interstate. To model contaminant transport within each cell, watershed data including land use, SCS hydrological soil group, surface cover type, and drainage pathways was obtained from aerial photos and site inspections.

The phase in which a contaminant exists largely determines its environmental fate. This information was not known for the contaminants considered here. Degradation by bacteria, sunlight, and hydrolytic actions could change the chemical form what was originally deposited. In addition dramatic pH changes can occur from bock to block in industrial areas. To simplify the development and implementation of the Mobilization Coefficient Model, it was assumed that 100% of all metals and PAHs which accumulate during a typical dry period are sorbed to fine-particulate matter by the beginning of the next rainfall.

The mobilization coefficient is a number between 0 and 1 that represents the fraction of the land-deposited contaminants that will be carried by surface water runoff, by groundwater, or through a series of pipes into the waterway. Where the cell is over Commencement Bay or the Puyallup River the coefficient is unity, and where it is partially over the Bay, a lower limit to the mobilization coefficient is that fraction of the cell that is subtended by water. For cells over land areas, the linear model predicts that less than 10 percent (mobilization coefficient less than or equal to 0.1) of the deposited contaminants will reach Commencement Bay through "prompt runoff" (runoff occurring during the period of this study). Factors contributing to this relatively low value include the existence of significant areas of vegetated open space, unlined vegetation drainage ditches, and the flatness of the land. Another factor in the low mobilization is the predominance of small storms in the annual rainfall pattern of the Pacific Northwest. For exceptional storms, where large and sudden flows mechanically scour the drainage ditches, it is plausible that deposits that have accumulated over fairly long periods may be flash-mobilized. These deposits will likely have a reduced contaminant load, as compared with the original deposited material, due to photolysis, biodegradation, biological uptake or vertical migration through soils.)

Since mobilization coefficients were never experimentally determined, there are no values for comparison with the computed model values, and therefore the errors associated with the model values cannot be precisely determined. Potential sources of error include the "typical year" estimate of rainfall, the assumption that contaminants are bound to particles, the washoff model, the deposition estimates, and the assumption that contaminants not washed off by one storm will be unavailable for washoff by a later storm event. Without verification and error analysis the model can only provide rough, semi-quantitative estimates of pollutant mobilization coefficients.

Because of the above-noted uncertainties in the mobilization coefficients, the total fluxes to Commencement Bay have been computed twice: once with those coefficients derived by the Mobilization Model (Appendix F-6), and once with the same coefficients modified so as to never be less than 0.1 in any cell. The results of these computations are presented in Table 7-4.

Table 7-4. Estimates by the WV3 Model of Fractions of Emitted Toxic Contaminants Deposited Within the Modeled Domain (91.5 km²) and Mobilized Into the "Prompt-Runoff" Watershed of Commencement Bay:

I. With washoff coefficients estimated in Appendix F-6:

	Source Emissions	Deposition/Emission			Fractions of Emissions Transported		
		Modeled Domain			Commencement Bay		
	Q (kg/day)	Wet/Q %	Dry/Q %	Sum/Q %	W/Q %	D/Q %	Tot/Q %
Arsenic	0.74	4.74	2.46	7.20	1.97	1.42	3.39
Copper	3.85	5.53	2.47	8.00	2.12	1.09	3.20
Lead	7.07	3.65	2.42	6.07	1.53	1.47	2.99
Zinc	9.88	3.36	2.40	5.76	1.48	1.55	3.03
PAHs	1.00(*)	1.33	0.85	2.18	0.48	0.33	0.80

II. With washoff coefficients estimated so that they are never less than 0.1 in any cell:

	Source Emissions	Deposition/Emission			Fractions of Emissions Transported		
		Modeled Domain			Commencement Bay		
	Q (kg/day)	Wet/Q %	Dry/Q %	Sum/Q %	W/Q %	D/Q %	Tot/Q %
Arsenic	0.74	4.74	2.46	7.20	2.36	1.57	3.93
Copper	3.85	5.53	2.47	8.00	2.62	1.29	3.91
Lead	7.07	3.65	2.42	6.07	1.83	1.60	3.43
Zinc	9.88	3.36	2.40	5.76	1.76	1.68	3.43
PAHs	1.00(*)	1.33	0.85	2.18	0.60	0.41	1.01

NOTES:

(*) PAH emissions are nominal, and should be renormalized for each separate PAH compound (see Table 7-1).

Wet/Q values are the ratios of all of the rainborne deposits to all the emissions, within the modeled domain, expressed as percents.

Dry/Q values are the ratios of all of the dry deposits to all the emissions, within the modeled domain.

Sum/Q = Wet/Q + Dry/Q.

W/Q are the ratios of wet deposits times washoff coefficients, to all of the emissions. These are the fractions of emitted contaminants that are promptly deposited or washed into Commencement Bay by rain.

D/Q are the ratios of dry deposits times washoff coefficients, to all the emissions. These are the fractions of emitted contaminants that are either dry-deposited into Commencement Bay, or dry-deposited onto the nearshore watershed and washed into Commencement Bay by subsequent runoff.

Tot/Q = W/Q + D/Q Fractions of all emissions transported into Commencement Bay.

1. Assumed dry deposition velocities : 0.1 cm/s
2. Assumed washout ratios (metals) : 1000
   (PAH) : 300

(A washout ratio is the concentration of a tracer in rain/concentration of the tracer in air.)

From Sum/Q it can be noted that greater than 90 percent of the emitted tracers (PM_{10} size fraction) are advected beyond the boundaries of the modeled domain. Perhaps one to three percent of emitted contaminants reaches Commencement Bay directly within the "prompt-runoff" watershed. Based on the particle deposition processes as modeling in WV3 and the mesoscale meteorology and topography of Puget Sound, it is likely that an additional three to four percent of the airborne tracers (As, Cu, Pb, Zn, and PAHs) emitted in the Tacoma Tideflats will reach Puget Sound beyond the 91.5 km^2 modeling domain. This projected loading is summarized in Table 7-5.

Table 7-5. Projected Mass Loading of Airborne Toxic Contaminants to Puget Sound Based on Emissions in 91.5 km^2 WV3 Modeling Domain

Contaminant	Estimated Mass Loading kg/year (3-7% of emissions)
As	8 - 19
Cu	42 - 98
Pb	77 - 181
Zn	108 - 252
PAH[a]	11 - 19

[a]Based on nominal emission rate of 1 kg/day. Total Should be multiplied by total PAH emissions in Table 7-2.

Chapter 8. Comparison of Studies

This study examined atmospheric contaminants from a number of different perspectives. Each sampling program or model effort focused on a somewhat different array of particle sizes and time and space scales, in effect capturing a piece of the total picture. This chapter provides data comparisons to bridge between and reconcile the individual study components. This additional analysis is critical to fully test and evaluate the tools used and to address gaps in sampling. Both qualitative and quantitative comparisons are attempted within the bounds of the study assumptions and limitations.

PAIRED COMPARISONS

1. Aerosol/Deposition Sampling

Objective of Comparison: How predictive is one sample of the other? Can we forego one type of sampling and still have a reasonably good idea of what will be in the other sample? What do differences in the samples tell us about the sources and the transport/deposition processes involved?

Limitations in Performing the Comparison:

Aerosol

▸ Upper size range of particles sampled was limited to 25-50 μm (depending on wind speed); larger particles in the ambient aerosol may have been missed.

▸ Sampler performance is variable, affected by precipitation and wind speed; collection efficiency of smaller particles (<1.0 μm) unknown.

▸ Long time period for collection of the sample (three or four days) increased possibility of vapor breakthrough from the PUF and changes in vapor-particle partitioning. (Direct measurement of breakthrough not made for the field samples.)

▸ Limited number of samples analyzed.

Deposition

▸ Particle size spectrum in sample not measured.

▸ Long collection period (two weeks) introduced opportunities for revolatilization of samples or transformation of chemicals (e.g. photolysis, biodegradation), particularly during summer conditions.

▸ Performance of samplers for collection of large particles blown horizontally across the sampling surface not known.

▸ Samplers at all sites not at same height, therefore different potential to capture large particles.

Approach: 1) Compare mean aerosol concentration and mean deposition rate for samples that match up in time and space. Rely on metals data rather than PAH, to reduce potential sampling and analytical error in comparison. 2) Compare aerosol and deposition data for all sample dates analyzed for a particular station to examine patterns.

Results: Only three deposition samples had all aerosol samples during the corresponding sample period analyzed: the two week samples beginning on September 7, November 2, and November 30 at Alexander Avenue. The data for these samples are presented in Table 8-1. Figure 8-1 is a plot of the mean aerosol concentration and mean deposition rate for all three periods for As, Cr, Mn, Ni, Pb, and Zn. Figures 8-2 through 8-5 show all analyzed aerosol and deposition samples for the Alexander Avenue and Morse sampling sites plotted first for metals and then for PAHs. (Similar plots for the Sea-Land, Riverside, and Tyee Marina are included in Appendix G-1.)

Table 8-1. Mean Deposition Rate, Mean Aerosol Concentration, and Deposition Velocity (V_d) at the Alexander Avenue Site for Three Sampling Periods

	Mean Deposition $\mu g/m^2/day$	Mean Aerosol ng/m^3	Deposition Velocity (V_d) cm/sec
	September 7 - 21		
As	14.1	19.4	0.84
Cr	1.8	5.7	0.37
Mn	187	66	3.3
Ni	57	16.2	4.0
Pb	91	45.4	2.3
Zn	360	110	3.8
	November 2 - 16		
As	7.4	2.5	3.4
Cr	12.2	4.5	3.1
Mn	70.1	19.5	4.2
Ni	5.8	5.0	1.3
Pb	38	18.3	2.4
Zn	249	39.5	7.3
	November 30 - December 14		
As	5.4	5.0	1.3
Cr	7.4	6.8	1.3
Mn	61	61	1.2
Ni	44	19.8	2.6
Pb	21	41	0.59
Zn	147	161	1.1

Figure 8-1. Comparison of Mean Aerosol Concentration (ng/m³) and Mean Deposition Rate (µg/m²/day) at the Alexander Site for September 7 - 21, November 2 - 16, and November 30 - December 14. All Data for As, Cr, Mn, Ni, Pb, and Zn are plotted
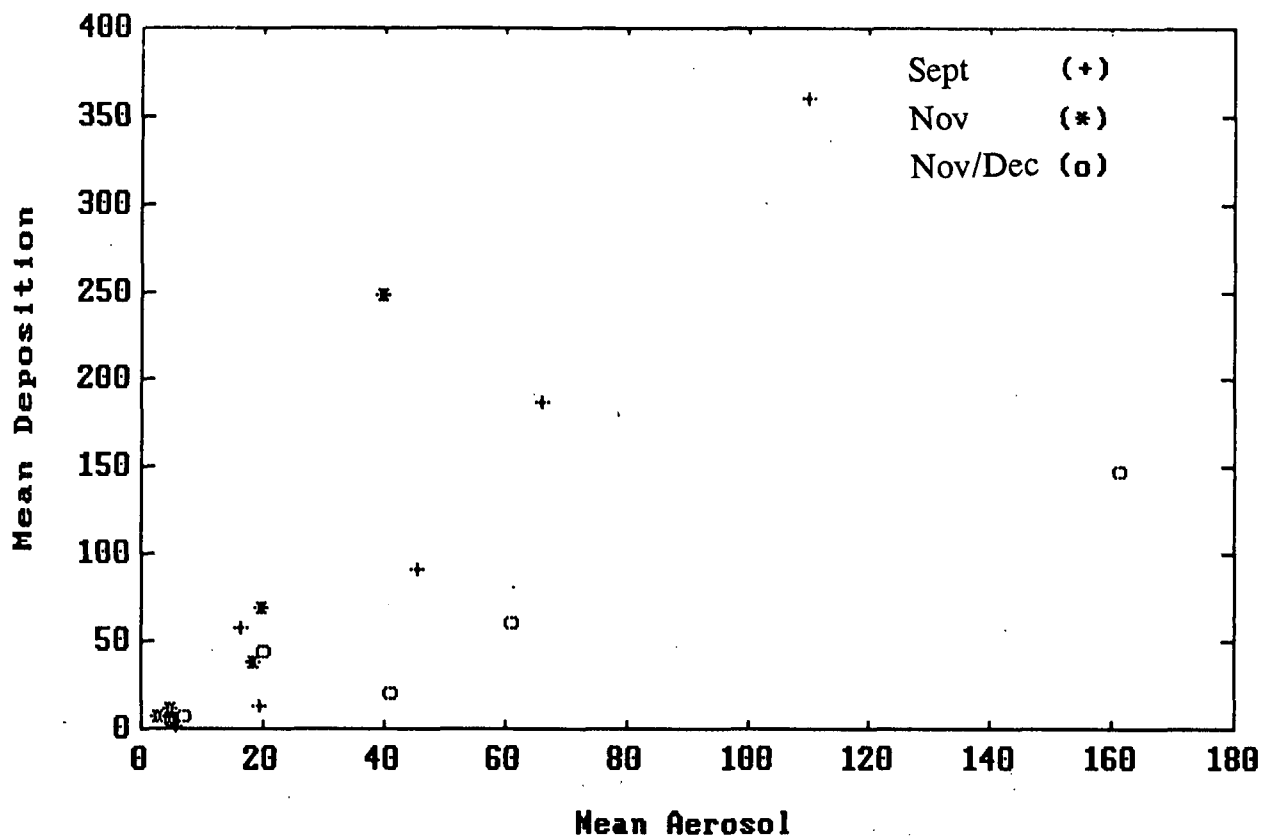
Figure 8-2(a). Aerosol Particulate Metal Concentrations (ng/m³) at the Morse Supply Site
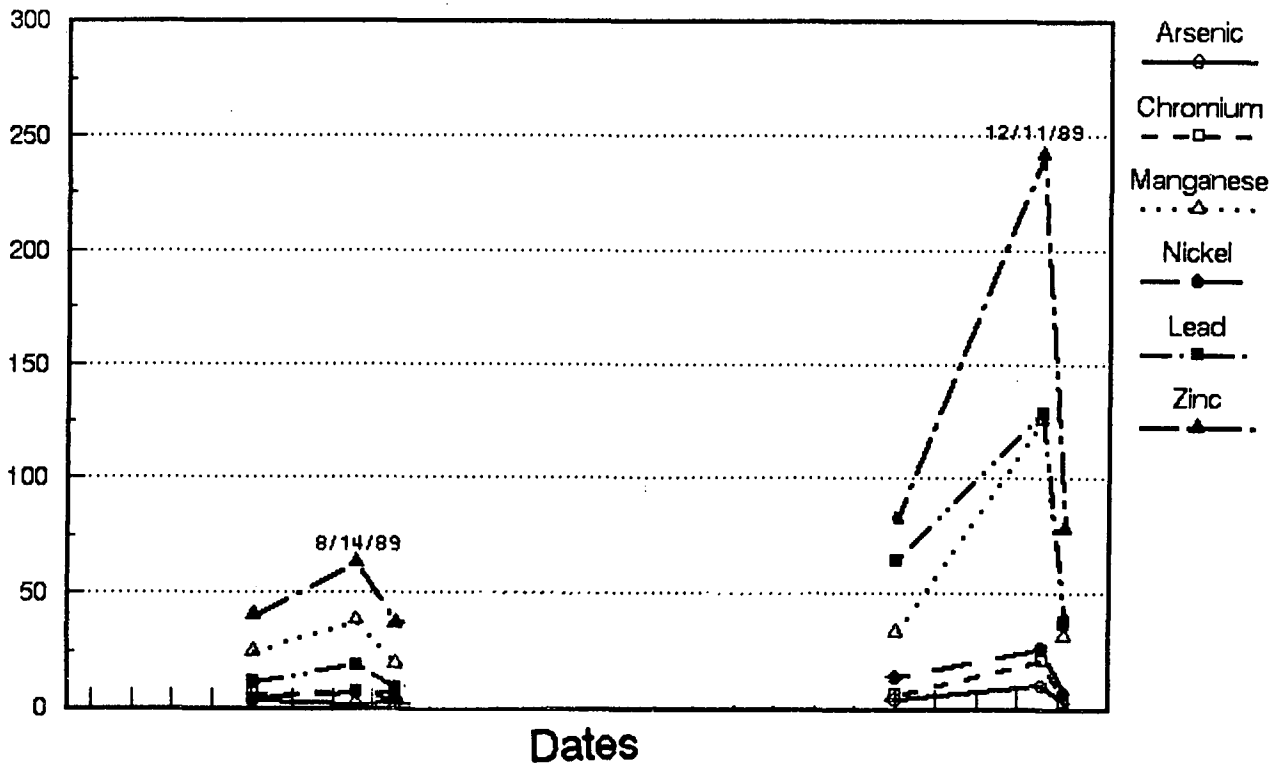
Figure 8-2(b). Metal Deposition Rate (μg/m²/day) at the Morse Supply Site.
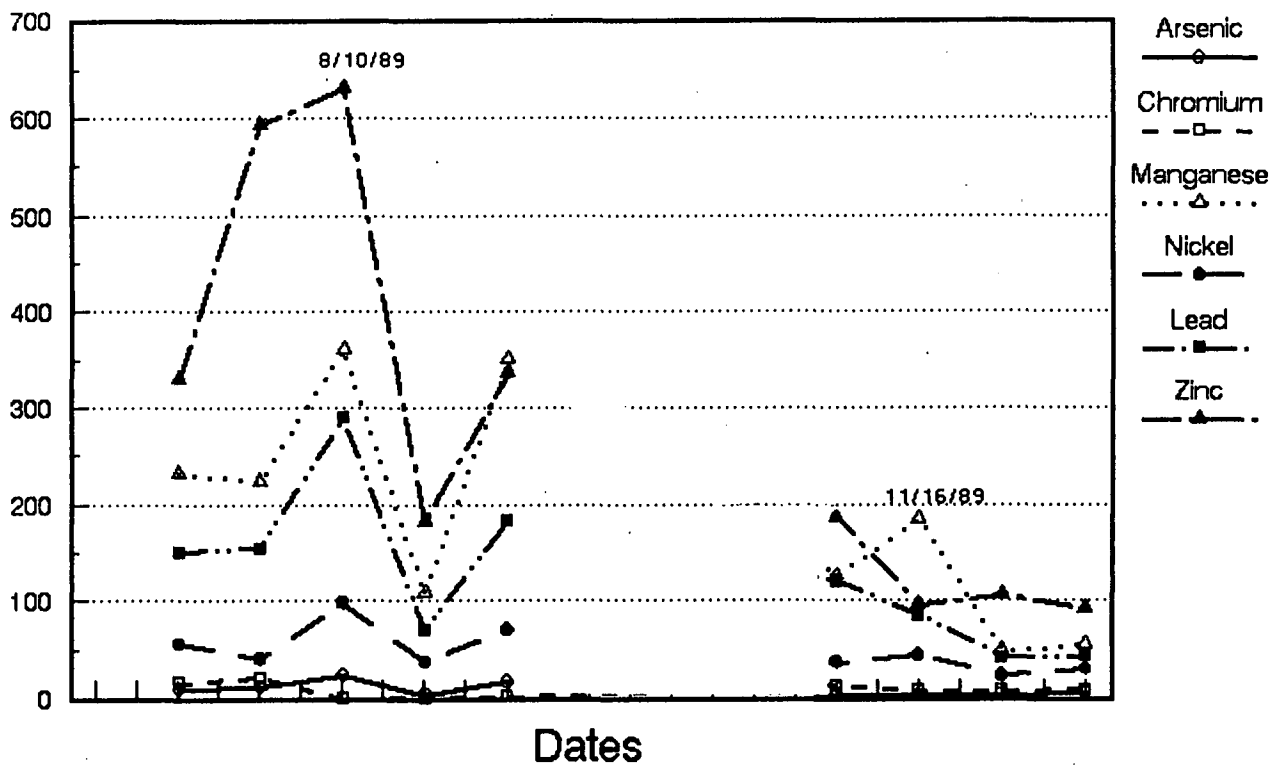
Figure 8-3(a). Aerosol Particulate Metal Concentrations (ng/m³) at the Alexander Avenue Site
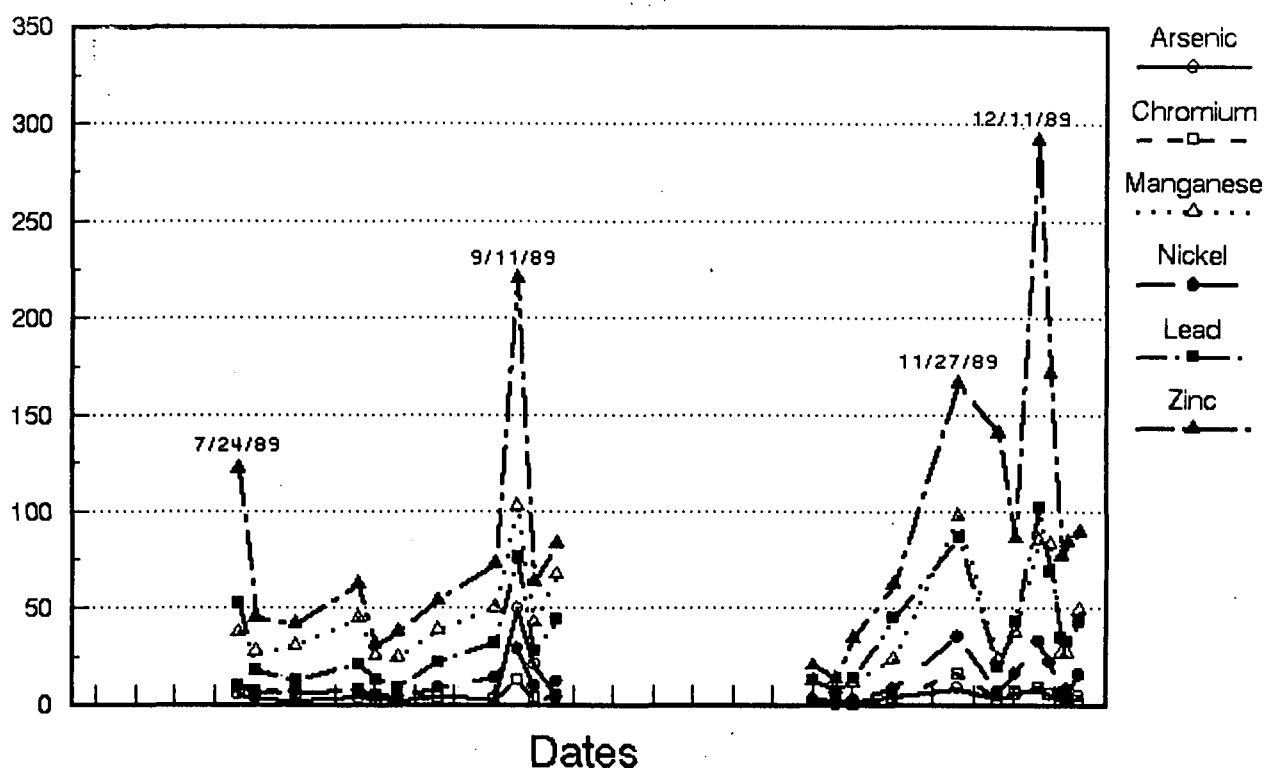
Figure 8-3(b). Metal Deposition Rate (μg/m²/day) at the Alexander Avenue Site
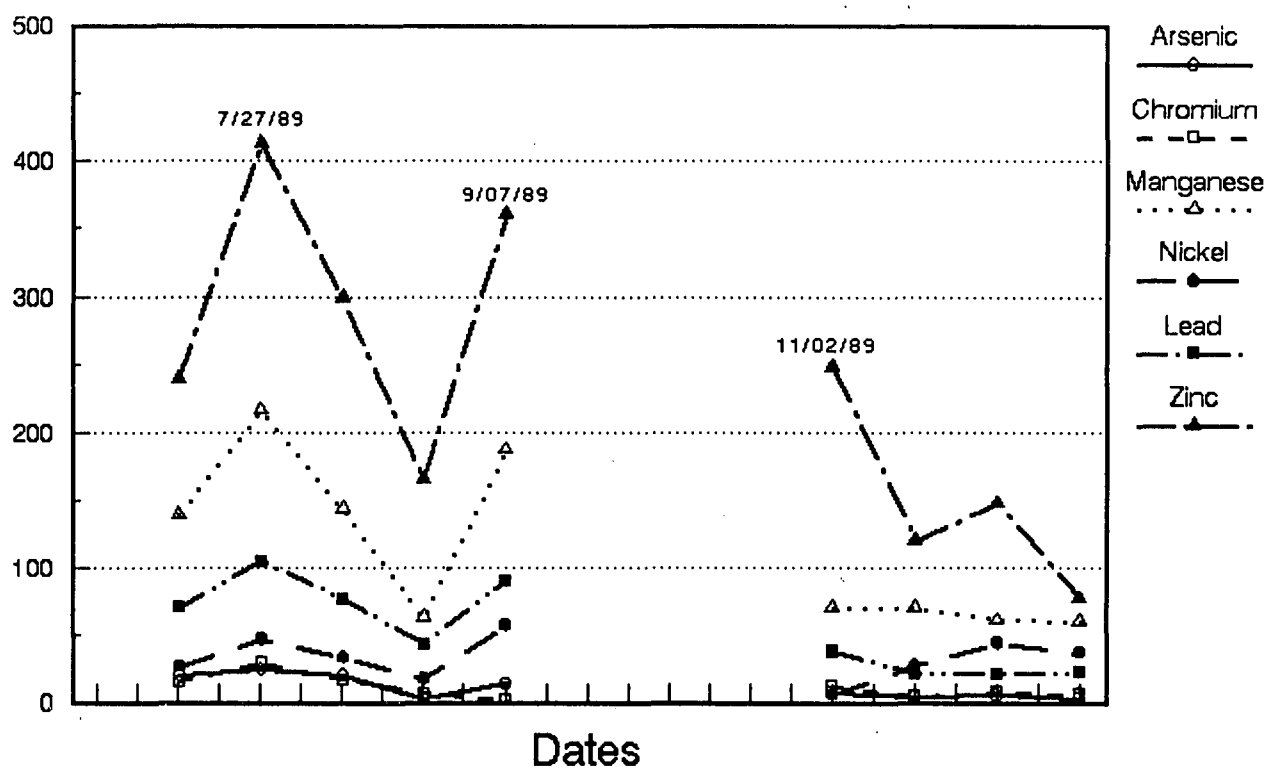
Figure 8-4(a). Aerosol Particulate PAH Concentration (ng/m³) at the Morse Supply Site
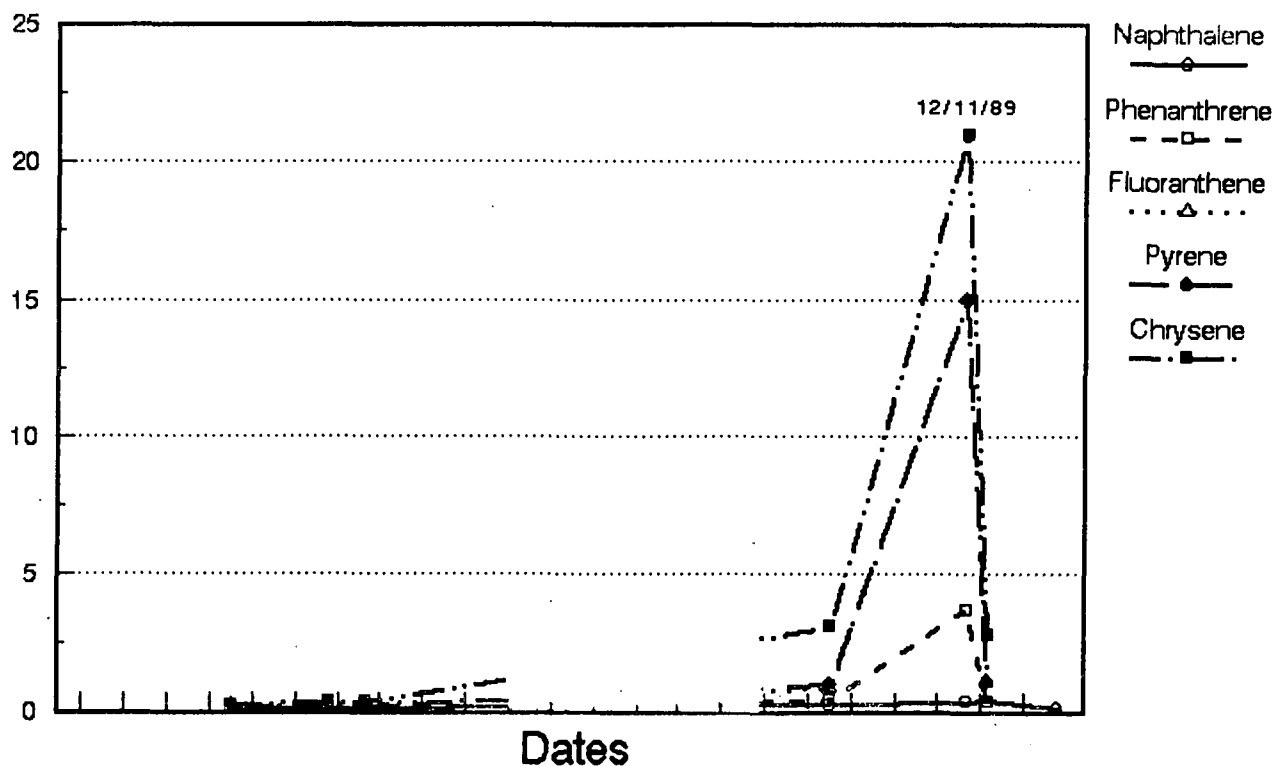
Figure 8-4(b). PAH Deposition Rate (ng/m²/day) at the Morse Supply Site
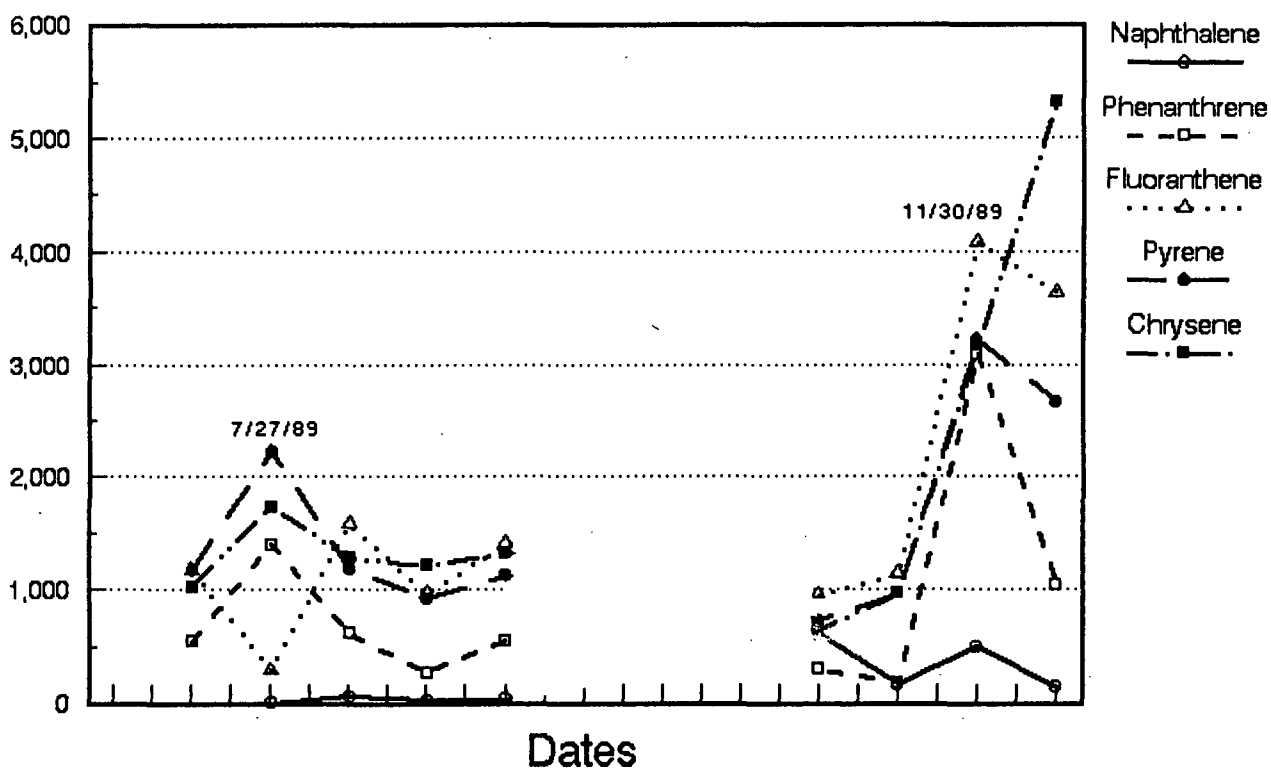
Figure 8-5(a). Aerosol Particulate PAH Concentrations (ng/m³) at the Alexander Avenue
Site
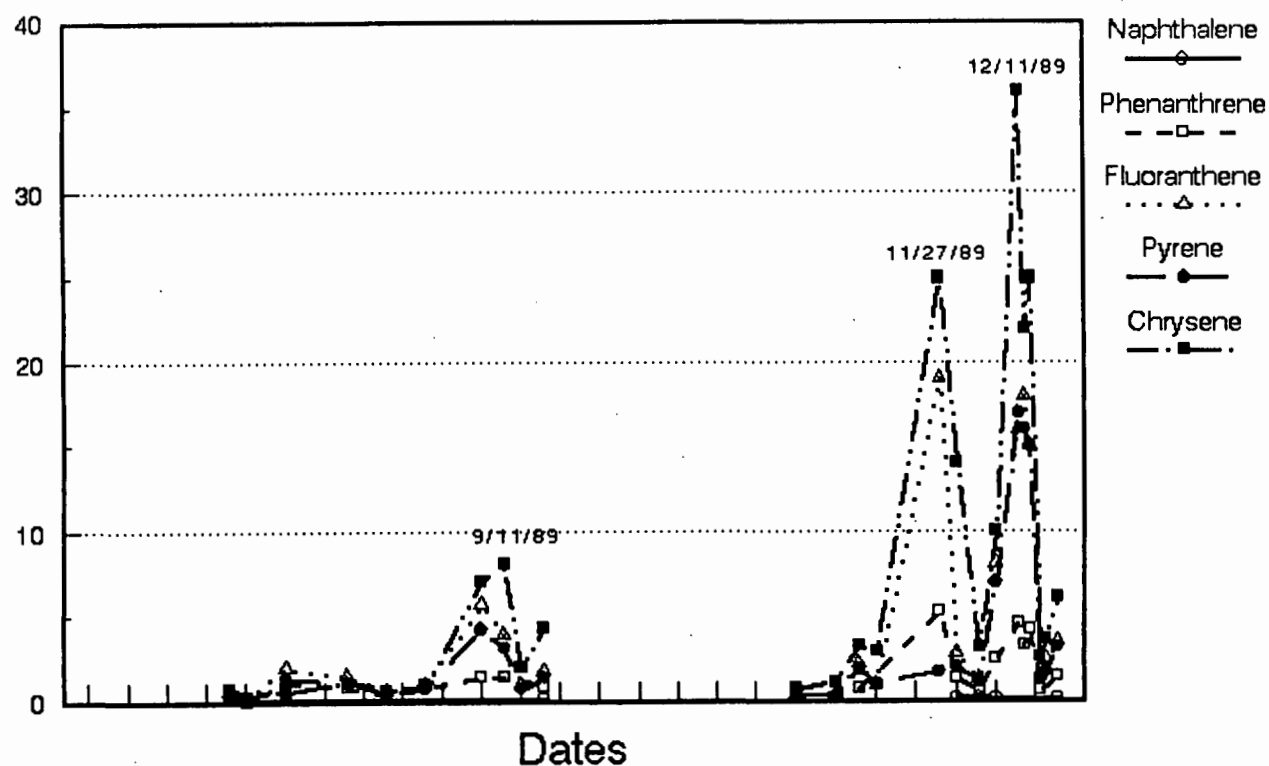
Figure 8-5(b). PAH Deposition Rate (ng/m²/day) at the Alexander Avenue Site
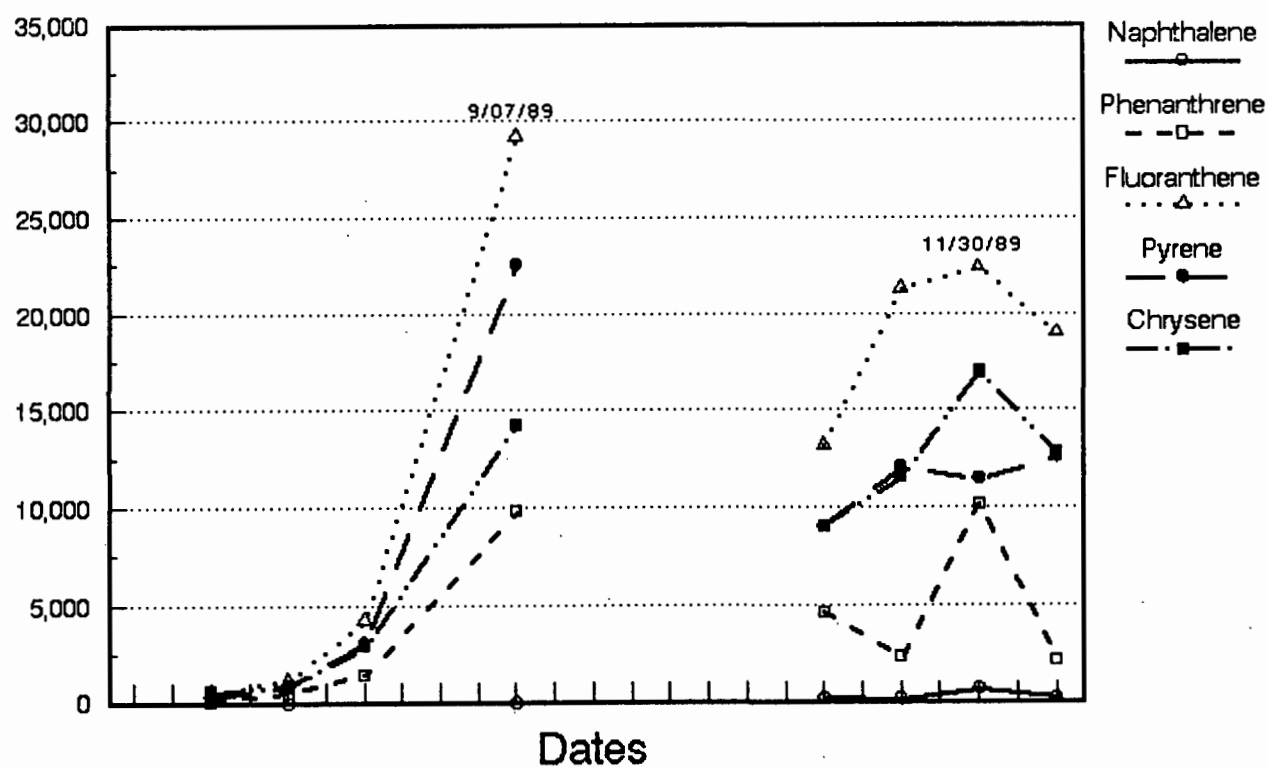
Analysis: For the reasons listed above under Limitations, direct comparison of the aerosol and deposition data is complicated by numerous potential unquantified biases in the sampling and analyses. It is not possible with the limited data to sort out the separate effects of meteorology, different particle sizes sampled, and different emissions mixes. The data in Table 8-1 reveal different deposition velocities for each month and each metal, with no clear pattern between the different metals. The September sampling period was dry, while November and December were wet (90 and 108 mm rain collected). November 2 corresponded with the beginning of a 48-hour Type 2 air stagnation episode for Tacoma. The data in Figure 8-1 are too limited to make definitive judgements, however they show a pattern of higher deposition versus aerosol concentrations in November and the opposite in September. These data cannot, however, be treated as independent, given the likelihood that certain metals co-occur on the same particle. Deposition velocities are quite high, far exceeding deposition velocities assumed for PM_{10} (0.1-0.3 cm/sec). The deposition velocities are within the range of measurements elsewhere for TSP (total suspended particulates) and are probably associated with very large particles. Observations of the deposition pans noted that particles in the sand/grit size range were collected.

Figures 8-2 through 8-5 must be viewed cautiously because the aerosol and deposition samples do not coincide precisely in time. However, these plots show an interesting pattern of generally higher metals deposition rates in the summer and early fall and higher aerosol metals concentrations in the December sampling period. These differences might be attributed to the potential for the two sampling devices to capture different size fractions of particles. PAH aerosol concentrations and deposition rate do not exhibit this same relationship. At the Morse site the pattern in deposition parallels the aerosol concentrations. At the Alexander Avenue site the deposition rate in early September is very high, not following the same pattern as Morse relative to the aerosol concentration. The September sampling period was characterized by construction activities at a site near Alexander Avenue.

Summary: Uncertainties in the data, based on the number of potential sampling biases, and the minimal number of samples analyzed preclude making any definitive comparisons. It would have been desirable to make comparisons chemical by chemical (taking into account co-occurring metals) and regime by regime (wet vs. dry, high temperature vs. low temperature, high wind vs. low wind, woodstoves on vs. off, etc.). From the data it cannot be concluded that one type of measurement is an adequate predictor of the other. Differences observed seasonally in the aerosol and deposition and the lack of comparison with each other might be attributable to variability seen in particle distribution by season, the chemistry in these distributions, and/or the particle size sampling efficiency of the methods.

2. Aerosol/Diffusion Modeling

Objective of Comparison: Can diffusion modeling be used with confidence in place of aerosol sampling or to extend it in space and time? Do the observations and simulations compare well quantitatively, qualitatively? Are there particular conditions under which there is better, or worse agreement? What do differences between the observations and simulations tell us about the sources or size fractions?

Limitations in Performing the Comparison:

Aerosol

- ▶ Upper size range of particles sampled was limited to 25-50 μm (depending on wind speed); larger particles in the ambient aerosol may have been missed.

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▶ Sampler performance is variable, affected by precipitation and wind speed; collection efficiency of smaller particles ($<1.0 \ \mu$m) unknown.

▶ Long time period for collection of the sample (three or four days) increased possibility of vapor breakthrough from the PUF and changes in vapor-particle partitioning. (Direct measurement of breakthrough not made for the field samples.)

▶ Limited number of samples analyzed.

▶ Range in the upper particle size captured by the aerosol sampler precludes using a single proportionality factor to relate aerosol (PM_{25-50}) and model (PM_{10}) numbers.

▶ Three- to four-day sampling times preclude finer temporal resolution of the data.

▶ Limited temporal and spatial scale of 18-day aerosol PM_{10} sampling (two stations separated by 3.5 km).

Diffusion Model

▶ Only the PM_{10} size fraction modeled.

▶ Spatial resolution of the model limited to 0.5 x 0.5 km grids; may not be descriptive of the smaller-scale, near field source-receptor relationships.

▶ Emission inventory accuracy limited by lack of information on the chemistry and mass emissions specific for Tacoma facilities and their temporal fluctuations.

▶ Emissions were limited to the inventory for the modeling domain; did not account for advection into the domain.

▶ Wind field data for the model limited to a single meteorological site at Alexander Avenue.

▶ Modeling did not account for chemical transformations or vapor emissions.

▶ Deposition velocities assumed by the model were very low compared to the range of measurements made elsewhere.

Approach: 1) Compare mass estimates of model with observations from PM_{25-50} and PM_{10} ambient aerosol sampling. 2) Compare model simulations with PM_{25-50} observations for metals and PAHs. 3) Further break down the data spatially and temporally and compare it for particular emissions and meteorological regimes.

Results: Observations (PM_{25-50}) and simulations (PM_{10}) of aerosol mass for all six sites sampled are plotted as a scattergram in Figure 8-6. Hourly output from the model for each receptor site was averaged over the sampling time of the corresponding aerosol sample. Table 8-2 contains a comparison of the observations and simulations based on 199 pairs of data. From the center "Mean" column it can be seen that the mean of all PM_{10} simulations underpredicts the PM_{25-50} measurements by 48 percent, 61.8 percent of the simulations agree with the observations within a factor of two, and the weighted mean relative error (wMRE) is 64.8 percent. This scoring factor (wMRE) expresses the root-mean-square fractional differences between the observations and simulations, weighted to give more emphasis to the larger measurements. (This is done because larger measurements are of more concern in a regulatory context.) The lower the wMRE, the better the model performance.

Table 8-3 contains site-by-site comparisons and summary scores that aggregate the data so that scores for all sites are compared with the scores for just the central Tideflats industrial area sites (Tyee Marina, Morse Industrial, Alexander Avenue, Sea-Land), omitting the two sites at the northwestern and southeastern boundaries of the Tideflats, Brown's Point and Riverside School. At Brown's Point and Riverside School (wMRE 106.4 and 155.8 percent) the model underpredicts the observations by factors of three and five (11.8 μg/m^3 versus 29.0 μg/m^3 and 9.0 μg/m^3 versus 49.6 μg/m^3). For the other sites combined the wMRE is 52.9 percent. For the four sites the average ratio of simulated PM$_{10}$ to observed PM$_{25-50}$ is 68 percent.

Figure 8-6. Scattergram of Observed PM$_{25-50}$ vs PM$_{10}$ Simulations by WV3 Model
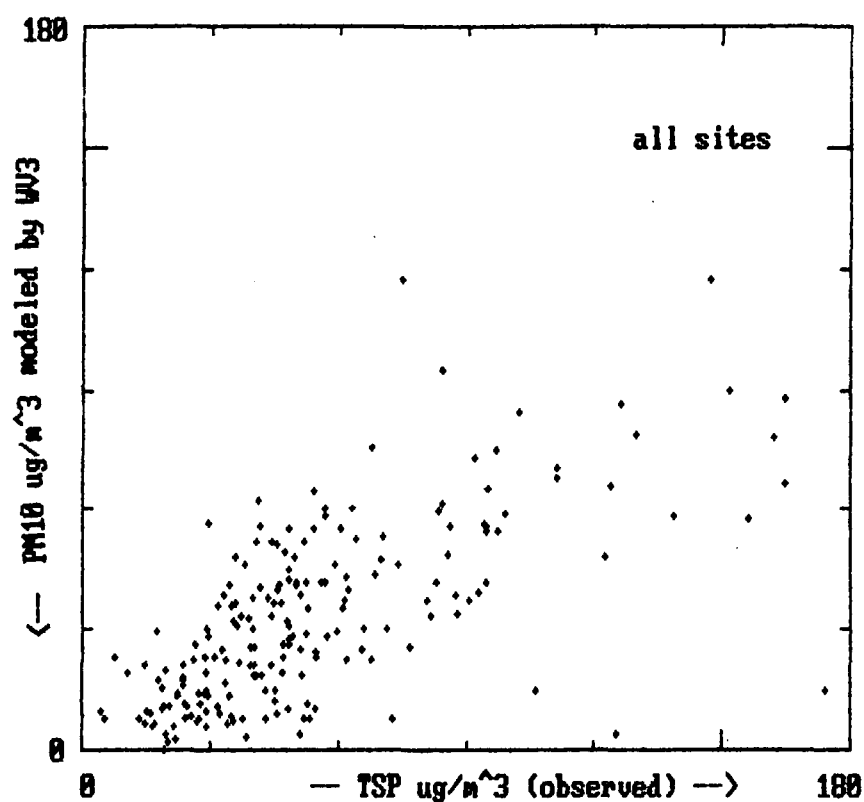
Table 8-2. Comparisons of Observed PM$_{2.5-50}$ with Simulated PM$_{10}$ by Various Protocols

NUMBER OF CASES = 199	90%	75%	Mean	25%	10%
Mean of Predictions	35.5	34.3	32.9	31.6	29.9
Mean of Observations	57.7	55.7	53.9	51.8	49.7
2*[P-O]/[P+O]	-0.41	-0.45	-0.48	-0.52	-0.55
S.D. of Predictions	24.6	23.9	22.5	21.0	20.0
S.D. of Observations	37.7	35.9	33.4	30.9	28.5
2*[P-O]/[P+O]	-0.24	-0.31	-0.39	-0.47	-0.52
FOR PAIRED DATA:					
Agree within a factor of two	67.3%	65.3%	61.8%	58.4%	55.4%
Slope: d[P]/d[O]	0.68	0.66	0.63	0.60	0.58
Correlation coefficient [r] 0.78	0.71	0.66	0.62	0.56	
wMRE= 2*rms<P-O>/rms<P+O>	72.7%	69.4%	64.8%	60.1%	56.4%
Robust MRE	74.1%	70.8%	66.1%	63.7%	60.4%

NOTE: S.D. = Standard deviation

Table 8-3. Comparisons Between Observed PM$_{2.5-50}$ and Simulations by WV3 Model

Site Name	Sample Size	PM$_{2.5-50}$ Mean μg/m^3	WV3 Mean μg/m^3	[--------------wMRE-------------] 75%	50%	25%
Browns Point	24	29.0	11.8	110.8	106.4	101.2
Tyee Marina	54	42.3	27.5	53.9	51.2	48.7
Morse Supply	22	63.5	51.4	45.3	44.1	40.4
Alexander Avenue	54	65.0	44.7	55.6	53.1	49.7
Sea-Land	22	77.1	46.8	66.1	60.4	54.2
Riverside	23	49.6	9.0	158.4	155.8	148.1
All Data	199	53.9	32.9	69.4	64.8	60.1
T+M+A+S	152	58.5	39.9	55.1	52.9	50.7

Simulations and observations are compared on a chemical basis in Tables 8-4 and 8-5. Table 8-4 is based on comparison of 104 pairs of data for the metals As, Pb, and Zn. The robust mean relative error (rMRE) is 59.7 percent. Table 8-5 is based on 229 comparisons for eight PAH compounds. The rMRE is 96.1 percent and observations and simulations agree within a factor of two for only 35.6 percent of the comparisons. For the comparison in Table 8-5, the PAH data were renormalized to attempt to correct for biases in the data.

Appendix G-2 contains data plots along a northwest (Brown's Point) to southeast (Riverside) axis for each sampling period. Measured PM_{25-50} and simulated PM_{10} are shown. This spatial segregation shows that samples beginning on 7/24, 11/27, 11/30, and 12/11 (periods characterized by generally southeasterly winds) show low simulation values at the southeast boundary of the modeling domain (Riverside School), and high observed values. The sample beginning on 12/4 shows an anomalously high aerosol observation at the Sea-Land site (156 $\mu g/m^3$).

Another way of segregating the data is to make comparisons by month and by season. (Within the study period, "summer" is defined as all data between July 7, 1989 and October 5, 1989, when the winds shifted abruptly from net westerly to net southerly.) Table 8-6 shows the wMRE scores by month, by season, and by season for non-stagnation periods only (here defined as $PM_{10} \leq 100$ $\mu g/m^3$). The winter season shows the best model performance (wMRE = 61.2 percent for all points and 46.7 percent for non-stagnant conditions).

Because of the differences in the size of particles measured and simulated, another more appropriate comparison to test the model's predictive ability is to use the PM_{10} data from the PSAPCA monitors at Fire Station No. 12 and Alexander Avenue. Table 8-7 contains these comparisons, showing a 50th percentile wMRE score of 41.7 percent. When these data are segregated by season and stagnation/non-stagnation the wMRE scores, are 39.8 percent in the summer, 42.2 percent for winter for all data, and 44.5 percent for winter without the stagnation period data (Table 8-8).

A similar comparison was made between the model simulations and the ambient PM_{10} measured during the 18-day receptor modeling study. Those ambient measurements never exceeded 100 $\mu g/m^3$, so there is no segregation into stagnation vs. non-stagnation cases (despite the actual stagnation event that occurred during December). Table 8-9 shows the wMRE scores. These scores are not as good as those achieved using the PSAPCA data.

Another possible temporal comparison of the simulations is with nephelometer b_{sp} measurements (particles < 1.0 μm) taken by PSAPCA at Alexander Avenue. Figure 8-7 shows the PSAPCA data composited by time of day for June and January. When compared with the modulation function used for traffic and woodsmoke (Figure 7-1), the June curve in Figure 8-7 shows a weak diurnal pattern consistent with the traffic pattern, while the January curve shows the highest b_{sp} at nighttime and a marked diurnal pattern with a minimum in the afternoon. The January data are consistent with some combination of increased nighttime sources and low nighttime air flow, and relatively better air flow in the daytime afternoons. Figure 8-8 shows a composited plot of PM_{10} simulations. Comparison with the b_{sp} observations shows that the winter nighttime maximum is missing and the traffic pulses are exaggerated for both summer and winter.

Table 8-4. **Comparison Scores for Model Estimates of Three Metals (As, Pb, Zn) vs Study Observations**

NUMBER OF CASES = 104	Actual	90%	Median	10%
Mean of Predictions	45.1	49.5	45.3	39.9
Mean of Observations	47.1	54.6	46.5	38.8
2*[P-0]/[P+0]	-0.04	0.07	-0.02	-0.13
S.D. of Predictions	36.2	38.1	36.1	33.0
S.D. of Observations	60.5	68.6	58.3	50.9
2*[P-0]/[P+0]	-0.50	-0.35	-0.48	-0.59
FOR PAIRED DATA:				
Agree within a factor of two	59.6%	66.3%	60.4%	53.5%
Slope: d[P]/d[0]	0.75	0.87	0.78	0.70
Correlation coefficient [r]	0.76	0.81	0.76	0.71
Robust MRE	59.6%	64.4%	59.7%	54.6%

NOTE: S.D. = Standard deviation

Table 8-5. **Comparison Scores for Model Estimates of Eight PAHs vs Study Observations-Renormalized**

NUMBER OF CASES = 229	Actual	90%	Median	10%
Mean of Predictions	3.5	4.2	3.4	2.7
Mean of Observations	3.5	4.6	3.4	2.5
2*[P-0]/[P+0]	-0.00	0.23	-0.01	-0.18
S.D. of Predictions	6.2	7.8	5.8	3.7
S.D. of Observations	7.0	9.1	6.0	3.9
2*[P-0]/[P+0]	-0.11	0.30	-0.08	-0.48
FOR PAIRED DATA:				
Agree within a factor of two	35.4%	42.6%	35.6%	29.7%
Slope: d[P]/d[0]	0.92	1.28	0.94	0.68
Correlation coefficient [r]	0.61	0.78	0.61	0.40
Robust MRE	96.0%	102.0%	96.1%	88.9%

NOTE: S.D. = Standard deviation

Table 8-6. Summary of Scores Comparing PM$_{25-50}$ Observations with WV3 Simulations, Stratified by Season

wMRE%	75%	50%	25%	
Jul	84.4	75.1	67.6	
Aug	69.8	65.6	78.0	
Sep	85.9	81.3	78.0	
Oct	56.5	53.7	50.8	
Nov	82.2	71.7	61.0	
Dec	61.9	56.8	51.8	
Summer	77.8	74.6	71.7	← all points
Winter	65.6	61.2	57.0	← all points
Summer	73.0	69.9	67.5	← TSP ≤ 100 μg/m^3
Winter	49.3	46.7	44.2	← TSP ≤ 100 μg/m^3

Table 8-7. Comparisons Between Observed PM$_{10}$ and Simulations by WV3 Model

Site Name	Sample Size	PM$_{10}$ Mean μg/m^3	WV3 Mean μg/m^3	[---------------wMRE---------------]		
				75%	50%	25%
Alexander Avenue	73	39.1	44.7	38.8	37.0	35.2
Fire Station No. 12	174	38.8	41.6	45.8	43.6	41.6
All Data	247	38.9	42.5	43.3	41.7	39.9

Table 8-8. Scores Comparing PSAPCAs PM$_{10}$ Observations with Simulations by WV3, Stratified by Season

wMRE%	75%	50%	25%	
Summer	41.9	39.8	37.5	← all points
Winter	49.3	42.2	40.2	← all points
Summer	41.9	39.8	37.5	← PM$_{10}$ ≤ 100 μg/m^3
Winter	46.3	44.5	42.0	← PM$_{10}$ ≤ 100 μg/m^3

Table 8-9. Scores Comparing 18-Day Receptor Modeling PM$_{10}$ ("Coarse+Fine") Observations with Simulations by WV3, All Points (Morse Supply and Alexander Avenue)

wMRE%	75%	50%	25%
PM$_{10}$	72.6	70.0	67.1

Figure 8-7. Composited B$_{sp}$ as a Function of Time of Day
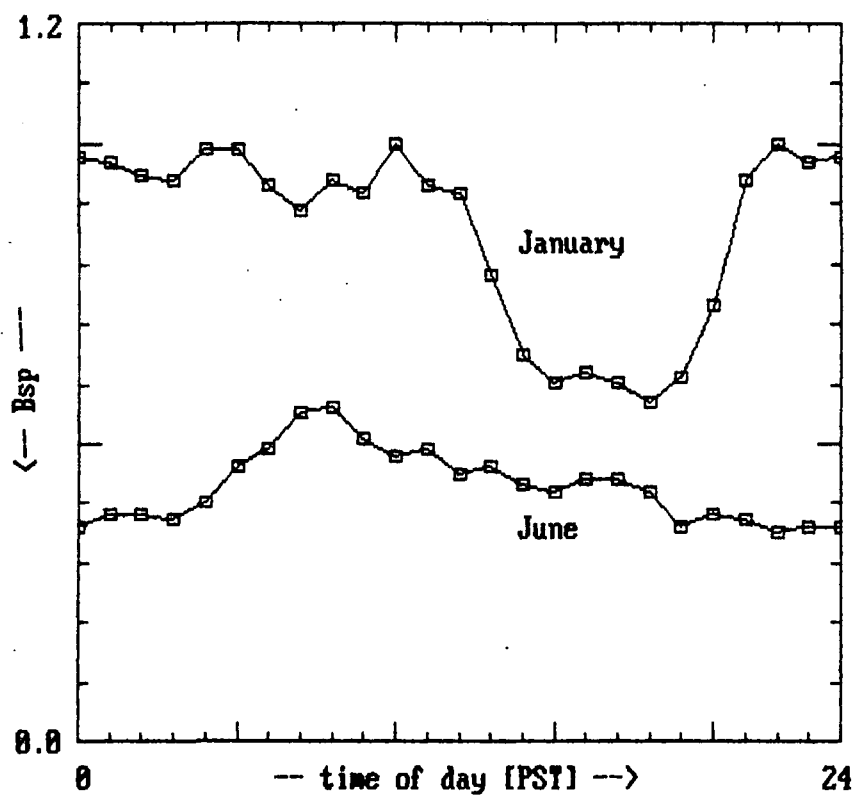
Figure 8-8. Composited PM$_{10}$ Simulations as a Function of the Time of Day
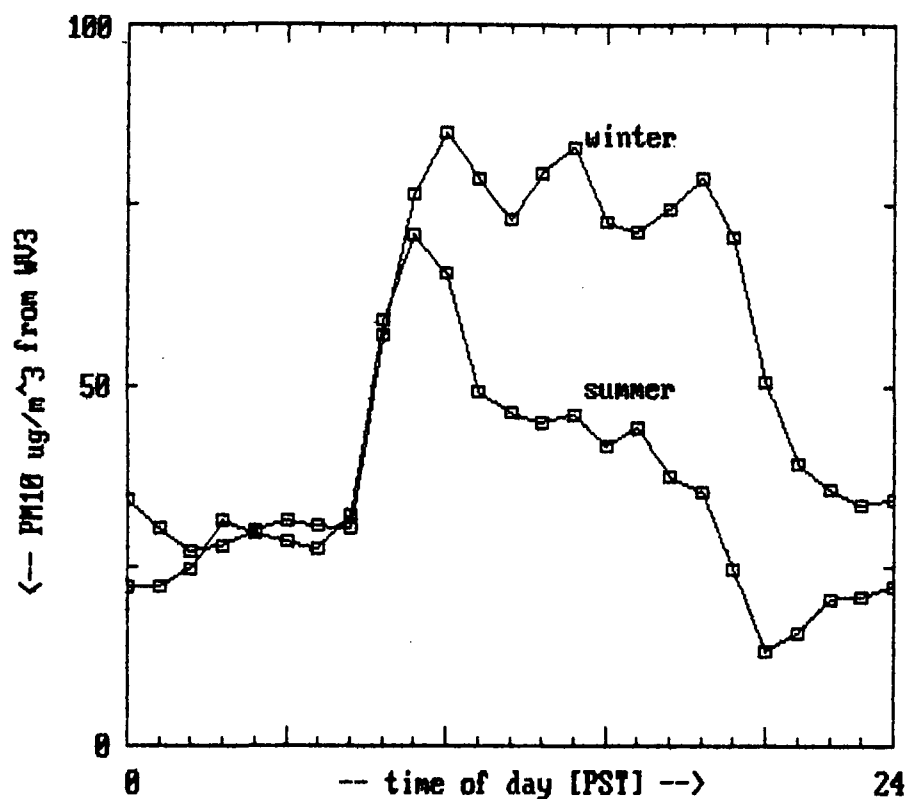
Analysis: The model underpredicted the PM_{25-50} observations, as might be expected, since only PM_{10} was modeled. However, when the sites at the northwestern and southeastern model boundaries were removed from the analysis, the model's predictive capability improved. One possible explanation is that the model neglects a background source which is relatively more important at the two sites removed from the industrial emissions core of the model domain. Based on the receptor modeling analyses in Chapter 6, one possible explanation is woodsmoke imported into the modeling domain from outside.

The model performed considerably better with the PSAPCA PM_{10} data than with the PM_{25-50} or 18-day receptor modeling aerosol data. The model overpredicted the PSAPCA data by only 9 percent, but overpredicted values from the 18-day study by 70 percent. One reason may be the difference in the sampling periods. The 18-day study sampled in 12-hour periods from 7 a.m. to 7 p.m. and from 7 p.m. to 7 a.m. PSAPCA samples are collected at midnight and noon.

The chemical-specific simulations are predictably less accurate than those for total mass due to a compounding of the inaccuracies in the emissions estimates used as input to the model and the potential sampling and analysis biases that could affect the aerosol data.

The patterns of discrepancies pointed out from the spatial plots of mass in Appendix G-2 are consistent with the theory of woodsmoke being advected into the modeling domain from upvalley. A likely source is the town of Puyallup, 11 km southeast of Fire Station No. 12. The b_{sp} comparison with the model for June and July also supports this theory. The winter b_{sp} maximum could be attributed to woodsmoke. A separate analysis done by Harrison (in press) calculates that the town of Puyallup, with a population of 24,000 people, could be responsible for woodsmoke emissions that are advected under certain conditions down valley to contribute up to 50 percent of the winter PM_{10} observed at Fire Station No. 12.

The high December 4 aerosol sample recorded on the contour map at the Sea-Land site could be attributed to a local source, such as the ore offloading facility nearby.

Comparison of the model simulations with the b_{sp} observations strongly suggests that the model overestimates traffic emissions, perhaps by a factor of two or more and underestimates woodsmoke, perhaps by a factor of three.

Appendix G-3 references several reports that served as a basis for much of the modeling and analysis discussion above.

Summary: The performance scores for the model using mass data were good, particularly when PSAPCA PM_{10} data are the basis of comparison. The temporal comparison and analysis pointed out some emissions (woodsmoke, traffic) that clearly need to be more accurately estimated to improve the model's predictive capability. Many of the observations and their "discrepancies" point towards an explanation that relies on a large woodsmoke emission component being advected into the model domain during winter light wind conditions. This could be corrected by using a larger modeling domain.

3. Aerosol/Receptor Modeling

Objective of Comparison: How well does the PM_{10} aerosol collected during the 18-day field study for receptor modeling agree with the PM_{25-50} aerosol collected at three- to four-day intervals in the six-month study? Are there certain conditions under which PM_{10} is a better estimator of PM_{25-50}? What do the differences between the two types of samples indicate about the likely sources?

Limitations in Performing the Comparison:

Aerosol

▶ Upper size range of particles sampled was limited to 25-50 μm (depending on wind speed); larger particles in the ambient aerosol may have been missed.

▶ Sampler performance is variable, affected by precipitation and wind speed; collection efficiency of smaller particles (<1.0 μm) unknown.

▶ Long time period for collection of the sample (three or four days) increased possibility of vapor breakthrough from the PUF and changes in vapor-particle partitioning. (Direct measurement of breakthrough not made for the field samples.)

▶ Limited number of samples analyzed.

Receptor Model

▶ Focus of all sampling was particles in <10 μm size fraction.

▶ Limited number (2) and short distance between the sites (3.5 km) used for PM_{10} aerosol sampling.

▶ Short temporal coverage of 18-day study; no seasonal comparison.

▶ Inadequate amount of sample for PAH analysis.

Approach: 1) Compare six-month and 18-day aerosol samples at the two sites in common (Alexander Avenue and Morse Industrial Supply) for fine mass (<2.5 μm), PM_{10} (fine plus coarse mass), and $PM_{2.5-50}$; 2) Compare PSAPCA TSP and PM_{10} data for entire study period to look at seasonal patterns.

Results: Figures 8-9 (a) and (b) show plots of total mass for $PM_{2.5}$, PM_{10} and $PM_{2.5-50}$ aerosol samples for Alexander Avenue and Morse Industrial Supply. The figures reveal similar patterns at both sites. Fine mass accounts for most of the PM_{10} fraction. PM_{10} tracks the changes in $PM_{2.5-50}$ quite well, with the possible exception of the December 12 sampling date at the Morse site. The PM_{10} mass is a larger fraction of the $PM_{2.5-50}$ mass when $PM_{2.5-50}$ is low (December 15).

Figure 8-10 shows a plot of the PSAPCA TSP versus PM_{10} data collected at Fire Station No. 12 during the entire study period. The two curves track fairly well. Qualitatively, the comparison appears to show a pattern of larger differences between the TSP and PM_{10} numbers during the summer period (July through September). During the fall/winter period there appears to be a pattern similar to that observed in Figures 8-9 (a) and (b), with PM_{10} mass constituting a larger fraction of the TSP mass during periods low when TSP levels are low.

Analysis: The relative proportions between the coarse and fine mass are as expected from other studies. Most combustion product emissions are in the <2.5 μm size range. The December 11 sampling date was the start of a significant air stagnation episode. The relative increase in $PM_{2.5-50}$ versus PM_{10} during this period is not consistent with the receptor modeling analysis that attributes much of the emissions during this period to woodsmoke. The larger difference between TSP and PM_{10} in the summer is consistent with the theory that resuspended dust is a more significant factor in the drier months.

Figure 8-9(a). Comparison of Aerosol Collected by Six-Month Study (PM$_{25-50}$) and the 18-Day Study (PM$_{2.5}$, PM$_{10}$) at the Alexander Avenue Site
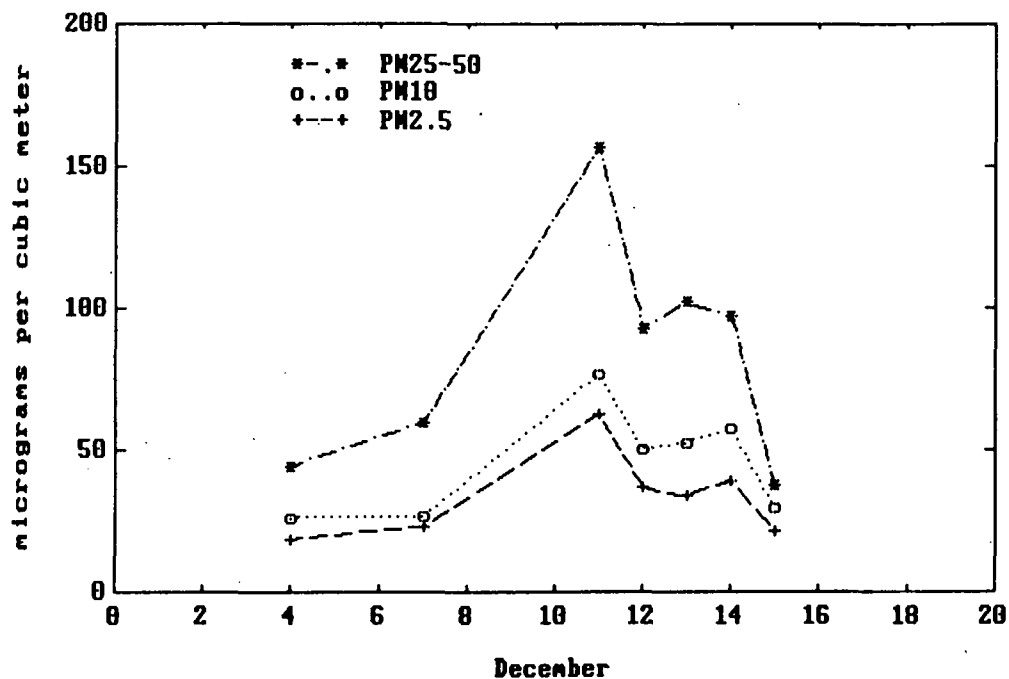
Figure 8-9(b). Comparison of Aerosol Collected by Six-Month Study (PM$_{25-50}$) and 18-Day Study (PM$_{2.5}$, PM$_{10}$) at the Morse Supply Site
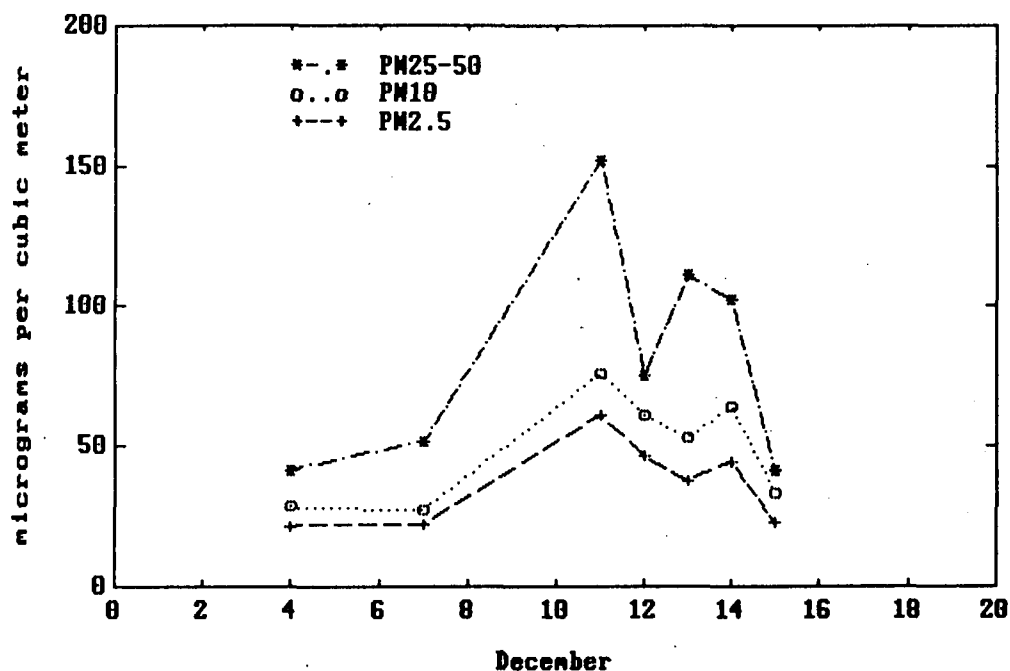
Figure 8-10. TSP and PM$_{10}$ Measured during the Study Period at Fire Station 12
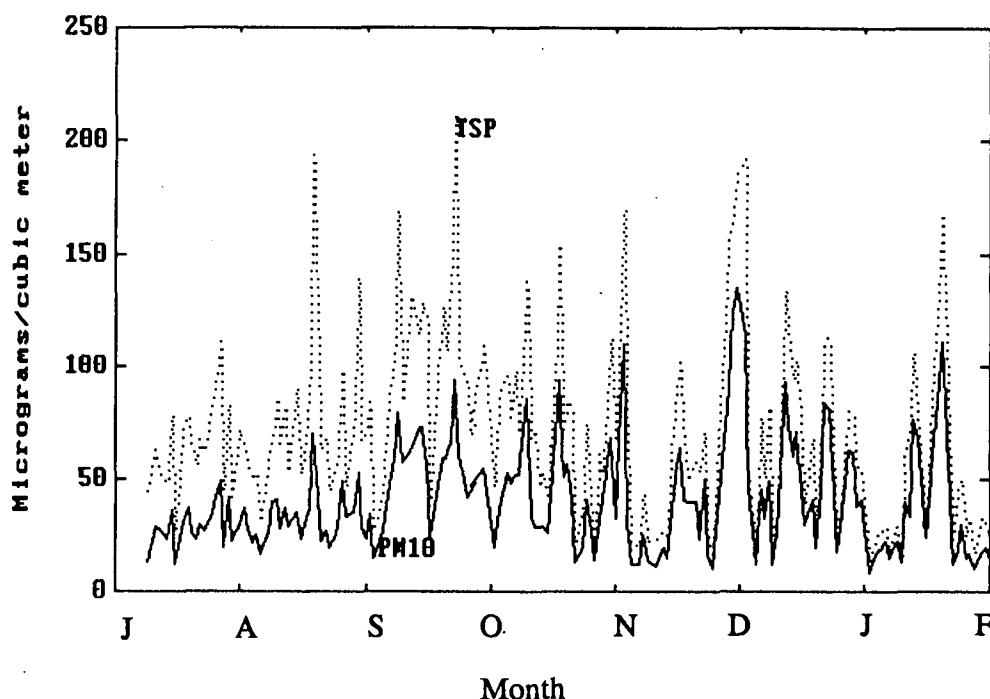
Summary: The comparison between PM$_{25-50}$ and PM$_{10}$ shows that the two size fractions reflect similar patterns, despite the high day-to-day variability in the ambient aerosol mass. The seasonal comparison using the PSAPCA data indicates that the ratio between the two size fractions may be different for summer and winter/fall conditions, so that a single constant proportionality factor shouldn't be assumed to attempt to convert one number to another. The seasonal difference is also consistent with the probability of a larger resuspended dust component during the dry months. The study data are for two sites relatively close together (3.5 km) and the PSAPCA data are for only one site, therefore the observations and conclusions should not be assumed to necessarily hold true for all sites.

4. Deposition/Diffusion Modeling

Objective of Comparison: How well does the model perform qualitatively and quantitatively in predicting the deposition at a receptor site? How do deposition velocities computed for the deposition samples compare with the deposition velocities assumed in the model; what does this comparison tell us?

Limitations in Performing the Comparison:

Deposition

▶ Particle size spectrum in sample not measured.

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▶ Long collection period (two weeks) introduced opportunities for revolatilization of samples or transformation of chemicals (e.g. photolysis, biodegradation), particularly during summer conditions.

▶ Performance of samplers for collection of large particles blown horizontally across the sampling surface not known.

▶ Samplers at all sites not at same height, therefore different potential to capture large particles.

Diffusion Model

▶ Only PM_{10} modeled, not total potential deposition.

▶ Deposition velocities used from literature may or may not be appropriate for ambient aerosol.

▶ Deposition calculations dependent on accurate aerosol modeling, which is subject to accuracy in emissions inventory, limited by scale of model, and affected by unknown temporal variation in emissions.

Approach: 1) Compare deposition velocities calculated from deposition samples with velocities assumed in the diffusion model. [Note: It would have been desirable to compare the deposition of particular metals on a station by station basis for discrete meteorological or emissions regimes. The model output for deposition was averaged over the 186-day study period, not allowing for these comparisons.]

Results: Table 8-10 presents net deposition velocities calculated from the deposition samples collected during the six-month study. The values in the table are the average deposition velocity (wet + dry) computed as:

Vd = (Flux of tracers to the surface)/(Concentrations of the tracers in the air)

The standard deviations are for determinations of the means. The ranges of the distributions are about six-fold greater than the standard deviations.

With the exception of the lighter PAHs in the middle block of the table (which are more likely to be affected by sampling and analysis errors), the remaining net (wet + dry) deposition velocities exceed 2.2 cm/sec, and all but one exceed 3.4 cm/sec.

By comparison the diffusion model used an assumed value for dry deposition velocity of 0.1 cm/sec.

Analysis: The numbers in Table 8-10 exceed by an order of magnitude reported deposition velocities for gaseous tracers or particles with diameters < 100 μm (McMahon and Denison, 1979). They also exceed estimates of deposition velocity calculated using the Monin-Obhukov similarity theory (Vd = 0.4 cm/sec). (These estimates are for small particles whose deposition is a function of turbulent mixing.) One possible explanation for the high deposition velocities is that large particles were advected into the deposition sampling pans. This is supported by the observations of sand and grit in the pans. The suspected source of these large particles is resuspended soil dust, which would not behave as the modeled eddy-driven deposition of particles < 10 μm. Biases in the ambient aerosol sampling may also have resulted in underestimates of the ambient aerosol. This would affect the calculation of Vd to yield a higher

deposition velocity. As noted under comparison #1 above, there is a suspected lack of correspondence between what was measured as ambient PM_{25-50} aerosol and what may have been deposited, particularly in the larger particle size range.

Resuspended dust may be transported over short distances (tens to hundreds of meters) most of the time. Strong gradients in the vertical distributions of resuspended dust are likely; therefore differences in the height of the deposition pans above the surface would be expected to be a factor in comparing between sites. A quantitative analysis of the objective effect of this is not possible.

Examination of the deposition data (Table 4-10) shows that the industrial sites (SL, AS, MS) have higher deposition concentrations than the sites more removed from the center of the Tideflats industrial area (TM, RS). These differences in concentration are not nearly as pronounced for the aerosol data (Table 4-6). The deposition pattern cannot be completely accounted for by the aerosol samples. The gradients in the deposition samples imply that local (nearby) sources are affecting deposition, which is consistent with resuspension of dust as one of the sources.

Table 8-10. Deposition Velocities Inferred from PSWQA Measurements at All Sites

	cm/s		
Arsenic	3.69	±	1.02
Chromium	2.22	±	0.34
Manganese	3.38	±	0.47
Nickel	4.27	±	0.70
Lead	3.83	±	0.86
Zinc	3.83	±	0.73
Naphthalene	0.69	±	0.13
Acenaphthene	0.06	±	0.02
Acenaphthylene	0.08	±	0.04
Fluorene	0.04	±	0.02
Phenanthrene	0.10	±	0.05
Anthracene	0.11	±	0.05
Fluoranthene	0.99	±	0.53
Pyrene	0.95	±	0.50
Benzo(a)anthracene	3.01	±	1.58
Chrysene	4.58	±	1.58
Benzo(a)fluoranthene	7.27	±	3.82
Benzo(k)fluoranthene	3.77	±	1.98
Benzo(a)pyrene	3.56	±	1.82
Indeno(1,2,3-c,d)pyrene	4.06	±	1.72
Dibenzo(a,h)anthracene	8.11	±	3.91
Benzo(g,h,i)perylene	3.45	±	1.38

Summary: The comparisons between the computed deposition velocities and those used in the model point strongly towards collection of larger size particles as part of the explanation for the much higher deposition velocities for the field data. The data would not be expected to compare precisely because the modeling only addressed particles < 10 μm. Model deposition

simulations were not available for station-by-station, regime-by-regime comparisons to attempt to further refine the analysis.

Attempting to model resuspension would be difficult due to uncertainties of lift coefficients as functions of particle size and land-surface type, and size-dependent transport distances. Most transport is concentrated into a few dry-windy episodes; thus, errors from statistical sampling would require simulations of many years.

5. Deposition/Receptor Model

Objectives of the Comparison: How well do measurements of ambient PM_{10} predict the qualitative and quantitative patterns in the deposition? Are the patterns in the deposition consistent with the receptor modeling analysis of emissions sources?

Limitations in Performing the Comparison:

Deposition

▸ Deposition samples collected over two week period, therefore limited number of samples (1) to compare with the 18-day PM_{10} aerosol.

▸ Lack of temporal match in initiation of the two-week sample with start of 18-day study.

Receptor Model

▸ Limited spatial and temporal scale for comparison.

Approach: As noted under Limitations there is insufficient data for a reasonable comparison of the receptor modeling aerosol and the deposition data. Analysis of comparisons #1 and 4 above suggests that the deposition samples may contain large particles not collected by the aerosol samplers. If so, the PM_{10} aerosol samples would be expected to have more discrepancies with the deposition data than was noted for the $PM_{2.5-10}$ aerosol.

6. Receptor Model/Diffusion Model

Objective of the Comparison: Do the two modeling approaches confirm each other as to the sources of the ambient aerosol?

Limitations in Performing the Comparison:

Receptor Model

▸ Limited number (2) and short distance between the sites (3.5 km) used for PM_{10} aerosol sampling.

▸ Short temporal coverage of 18-day study; no seasonal comparison.

▸ Inadequate amount of sample for PAH analysis.

Diffusion Model

▸ Spatial resolution of the model limited to 0.5 x 0.5 km grids; may not be descriptive of the smaller-scale, near field source-receptor relationships.

▶ Emission inventory accuracy limited by lack of information on the chemistry and mass emissions specific for Tacoma facilities and their temporal fluctuations.

▶ Emissions were limited to the inventory for the modeling domain; did not account for advection into the domain.

▶ Wind field data for the model limited to a single meteorological site at Alexander Avenue.

▶ Modeling did not account for chemical transformations or vapor emissions.

Approach: 1) Compare receptor model ($PM_{2.5}$) and diffusion model source apportionments. 2) Scale up receptor model to PM_{10} and compare with diffusion model source apportionment. 3) Compare model results with other approaches for identifying sources.

Results: Table 8-11 summarizes the information from the receptor model pie charts (using Pb and o-xylene as tracers of vehicle exhaust) found in Chapter 6, Figures 6-9 through 6-12. These source apportionments are for the fine particle fraction ($PM_{2.5}$), based on all samples collected during the 18-day study. At both sites residential woodsmoke accounted for the largest component of fine-particle mass, followed by vehicle exhaust.

Table 8-12 contains fractional source apportionments for the diffusion model, grouped into categories that were used to modulate emissions in the model over a 24-hour period. Vehicle exhaust and industrial sources operating around the clock are the primary contributors.

Table 8-11. Receptor Modeling Results (Normalized Percent Contribution) for Fine Particulates ($PM_{2.5}$) Using Lead (Pb) and a VOC (o-xylene) as Tracers of Vehicle Exhaust

	Alexander Avenue		Morse	
	Pb	o-xylene	Pb	o-xylene
Vehicle Exhaust	7 ± 4	18 ± 5	10.0 ± 5	20 ± 6
Woodstoves	62 ± 7	55 ± 6	72.0 ± 7	64 ± 6
Hogged Fuel	2.0 ± 0.3	1.6 ± 0.3	3.0 ± 0.4	2.4 ± 0.3
Al Production	12.0 ± 3	10.7 ± 2.5	---	---
Scrap Metal	7.0 ± 1	6.3 ± 0.8	5.0 ± 1	5.0 ± 0.9
Residual Oil	10.0 ± 3	8.9 ± 2.5	10.0 ± 3	9.0 ± 2.3

Table 8-12. Fractional Source Attributions from WV3 December 1 Through 31, 1989

	Morse Supply		Alexander Avenue	
3-shift factories	0.037	± 0.053	0.360	± 0.051
1-shift factories	0.170	± 0.057	0.157	± 0.043
woodstoves	0.079	± 0.066	0.100	± 0.067
transportation	0.446	± 0.051	0.379	± 0.057
	1.002		0.996	

Table 8-13 contains the results of the receptor model scaled up to PM_{10}. The Fine CMB (Chemical Mass Balance) was calculated using fine particle data only and fine particle source profiles. Values in the table under this column were calculated as follows:

$$\frac{\text{calculated fine mass concentration from source}}{\text{total measured fine + coarse mass concentration}} \times 100$$

Fine particles were overpredicted in the Fine CMBs by 16-24%. The columns under "PM_{10} CMB" were calculated using PM_{10} data and source profiles. Woodstoves could not be included directly in these calculations because organic and elemental carbon were not measured for the coarse particle size fraction. The unexplained mass ("other") could be considered an upper limit for woodstoves.

To examine the influence of meteorology, source apportionments were performed separately for high-wind and low-wind days, again using the fine particle data scaled up to PM_{10}. From the 18-day study the days identified as very windy were December 8, January 3, 4, 5, 6, and 7. Of these six days the only days when there were both a.m. and p.m. samples for both receptor sites were January 4 and 5. Winds were mostly from the south (SW - SE) on those two days. The days identified as having very little wind were December 5, 12, and 14. Of these three days, the only days when there were both a.m. and p.m. samples for both sites were December 12 and 15. Winds were mostly from the NE - E - SE sectors during those days. Results of this CMB modeling are presented in Figures 8-11 through 8-14. At the Morse site on windy days there was a much larger "other" contribution than on non-windy days. This is a result of the higher concentrations of coarse particles at that site on windy days. At the Alexander site the fine-particle mass was overpredicted for most of the windy-day samples. The result of overpredicting the fine particles is to reduce the "other" category.

Table 8-13. Receptor Modeling Results (% Measured PM_{10}) Using Two Alternative Methods of Calculation

	Alexander Avenue		Morse Supply	
	Fine CMB[a]	PM_{10} CMB[b]	Fine CMB	PM_{10} CMB
Crustal Dust	---	14.1 $\pm$ 2.8[c]	---	9.4 $\pm$ 1.9
Autos	6.0 $\pm$ 3.0	5.9 $\pm$ 3.4	9.0 $\pm$ 4.2	9.4 $\pm$ 4.0
Woodstove	55.2 $\pm$ 6.1	---	63.4 $\pm$ 6.3	---
Hogged Fuel	1.6 $\pm$ 0.3	6.0 $\pm$ 1.0	2.3 $\pm$ 0.3	6.5 $\pm$ 1.1
Al Potlines	10.8 $\pm$ 2.5	9.2 $\pm$ 5.0[c]	---	---
Al Fugitives	---	---	---	12.1 $\pm$ 4.9
Metals	6.3 $\pm$ 0.8	9.0 $\pm$ 1.5	4.9 $\pm$ 0.9	6.7 $\pm$ 1.1
Residual Oil Boilers	9.0 $\pm$ 2.5	23.7 $\pm$ 6.9[c]	8.9 $\pm$ 2.3	21.3 $\pm$ 5.8
Other	11.1 $\pm$ 7.7	32.1 $\pm$ 9.8	11.5 $\pm$ 8.0	34.6 $\pm$ 8.9

(a) Fine CMB indicates that CMB was performed on fine particle data using fine-particle profiles. Both fine CMBs overpredicted total fine mass (by 16% for Alexander Avenue and 24% for Morse Supply). Calculated source contributions were divided by measured fine plus coarse (PM_{10}).

(b) PM_{10} CMB indicates that CMB was performed on PM_{10} data (fine + coarse) using PM_{10} profiles, where available. If PM_{10} profiles were not available (as for Simpson hogged

fuel), fine profiles were used. (Note: for other hogged fuel profiles, fine + PM_{10} were nearly the same because most of the emissions are fine.) Woodstoves could not be included in the PM_{10} CMB. They may be at least partly attributed to "other". Calculated source contributions were divided by measured PM_{10}.

(c) Crustal dust, aluminum potlines, and residual oil boiler (and possibly metal shredding) are listed as a similarity cluster in the CMB.

Two other methods were attempted to gain information about the source apportionment and the behavior of the emissions: covariance analysis and construction of polar fluxgrams or PM_{10} tracer roses. A covariance analysis is a mathematical technique used to isolate sets of chemical species that behave similarly in time and space. Vectors or sets of chemical species are identified that minimize the residual variance. These sets of chemicals are then used to identify sources or source categories that significantly impact receptor sites. The covariance analysis is described further in Appendix G-4. Two significant vectors were identified from the metals data:

Vector 1: Pb + Zn + Mn + Ni + Br + (S) - Ca
Vector 2: Ti + Fe + Mn + Cr + K - Cl - (S)

The relative contributions of vector 1, associated with automotive transport, were higher at Brown's Point and Riverside School and lowest at Morse Supply and Alexander Avenue. The relative contributions of vector 2, associated with soil minerals, were lowest at Brown's Point and Riverside School and highest at Morse and Alexander Avenue. From the PAH data two vectors were identified, one representing all 17 PAH compounds, and associated with the Kaiser emissions, and the other representing naphthalene, benzo(k)fluoranthene and benzo(g,h,i)perylene, with an unidentified source.

PM_{10} tracer roses were constructed from the PSAPCA data from Alexander Avenue and Fire Station No. 12 during the period of the study (Figures 8-15 and 8-16). Vector amplitudes are proportional to the tracer concentrations measured at the receptor, and the vector direction points upwind. Figure 8-15 displays the results of 175 daily-averaged PM_{10} measurements from Fire Station No. 12, Figure 8-16 the results of 73 daily-averaged measurements between July 7, 1989 and January 7, 1990 for Alexander Avenue. Each small circle represents one of the daily measurements. The lobes "point fingers" at conspicuous upwind sources. An interior thin circle in each curve depicts a normalized isotropic distribution. Inner and outer thin irregular curves bracket this isotropic circle with expected sampling errors of ± one standard deviation. Both figures show a common southeasterly lobe which runs parallel to the Puyallup valley axis. At Alexander Avenue there is a similar lobe to the northwest. Further discussion can be found in Appendix G-5.

Analysis: The source apportionments for residential woodsmoke and vehicle exhaust differ quite dramatically among the several methods employed for calculations. Very high values are computed for woodsmoke using Pb as a tracer of vehicle exhaust. These numbers remain high in the "Fine CMB" because the fine mass dominated the measured PM_{10}. The PM_{10} CMB cannot be reconciled with the apportionment from the diffusion model. However, the comparison between the diffusion model simulations composited for January and the b_{sp} observations (see comparison #2) points strongly towards the diffusion model using too large a vehicle exhaust emission input and too small a woodsmoke input. The high-wind versus low-wind comparisons of the receptor model were based on very limited data, but showed a higher contribution of woodsmoke on low-wind days. The difference in the amount of coarse particles measured at the Morse site is likely to be a reflection of the sampler being located closer to the ground than the Alexander Avenue sampler.

Figure 8-11. Receptor Model Results for Low Wind Days (December 12 and 14) at the Morse Supply Site

Hogged Fuel (1.4%) — All Autos (6.9%) — Scrap Metals (4.7%) — Residual Oil (10.8%) — Other (10.4%) — Woodstoves (65.7%)
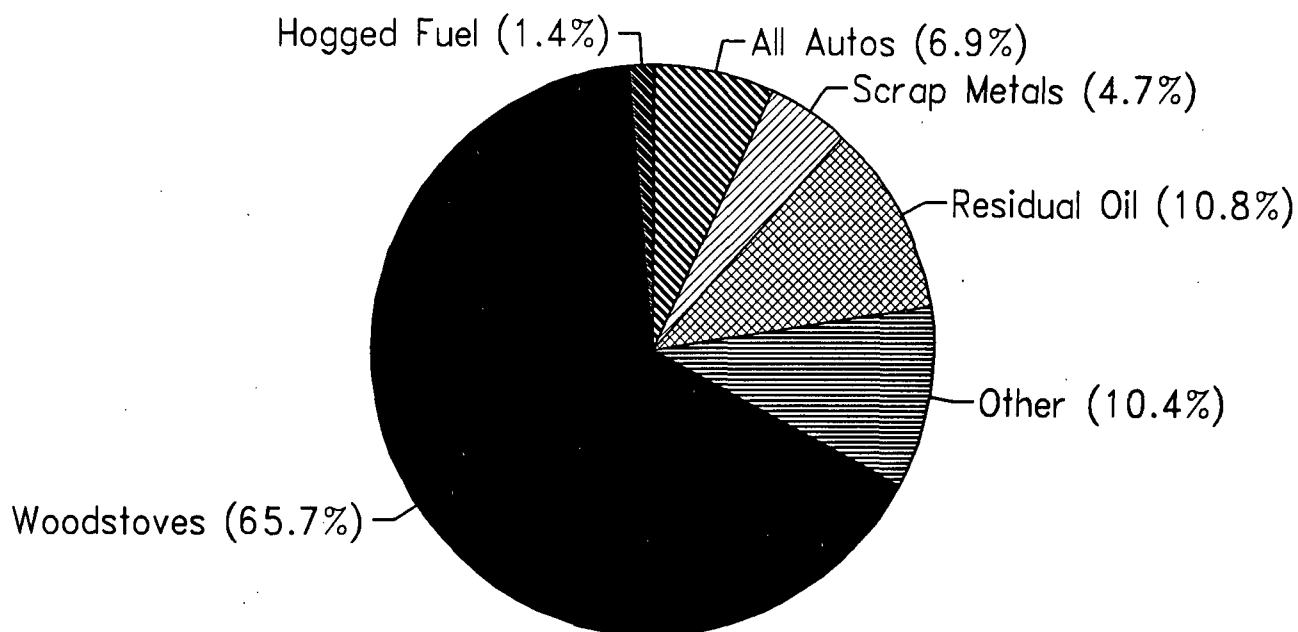
Figure 8-12. Receptor Model Results for High Wind Days (January 1 and 5) at the Morse Supply Site

Hogged Fuel (2.0%) — All Autos (6.3%) — Scrap Metals (5.9%) — Residual Oil (5.2%) — Other (36.9%) — Woodstoves (43.7%)
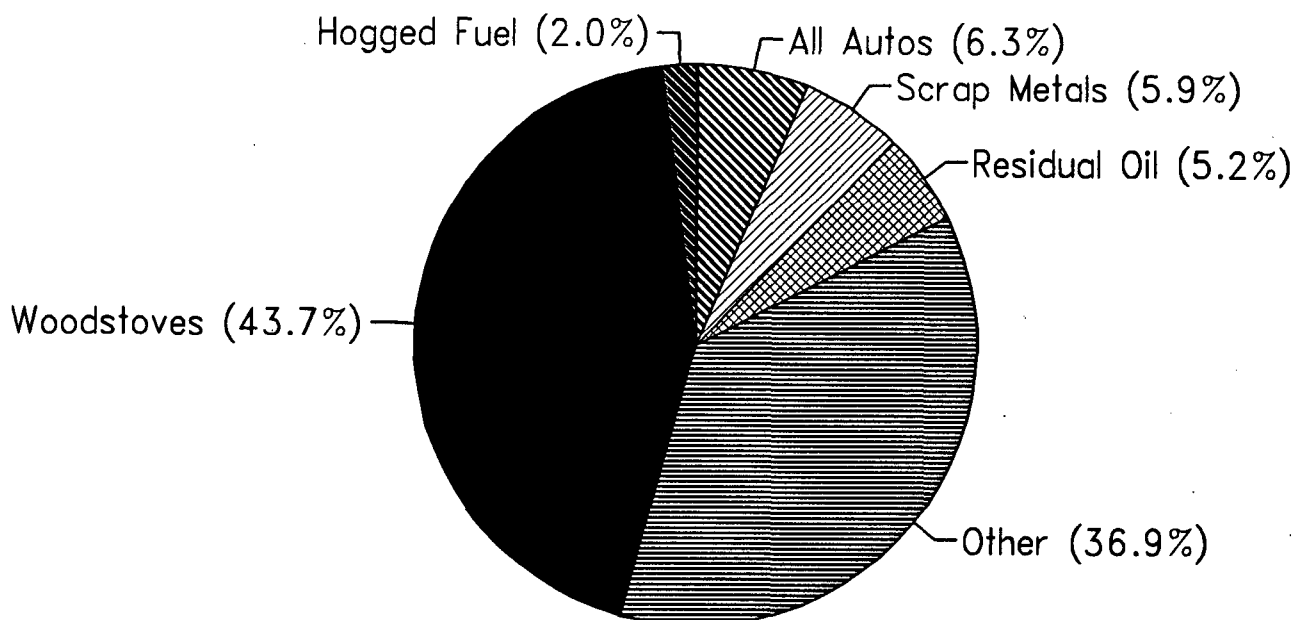
Figure 8-13. Receptor Model Results for Low Wind Days (December 12 and 14) at the Alexander Avenue Site

Other (16.0%)
All Autos (5.8%)
Residual Oil (10.9%)
Scrap Metals (5.9%)
Al Production (4.5%)
Hogged Fuel (1.1%)
Woodstoves (55.8%)
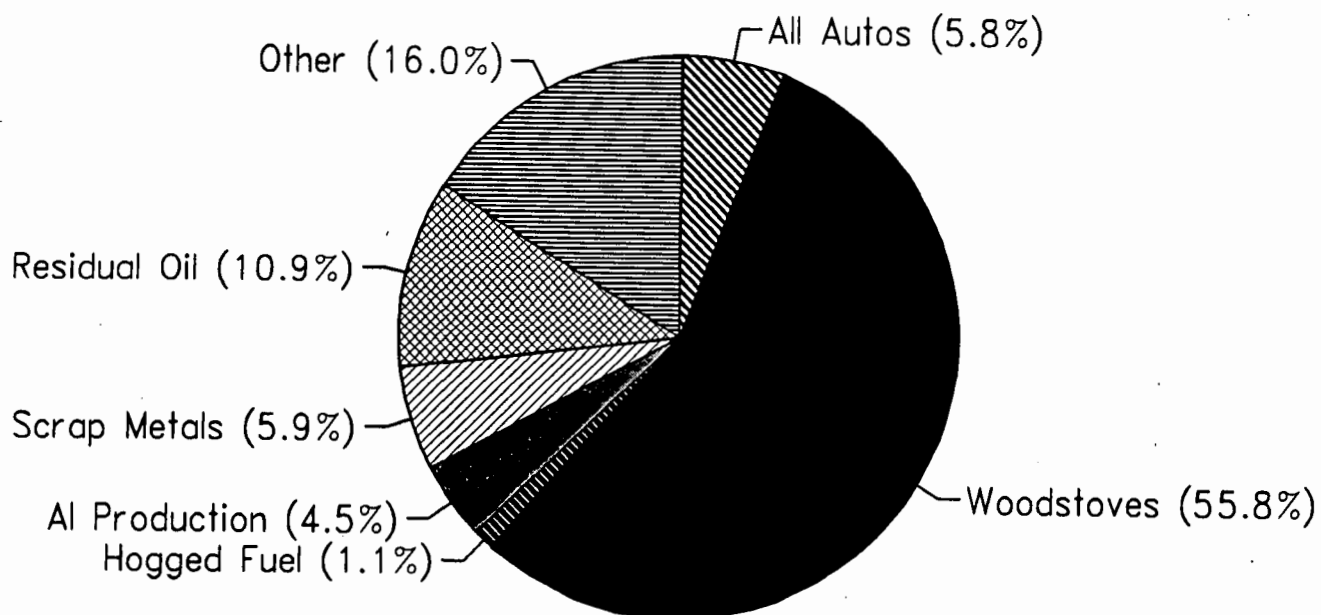
Figure 8-14. Receptor Model Results for High Wind Days (January 4 and 5) at the Alexander Avenue Site

Other (2.6%)
All Autos (9.9%)
Residual Oil (19.7%)
Scrap Metals (3.4%)
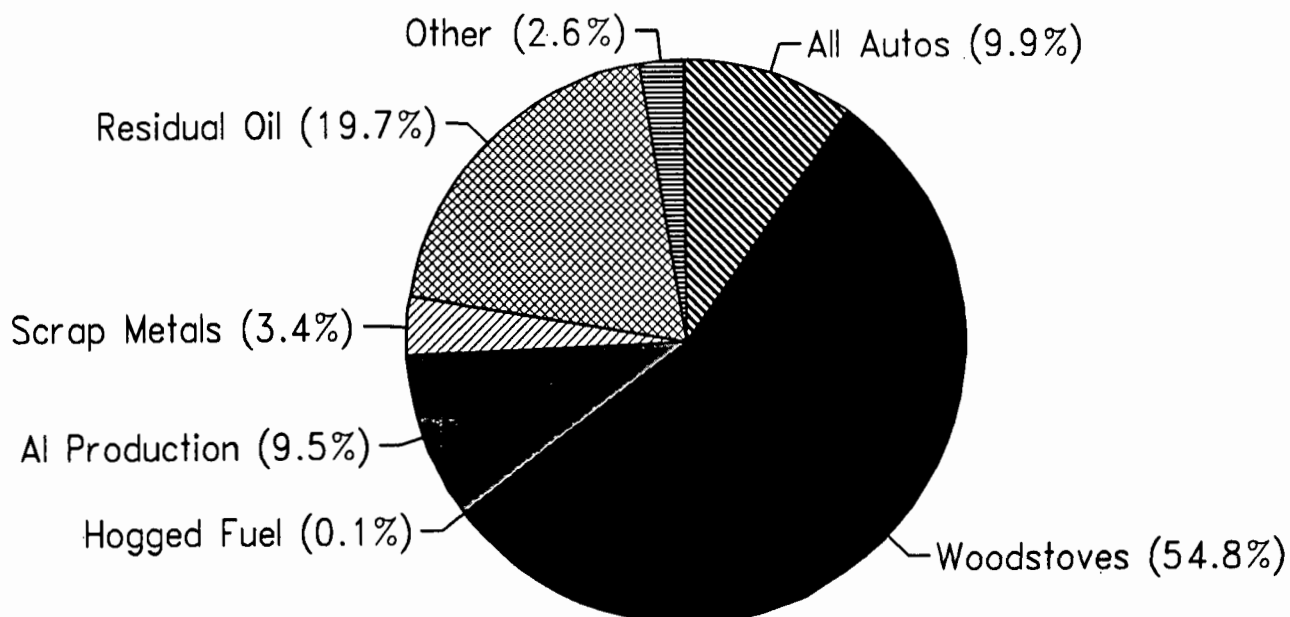Al Production (9.5%)
Hogged Fuel (0.1%)
Woodstoves (54.8%)

Figure 8-15. Tracer-Rose Using Fire Station No. 12 PM₁₀ Data
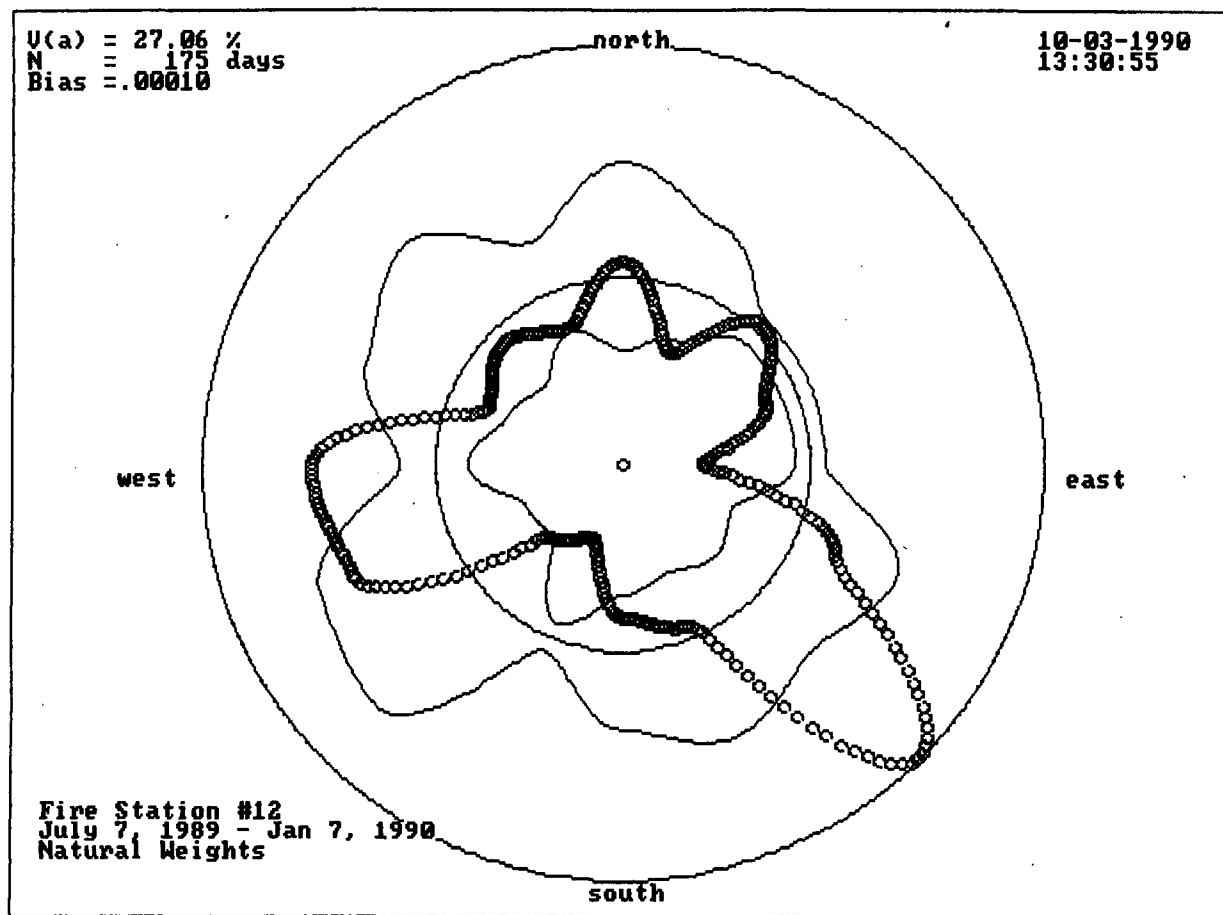
Figure 8-16. Tracer-Rose Using Alexander Avenue Site PM$_{10}$ Data
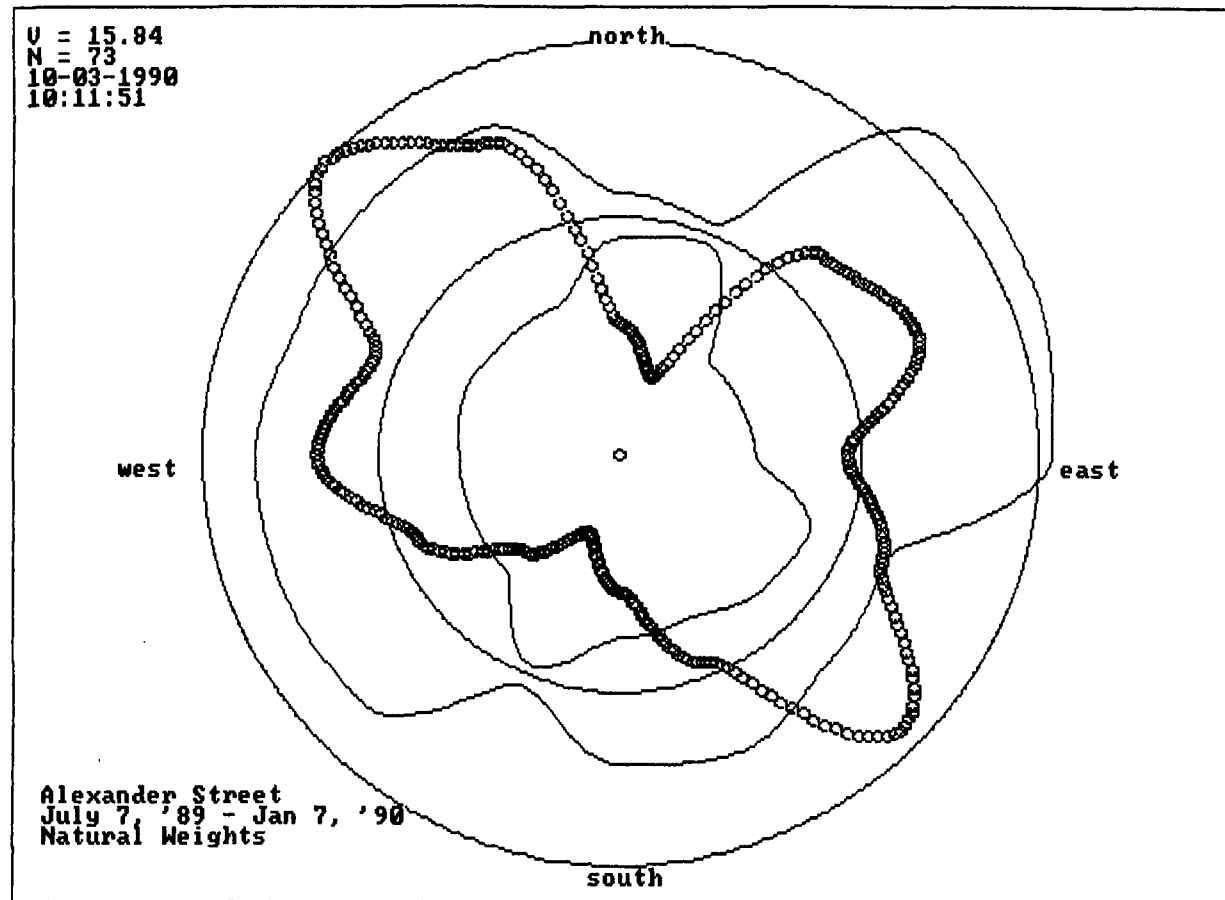
Results of the covariance analysis support the theory that resuspended dust plays an important role in the input of metals measured at the sampling sites in the industrial area.

The southeasterly lobe in the PM_{10} tracer roses at both sites may be attributable to emissions from a source at Kaiser, which is two miles east-southeast of Fire Station No. 12 and one mile southeast of Alexander Avenue. This lobe and the one pointing northwest at Alexander Avenue are also aligned with the valley axis. This would be consistent with the theory that woodsmoke is advected down the valley, commingling with industrial emissions from the northwest at the Alexander Avenue site.

Summary: While the current diffusion model run and the receptor modeling don't agree on the relative importance of woodsmoke and vehicle exhaust (during the 18-day receptor model sampling period) subsequent analyses argue that the woodsmoke component is larger than that anticipated in the diffusion model.

The tracer rose developed using the PSAPCA data shows the potential for a strong woodsmoke influence on the Tideflat monitoring stations from a source in a southeasterly direction.

SUMMARY

The following conclusions are drawn from the study comparisons. Individual paired comparisons were limited by the data available and the inherent sampling biases and assumptions used in sampling and modeling. Collectively, the comparisons reinforce the individual study results and help develop a more coherent picture of the processes and parameters affecting the atmospheric contaminants in the Tideflats.

▶ Aerosol and deposition samples, as collected in this study, are not sufficiently similar that one can serve as a predictor of the other. The differences are confounded by the different particle capturing abilities of the aerosol and deposition samplers, which are a function of sampler design and location. The differences suggest that large particles (>50 μm) not collected by the aerosol samplers, are a significant component of the deposition samples at certain times (e.g. summer dry weather and moderate to high wind speeds).

▶ Diffusion modeling, focused on the PM_{10} size fraction, performs best when compared with measurements of the PM_{10} aerosol mass. The model's ability decreases as a larger size spectrum of particles or specific chemical constituents are examined. The differences suggest that the model's predictive ability would be improved by enlarging the modeling domain and thereby increasing the emissions inputs for woodsmoke. Additional refinement in all the emissions inputs to the model (e.g. their temporal variability, chemistry, size fraction of particles) is needed to improve the performance in simulating the ambient aerosol.

▶ From samples at a limited number of stations, it appears that the patterns in PM_{10} aerosol and $PM_{2.5-50}$ track each other quite well, however the proportion of the total mass that is PM_{10} changes seasonally, being higher in the winter. This is consistent with resuspended dust (generally larger particles) comprising a larger component in the summer, and woodsmoke (primarily <2.5 μm) comprising a larger component of the aerosol in the winter.

▶ Differences between the model assumptions of deposition velocity and the deposition velocities computed from the deposition samples suggest that the samples collected particles considerably larger than PM_{10}. The model's predictive capability would be improved by assuming a range of deposition velocities, including values appropriate for TSP.

▶ Comparison of the diffusion modeling and receptor modeling source attributions suggests that during winter stagnant air conditions, woodsmoke is an important component of the ambient fine (<2.5 μm) aerosol. Tracer rose analysis also supports the concept that this woodsmoke is imported into the modeling domain from the southeast.

Chapter 9. Synthesis of Results

Results of individual studies have been summarized at the end of the chapters. This chapter assembles all of the information into a synthesis of what has been learned. First, study conditions are compared with non-study periods to set a larger context for interpreting and applying study results. Results are presented and discussed pertinent to the components of the ambient aerosol, the sources of the aerosol, deposition, and the transport of atmospheric contaminants to Commencement Bay. The chapter concludes with an assessment of the significance of these inputs to Commencement Bay relative to other sources of toxic contaminants to the water.

CONTEXT

A reasonable question in assessing the study results is to inquire whether the conditions during the study represented a worst case scenario. The spatial, temporal, meteorological, and emissions characteristics of the study are examined below to attempt to make this determination. Historical data and projections of future conditions are used for comparison where available.

Spatial

Sampling stations for ambient aerosol and deposition were centered within the Tacoma Tideflats industrial area, with more distant stations both "upwind" at Riverside School, and "downwind" at Brown's Point. The upwind and downwind orientations are geared to the dominant local wind patterns. Sampling did not include equivalent downwind stations for other wind directions, nor was it able to include stations further out over Commencement Bay. Brown's Point, while generally in a downwind direction, is physically "around the corner" and therefore removed from the direct downwind path. Tall stacks from some of the major industrial emissions sources, such as Simpson Tacoma Kraft, may also move the emissions beyond the relatively close-in sampling network of the study.

The diffusion modeling domain of 91.5 km^2 included the Tideflats and the communities of Milton, Fife, and SE Tacoma. As discussed in Chapter 8, this is probably not the only source of emissions affecting the ambient air in the Tideflats, and it only includes a small portion of the total watershed that drains into the Puyallup River and Commencement Bay. For example, the modeling domain was bounded by the bluffs on either side of Commencement Bay and therefore did not include all of Tacoma. As a consequence, the projected loading from atmospheric deposition on land and runoff to Commencement Bay is probably underestimated. Because of paved surfaces and steep slopes in downtown Tacoma, mobilization (the percentage of contaminants available for runoff into Commencement Bay) will be relatively high from this source compared with rural, unpaved regions of the watershed, where sediment and vegetation filter out most contaminants prior to washoff. The sampling and modeling domain probably captured a worst case for examining the effects of woodstove emissions on ambient air.

Temporal

The overall study period extended from July 1989 to January 1990. Ambient aerosol (PM$_{2.5-50}$) and deposition samples were collected during the entire six-month study; stations in use varied according to the "intensive" and non-intensive sampling regimes described in Chapters 2 and 4.

A separate short-term aerosol study to support the receptor modeling was conducted for eighteen days in December 1989 and January 1990. The measurements therefore are a series of "snapshots" over the equivalent of half of a year and encompass a range of meteorological and emission conditions.

Meteorology

State climatological summaries issued by the National Weather Service were used to plot monthly means and minimum and maximum readings of temperature and precipitation for the period from 1980 through 1988. Figures 9-1 and 9-2 illustrate the conditions during the study period relative to the nine-year historical data. For the most part the study period is typical of the normal pattern. Figure 9-2 shows, however, that the study period included two apparent variances in precipitation from the historical conditions: extremely low precipitation in September 1989 (0.18"), and an extraordinarily wet January 1990 (10.90"). However, the highest rainfall in January occurred on January 9 (3.66"), just after completion of the sampling studies.

Winds during the study period are summarized in Chapter 7 with a wind rose and a plot of the cumulative trajectory of winds during the study period. The latter figure shows the expected seasonal shift from net westerly summer winds to south or southeasterly winds during late fall and winter. Air stagnation, which occurs during periods of light winds and increased stratification, is more likely in the fall and winter. Air stagnation in the Tacoma region is often accompanied by a light drainage wind that flows from the Puyallup area, down the river valley, and over Commencement Bay. During the summer and fall there is a daily reversal in the winds due to land-water temperature differences; this does not occur or rarely occurs during the late fall when the land is cold. January and December are the two months of the year that usually have the strongest temperature inversions and therefore the greatest potential for air stagnation and elevated air contaminant levels.

During the study period Ecology issued two air stagnation forecasts covering the Tacoma region: one on November 30, which lasted not quite 24 hours; and one on December 11, which lasted until December 17. This compares with two forecasts issued in 1987 and one in 1988. As described in Chapter 3, an analysis of meteorological conditions after-the-fact confirms the air stagnation that was forecast in mid-December and notes a lesser episode in late December. These episodes were of shorter duration (and severity) than some earlier episodes of prolonged air inversion (e.g. approximately two weeks in late December 1985).

Besides the light wind/stagnant air conditions found at times in the winter, the study period also included winter periods with strong winds, and summer and fall periods with prolonged dry weather and moderate-to-high wind speeds. While this did not include all potential meteorological conditions during a year, it did reflect conditions under which individual emissions sources varied in their relative influence.

Emissions

An accurate accounting of all emissions sources, including their chemistry, particle size fractions, and temporal variations is extremely difficult to construct. PSAPCA is continually receiving updated information on specific Tacoma sources as well as revisions of the emission factors used to estimate the emissions of particular source categories. The air emissions inventory for the Tacoma Tideflats is not continuously updated to incorporate these changes. To attempt to set emissions levels during the study into a longer-term context, one can look at the PM_{10} measured by PSAPCA at their Alexander Avenue site during the study period and compare this with the preceding three years of data from the same site during the same portion

Figure 9-1. Comparison of Monthly Mean Temperatures for the Study Period with the Monthly Mean, Average Maximum, and Average Minimum for 1980-1988

Monthly Temperature at Tacoma

. Study year only
_ Excluding study year
+ Monthly min and max
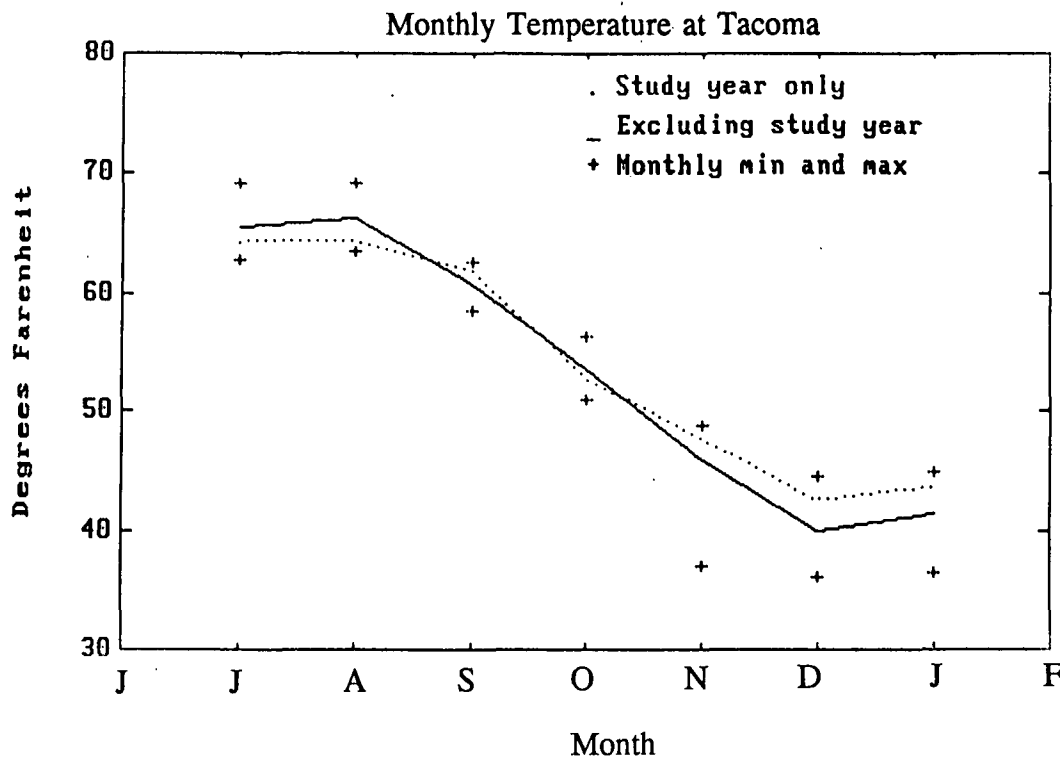
Figure 9-2. Comparison of Monthly Mean Precipitation for the Study Period with the Monthly Mean, Average Maximum, and Average Minimum for 1980-1988

Monthly Precipitation at Tacoma

. Study year only
_ Excluding study year
+ Monthly min and max
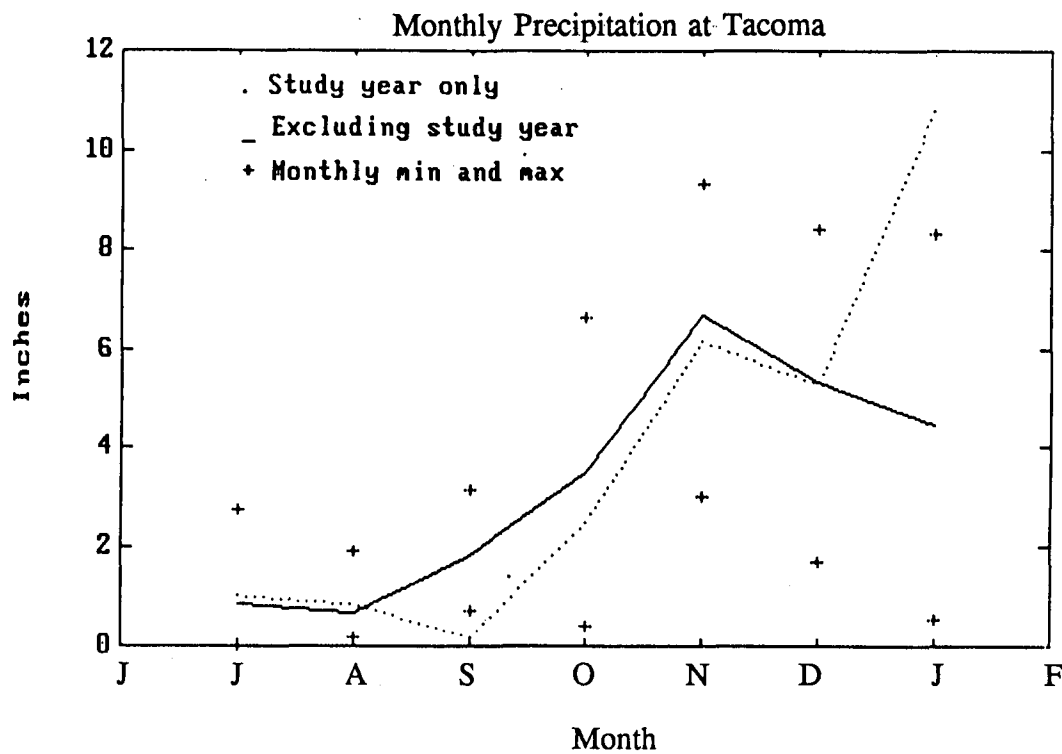
of the year. Figure 9-3 illustrates this comparison. PM_{10} during the study was higher than the average maximum during September 1989, when precipitation was very low, and lower than the average minimum level during January, when precipitation exceeded the norm.

Woodstoves are a clear example of a source with emissions modulated over a seasonal cycle. The study period captured portions of the two extremes in this cycle: high and minimal emissions.

Various earth-moving and construction projects, which probably contributed increased fugitive dust, were underway in the Tideflats industrial area during the summer and fall months of the study. Anecdotal information on these activities has been incorporated into some of the discussion of study results.

The Simpson Tacoma Kraft pulp mill, which is the major source of particles less than PM_{10} in the Tideflats, was not operating during part of December 1989, when the field sampling was conducted for the receptor modeling study. In addition, the two monitoring sites for that study were not downwind of Simpson, so this source was not fully reflected in the receptor modeling analysis.

Since the period of the study several actions have or are taking place to further control emissions: in the summer of 1990 Kaiser consolidated and covered eight acres of PAH-contaminated scrubber sludges that were exposed and had the potential of becoming airborne; in July 1991 the off-loading of "black ore" (ore from which lead, zinc, silver and gold are extracted by smelting) at the Port of Tacoma's Terminal 7 was scheduled to cease; PSAPCA is continuing efforts to improve the effectiveness of its communication and enforcement of burn bans, thereby aiming to decrease this emissions source during the most sensitive meteorological conditions; more stringent regulations on wood stove performance for new stove installations are also now in effect. The likely overall effect of these actions will be to reduce air emissions, particularly some local sources of fugitive dust. It therefore seems reasonable to conclude that portions of the study period (summer/fall dry conditions and moderate to high winds, winter stagnant air/heavy wood stove use) represent "worst case" emissions relative to current and anticipated conditions.

Figure 9-3. Comparison of Monthly Mean PM$_{10}$ at the Alexander Avenue Site for the Study Period with the Monthly Mean, Mean High, and Mean Low PM$_{10}$ from 1986-1988 (Data is from PSAPCA monitoring)
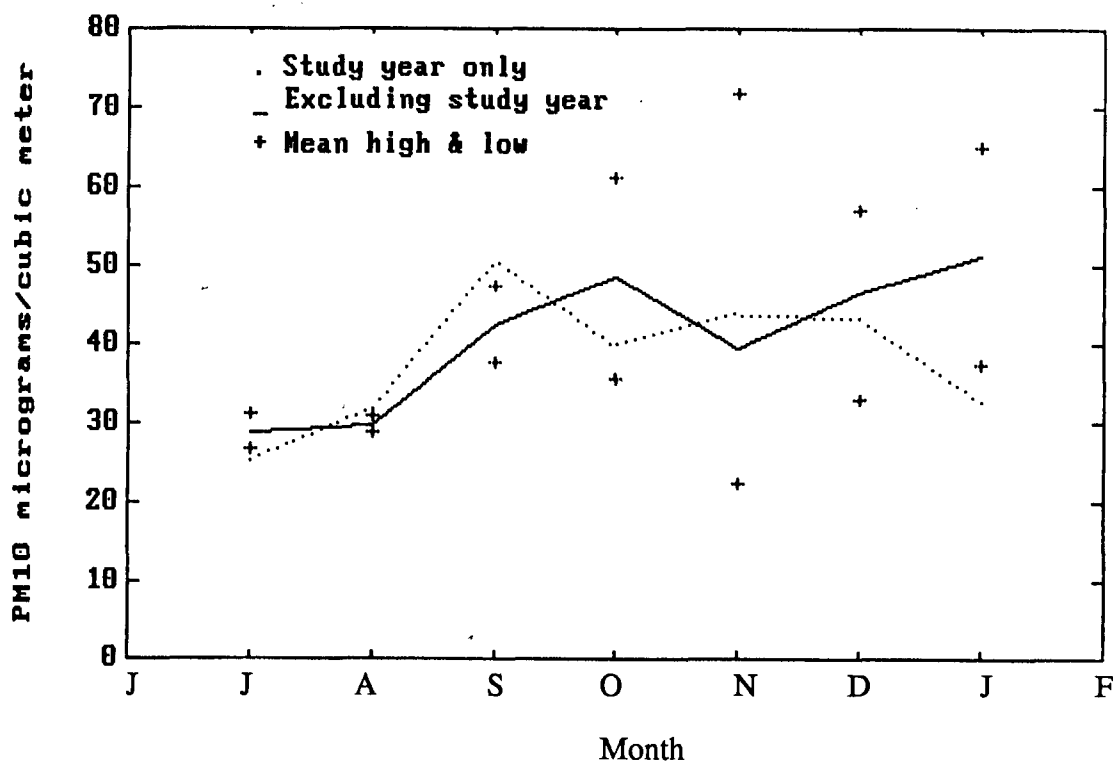
SYNTHESIS

Components of the Aerosol

► The summer and winter high-concentration[2] aerosols were qualitatively different. The composition, concentration gradients between stations, and the differences measured between co-located aerosol and deposition samplers suggest that the high-concentration summer aerosol may have consisted largely of resuspended larger particles, such as fugitive dust. These larger particles could be composed of, or serve as transport media for, metals and PAHs. Larger particles tend to settle nearer their source than fine particles, and may not be collected efficiently, or at all, by the aerosol sampler used in this study. The highest concentrations of metals were found in the industrial area, particularly at the Sea-Land site (Pb and Zn). The highest concentrations of PAHs were measured at the Alexander Avenue site. The set of meteorological conditions favoring transport of the summer aerosols from their sources to their receptors consisted of prolonged periods of dry weather followed by moderate-to-high wind speeds. Concentrations of crustal metals, such as Fe and K, were relatively higher in the summer at Alexander Avenue. A covariance analysis of the data identified several soil minerals that contributed most strongly in the industrial area at the Morse and Alexander Avenue sites.

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[2]High-concentration aerosol refers to episodes during the study period when the highest concentrations of aerosol were observed.

▶ The 18-day study showed that on average the late fall/winter PM_{10} aerosol consisted largely of fine particles. A large percentage of the total fine-particle mass consisted of organic compounds. High fine-particle aluminum concentrations were measured at the Alexander Avenue site when there were light southeast winds or stagnant air. The similar $PM_{2.5-50}$ aerosol concentrations throughout the five-site sampling area during air stagnation periods suggest a substantial influence of regional sources relative to local sources. High concentrations of the particles were most often associated with air stagnation episodes and low wind speeds predominantly from the southeast.

Sources of the aerosol

▶ All of the industrial sources, mobile sources, and residential and commercial combustion sources in the Tideflats area contributed to some degree to the aerosol. The primary parameters affecting the estimated contribution of each source to the aerosol at each sampling point included the emissions levels, the particle sizes emitted, the location of the emission source relative to the sampling point, and the meteorological conditions.

▶ During the summer/early fall sampling period, when larger particles appear to have been an important component of the aerosol, earth-moving and construction activities (with accompanying exhaust and road dust from heavy machinery) occurred in the vicinity of the industrial area sampling sites. Fence posts were moved on the Reichhold property adjacent to the Alexander Avenue site. An unpaved field 80 meters west of the Alexander site was used for parking and short-term storage of large diesel trucks. Also during the study period Kaiser had at their site approximately eight acres of wet scrubber sludge containing PAHs, some of which had the potential of becoming airborne dust during the dry season (Schmeil, personal communication). Two ore offloading operations of note occur near the Sea-Land site. Kaiser offloads alumina, which is removed from the hold of the ships by open crane and moved by conveyor belts to a storage dome. The Port offloads lead and zinc at an adjacent berth and loads the ore into open rail cars. These sources can only be inferred at this point based on the patterns of chemicals in the deposition samples and their proximity to these industrial sites.

▶ The major source of the late fall and winter high-concentration fine-particle aerosol (<2.5 μm) appears to be woodsmoke that drains downslope and downwind from residential areas into the industrial area. This was one of the more surprising results of the study, however a number of different analyses bear out this conclusion. Receptor modeling indicated woodsmoke was the largest contributor to fine-particle aerosol. The tracer rose analysis of PM_{10} data (which projects concentrations of contaminants measured at a receptor as vectors pointing upwind) indicated that a southeastern emissions source was dominant. Followup studies comparing diffusion model simulations to PSAPCA data revealed that the model input for woodsmoke emissions was an underestimate by a factor of three. Calculations based on the population of the town of Puyallup (to the southeast) and the assumed woodstove usage per capita were sufficient to account for the woodsmoke needed to reconcile the model results with the PSAPCA measurements (Harrison, 1990).

▶ The sampling times and locations may not have been adequate to accurately reflect the relative influence of the Simpson emissions. The Simpson mill is the largest emissions source for PM_{10} in the study area. During most of the receptor modeling field study the Simpson hogged fuel boilers were shut down for maintenance. The tracer rose analysis also raises this question; there is only a modest western "finger point" despite Simpson's location one mile east of the Fire Station No. 12 PSAPCA sampler. One reason for this may be the effectiveness of the tall emissions stack in mitigating the ground level impacts in the study area. Wind analysis shows that with the seasonal shift from summer to winter

the percentage of winds from the SE increases. Therefore, samplers may not have been in the prevailing downwind direction for Simpson.

▶ A number of the sampling locations were a short distance from major roadways. The study results did not reach a clear conclusion on the relative importance of automotive sources. They ranged from three to 20 percent of the source apportionment in the CMB analyses, but the error in that analysis was estimated at ±50 percent. Diesel powered vehicles accounted for most of the emissions. The covariance analysis found auto emissions (vector 2) to be most important at Brown's Point and Riverside School, the sites furthest removed from the industrial emissions sources.

Deposition

▶ Deposition rates for all the metals were greater at the industrial sites than at the Brown's Point and Riverside School sites. PAH deposition rates were five to ten times higher at the Alexander site than at Tyee Marina, Morse, and Sea-Land. Deposition rates for both metals and PAHs were higher in the summer. PAH deposition was dominated by the most abundant compounds in the particulate air samples.

▶ Kaiser appears to be the major source of the high-concentration deposition PAHs. Kaiser is by far the largest PAH emissions source in the Tideflats area (546 kg/day of PM_{10} PAHs versus an estimated 14 kg/day from all other area and point sources) and is in close proximity to the sampler with the highest PAH deposition rates. As described above, the measured PAH deposition could be either from stack emissions or from resuspended dust contaminated by scrubber sludge held on the Kaiser property. It is also worth noting that >70 percent of Kaiser's emissions are larger than PM_{10}, and therefore more likely than fine emissions to be deposited nearby.

▶ Deposition velocities calculated from the deposition samples were very high (most were >2.2 cm/sec) compared to the deposition velocities assumed in the diffusion model (0.1 cm/sec). The high numbers may be an artifact of biases in aerosol or deposition sampling; they could also be consistent with deposition of larger particles (compared with the PM_{10} fraction used for the diffusion model). This cannot be determined without data on the specific size fractions in the deposition samples.

Transport to Commencement Bay

▶ The diffusion model attempted to simulate deposition and transport within the 91.5 km^2 modeling domain. A separate Mobilization Coefficient Model was used to predict transport to the receiving water. The models did not include all of the Puyallup River drainage basin. The models calculated that one to three percent of the PM_{10} emissions would be deposited and reach Commencement Bay in "prompt runoff." The diffusion model further estimated that more than 90 percent of the PM_{10} emissions would be advected beyond the boundaries of the model domain. As fine particles moving away from the source are vertically transported into air above the surface boundary layer, their dry deposition fluxes (which are proportional to concentration at the surface) drop rapidly with increasing downwind range. The best guess is that another three to four percent of exported emissions may be deposited farther afield in Puget Sound. It is important to note that these results are based on modeling of the PM_{10} size fraction. Other researchers have estimated deposition velocities closer to 0.3 cm/sec (Sehmel, 1984), which would increase computed net deposition by a factor of three. Higher deposition rates, as suggested by the deposition sampling results, are more likely with larger aerosol particles, however this deposition will be limited to the area close to the emissions sources.

▶ The transport calculations used mobilization coefficients that are not based on direct measurements. These coefficients are quite low and assume that soils and vegetation will absorb most of the deposited contaminants. The coefficients also assume typical year rain events. If complete washoff is assumed for the modeled deposition during a severe storm event, the model still predicts that less than 10 percent of the emissions will be transported to Commencement Bay.

▶ The modeled transport numbers cannot be verified without direct measurements of runoff.

APPLICATIONS TO COMMENCEMENT BAY AND PUGET SOUND

Taking what was learned from the measurements of deposition and the model simulations of deposition and runoff, some first order estimates of atmospheric loading to Commencement Bay and Puget Sound can be computed and compared with other sources of contaminants to these waters. Only limited conjectures and conclusions can be drawn from these comparisons with the data presently available.

Mass Loading to Commencement Bay

One approach is to calculate mass loading by atmospheric deposition, using as upper and lower bounds the mean deposition rates measured at Riverside School (a sampling site with low rates of deposition) and the rates measured at Sea-Land (the sampling site with the highest metals deposition rates). These rates were multiplied by an assumed area of Commencement Bay (10 km^2). Table 9-1 demonstrates that these estimates are significantly lower than mass loading estimates from point source water discharges given by Tetra Tech (1988) and Paulson et al. (1989). Though the Tetra Tech and Paulson data differ by up to a factor of four, they are both significantly greater than the upper bound of the atmospheric contributions. (Note: The Paulson et al. estimate includes the Ruston shoreline and therefore covers a larger source area than that considered by Tetra Tech.) The Puyallup River contributes more Cu, Pb, and Zn than the point sources. One would conclude from these data that atmospheric deposition of metals to Commencement Bay is of minor importance relative to other sources.

Table 9-1. Contaminant Mass Loading to Commencement Bay

	Sources (mt/y)				
Contaminant	Atmospheric Deposition RS[a]	SL[b]	Point Sources Tetra Tech (1988)	Point Sources Paulson et al. (1989)[c]	Puyallup River Curl et al. (1982)
As	0.007	0.07	5.2	---	---
Cu	0.07	0.5	3.4	17	19.2
Pb	0.08	2.4	3.1	15	7.4
Zn	0.1	2.4	8.4	21	24
CPAH	0.013	0.055	---	---	---

(a) Mean deposition rate based on Riverside School deposition samples.
(b) Mean deposition rate based on Sea-Land deposition samples.
(c) Paulson et al. numbers have been adjusted to subtract the ASARCO discharges and the nonpoint contributions.

This comparison is still not definitive because of how the atmospheric deposition was computed. The Sea-Land deposition rate is probably atypically high due to site-specific activities nearby that generate fugitive dust. Therefore, extrapolation of this rate to the entire bay is probably an overestimate of the direct deposition over the water surface. Conversely, because these estimates for atmospheric deposition are based solely on direct deposition to the water, there is an unquantified contribution of runoff from the watershed that is missing. Including the runoff would yield a higher estimate for the overall contribution of atmospheric deposition.

To try and incorporate runoff, another approach for a mass loading budget is to rely on the diffusion model and the runoff calculated using the mobilization coefficient model. A range of one to three percent of the emitted contaminants is calculated to reach the modeled region of Commencement Bay, either by direct deposition or "prompt" runoff (see Table 7-4). These estimated atmospheric loadings are presented in Table 9-2.

Table 9-2. Estimated Mass Loading to Commencement Bay Based on WV3 Model (modeling domain of 91.5 km^2)

Contaminant	4 - 7% of Emissions
As	.0027 - .0081 mt/y
Cu	.0141 - .0422 mt/y
Pb	.0258 - .0774 mt/y
Zn	.0361 - .1082 mt/y
PAH	2.044 - 6.132 mt/y
CPAH	.269 - 0.087 mt/y

These rates are almost certainly an underestimate: they are based on a very low assumed particle deposition velocity (0.1 cm/sec), only the PM$_{10}$ fraction of emissions is modeled (thereby missing the large particles), some emissions sources outside the modeling domain may be important and are not included, and the mobilization coefficients used are very low (assuming that most contaminants will be filtered out before stormwater flows into the bay). In addition, the modeling domain did not include downtown Tacoma, and runoff from this source into Commencement Bay. If deposition velocities are increased by a factor of three, which is not unreasonable, this would increase the runoff by a factor of three. Another adjustment that might be made in these calculations is to assume a worst case scenario of all the deposited contaminants being available to be mobilized into runoff to the bay during severe storms. This would further double the estimates. Using the upper range estimates from Table 9-2, the recalculated loadings from the model would be:

Table 9-3. Estimated Mass Loading to Commencement Bay Based on Adjusting WV3 Model Results for Increased Deposition Velocity and Mobilization

Contaminant	Estimated Mass Loading
As	.0486 mt/y
Cu	.2532 mt/y
Pb	.4644 mt/y
Zn	.6492 mt/y
PAH	36.792 mt/y
CPAH	4.842 mt/y

These loadings are still significantly less than the point source loadings for metals included in Table 9-1. It is not reasonable to project further with these data without better measurements of runoff. While many studies have been undertaken in recent years to examine stormwater, particularly in the Tideflats area, most are not able to separate the measured stormwater contaminants into their respective sources to arrive at a reliable estimate for the airborne contribution.

Input Timing and Location

An alternative approach to examine the potential significance for Commencement Bay and Puget Sound of atmospheric deposition is to look more closely at how the atmospheric inputs are occurring and the specific zones in the receiving water that are most likely to be affected. Direct deposition to the bay and some intertidal stormwater enter the receiving water at the sea surface in a 50 - 100 micron-thick zone that has been described as the sea surface microlayer. The residence time of metals in the sea surface microlayer was determined by Hardy and Apts (1983) to be on the order of three to 20 hours for urban air particulate matter [using a microlayer thickness of 50 microns and a wind speed of 3.6 m/sec (average wind speed in Puget Sound)]. The concentrations of metals in the sea-surface microlayer of Commencement Bay can be estimated using the mean deposition rates for Sea-Land and Tyee Marina sites from Table 4-11 and using the assumptions of a thickness of 50 microns and a residence time of three or twenty hours.

The estimated bounds of chemical concentrations in the sea-surface microlayer are presented in Table 9-4 for (1) the Tyee Marina site (representing the low end of deposition rates) at a residence time of three hours, and (2) the Sea-Land site (representing the high end of the deposition rates) at a residence time of 20 hours. The last column of the table contains literature values for actual chemical analyses of sea-surface microlayer from Puget Sound urban bays (Hardy et al., 1987).

Table 9-4. Predicted Concentrations of Specific Contaminants in the Sea-Surface Microlayer[a]

	μg/L		
Contaminant	TM 3-hour	SL 20-hour	Literature Value Hardy et al. (1987)
As	4.5	300	----
Cu	144	2,470	51 - 3,200
Pb	87	10,800	38 - 650
Zn	267	14,500	135 - 1,420
CPAH	11	225	8 - 148

(a) Concentrations assume a 50 micron-thick microlayer, three-hour or 20-hour residence times, and mean deposition rates at Tyee Marina or Sea-Land.

The estimates of contaminant concentrations from atmospheric deposition (Table 9-4, columns 2 and 3) indicate that it is possible to account for the high measured concentrations (column 4) with the cross-media transfer of these toxic contaminants from the air, even at the lower input rate.

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The calculated runoff loadings also do not take into account that this input is usually delivered in a pulsed manner, as a result of rainfall, and is likely to be channeled into the Bay via an intertidal or subtidal pipe, generally nearshore. As with the microlayer, it is conceivable that despite low overall loadings, the pulsed timing and the input location may make atmospheric runoff a critical factor in determining the water quality in a circumscribed zone near the stormwater pipe. The study results also suggest that large particles, which settle near their source, are an important component of the deposition resulting from the Tideflats emissions. If so, this would act in concert with the stormwater inputs to subject the nearshore zone to the highest contaminant levels from atmospheric inputs.

Loading to Puget Sound

If large particles, such as fugitive dust, are likely to deposit close to their source, a remaining question is the fate of the fine (<2.5 μm) particles in the ambient aerosol. The study identified woodsmoke as a significant component of the fine-particle mass during winter air stagnation periods. As described above, the diffusion model predicted that only one to three percent of the particles <10 μm would be deposited and transported to Commencement Bay in "prompt" runoff. Combining the diffusion model results with some general information about dominant wind patterns and the topography of Puget Sound results in an estimate that an additional three to four percent of the Tideflats PM_{10} emissions would reach Puget Sound beyond the immediate modeling domain of Commencement Bay (see Chapter 7). As the emissions move downwind their probability of being deposited decreases rapidly with distance from the source. The prevailing regional wind direction is towards the northeast, therefore the emissions from the Tideflats will not be carried over the bulk of Puget Sound. Data from the sampling done for this study are inadequate to allow further speculation on the fate of these fine particle emissions.

Chapter 10. Conclusions and Recommendations

This study addressed two related management concerns:

▶ Developing a better understanding of the importance of atmospheric deposition relative to other inputs of toxic contaminants to Commencement Bay; and

▶ Developing efficient and cost-effective tools for assessing this question in other reaches and embayments of Puget Sound, and other water bodies as well.

The study was scaled as a pilot-level effort to develop a first-order approximation of the relative significance of atmospheric deposition. The results provide: 1) new insight into the contributing sources and the composition of the ambient aerosol in the Tacoma Tideflats, 2) first order estimates of atmospheric deposition in regions adjacent to Commencement Bay, and 3) recommendations on how the tools used for this study need to be refined for future application. This was a relatively short-term study of a complex air emissions system; not surprisingly, some important questions remain unanswered, particularly how the study results apply beyond Commencement Bay to other regions of the Sound.

CONCLUSIONS

Relative Importance of Atmospheric Deposition

[Note: These conclusions set atmospheric deposition in perspective relative to other sources of contaminants in a heavily industrialized region of Puget Sound, where the overall contaminant loading is high. It should not be assumed that the relative contribution of atmospheric deposition is the same elsewhere in the Sound.]

▶ Direct atmospheric deposition of metals (i.e. atmospheric contaminants falling directly on the surface of Commencement Bay) appears to be a small contributor, in terms of mass loading, relative to point source water discharges of metals to Commencement Bay.

▶ The data available do not allow definitive conclusions on the relative importance of atmospheric inputs of PAHs. The deposition measurements of PAHs showed a marked gradient between sites, with Alexander Avenue, the closest site to the Kaiser Aluminum facility, exhibiting the highest PAH deposition by more than a factor of three. Kaiser is the largest PAH emissions source in the Tideflats area. Because greater than 70 percent of Kaiser's emissions are particles larger than 10 microns, these emissions are likely to settle nearby, and therefore may be an important local source of PAHs. [Note: After the sampling was conducted for the study, Kaiser covered PAH-contaminated scrubber sludges on their property that had the potential to become part of the fugitive dust loading of PAHs to the Bay.]

▶ Woodsmoke, another source of PAHs, is an important contributor to the ambient aerosol during winter periods of air stagnation. However, PAHs generally make up less than 1 percent of the woodsmoke emissions mass. In addition, woodsmoke emissions are predominantly in the less than 2.5 micron particle size fraction, therefore they are not expected to settle nearby and be an important component of atmospheric deposition to Commencement Bay.

▶ The total input from atmospheric deposition cannot be assessed from the results of this study because of uncertainty in the estimates of atmospheric deposition on land and its subsequent runoff to the Bay.

▶ Atmospheric deposition may be significant relative to other inputs in particular zones, especially close to large sources of fugitive dust, near discharge pipes for stormwater, and at the sea-surface microlayer (top 50-100 μm of the water column). These focused entry points into the water, coupled with pulsed inputs (such as stormwater) create periodic conditions where atmospheric deposition may be the dominant source of toxic contaminants, resulting in a steep gradient in contaminant concentrations in the receiving water.

▶ The samples obtained for nutrients, PCBs, and aliphatic hydrocarbons were inadequate to serve as a basis for assessing the relative importance of these atmospheric contributions.

▶ It is not possible from the data to make a definitive prediction of deposition in the far field (Puget Sound beyond Commencement Bay). Emissions that are likely to be carried beyond Commencement Bay are generally made up of vapors and particles less than 10 microns in diameter. For this size particle there is a rapidly decreasing probability of deposition with distance from the source.

Effectiveness of the Tools

Aerosol and Deposition Study

These measurements were central to the study. There were a number of potential unquantified biases in the sampling, however the data reveal patterns that were fundamental to developing the overall understanding of the components and behavior of the ambient aerosol. These data were verified and supported by the other studies and analyses. In designing future sampling the following factors deserve particular attention:

▶ Consistency in the particle size fraction sampled for each study component;

▶ Length of sample collection period;

▶ Number of samples chemically analyzed;

▶ Sampling protocol/amount for PCBs, aliphatic hydrocarbons, nutrients, and vapor PAHs;

▶ Sampling locations relative to wind field and primary sources.

Receptor Modeling

This modeling effort was based on a very short (18 days) and spatially limited (two sites 3.5 km apart) monitoring study. Nevertheless, the chemical mass balance (CMB) or receptor modeling discerned some important features of the ambient "fine" aerosol (particles less than 2.5 microns), which were later borne out in the paired comparisons of studies. Specifically, the model highlighted the importance of woodsmoke in the fine aerosol during winter air stagnation. The design of future receptor modeling applications should pay particular attention to:

▶ Temporal and spatial representativeness of sampling;

▶ Information on the chemical signatures specific to the local sources and their variability over time;

► Sample quantity for organic chemical speciation.

Diffusion Modeling

The diffusion model showed promise when compared with field measurements of the aerosol mass, particularly for particles in the less than 10 micron size fraction. There was less agreement between model simulations and field measurements for specific chemicals, but this is not surprising given that the representativeness of sampling sites is uncertain when there are significant local sources and variability in emissions with time. CMB modeling and additional model comparisons with PSAPCA data (Harrison, 1990) helped to diagnose some potential emissions input errors in the model. In addition, the intercomparison with the field deposition measurements suggests that deposition velocities need to be varied to more realistically represent the behavior of different chemicals and different particle sizes. For future applications, model refinements should address:

► Site-specific chemical and particle distribution information;

► Extension of the modeling domain;

► Particle size fractions modeled;

► Deposition velocities specific to a range of particle sizes.

Mobilization Coefficient Model

Mobilization coefficients were a critical component of computing total transport to Commencement Bay. The coefficients used were theoretically derived and were not field verified. The following should receive particular attention in future development of these coefficients:

► Field validation of the mobilization coefficients;

► Incorporation of severe storm events;

► Size of model domain.

RECOMMENDATIONS

Analysis of the study results and performance of the tools suggests several areas where further basic research is needed on certain critical technical methods and physical processes, including:

► Aerosol particle distribution and associated chemistry;

► Fugitive dust transport relative to wind speed, soil moisture, and vehicle activities;

► Particle deposition dynamics for different particle sizes and chemical constituents;

► Deposition sampling techniques;

► Chemical and physical dynamics of contaminant mobilization;

► Hybrid dispersion modeling (a combination of models).

The current study produced first order estimates of some important processes. Significant refinements in the methods are recommended if a more definitive picture of the relative importance of atmospheric deposition is desired. To augment what has already been done, additional studies that might be pursued either independently or as part of a larger program include:

► Extensive characterization of ambient and source particle size distributions and chemistry;

► Sampling of the microlayer and nearshore zones to complement the deposition sampling;

► Combined sewer overflow (CSO)/stormwater monitoring;

► Refinement of emissions inventories, including temporal variations;

► Vertical and horizontal wind profiling;

► Hybrid dispersion modeling.

GLOSSARY

ADSORPTION
Adhesion of the molecules of a gas, liquid, or dissolved substance to a surface.

AEROSOL
A suspension of colloidal particles in a gas.

AEROSOL WASHOUT
Below-cloud scavenging of particles in the air by falling water (in liquid or solid form).

CHEMICAL MASS BALANCE MODELING
Apportioning the chemicals measured at a site to the potential sources.

COLLOIDAL
Very small particles larger than molecules, but small enough they remain suspended in a fluid medium.

COMBUSTION-DERIVED PAHs (CPAHs)
Polycyclic aromatic hydrocarbons resulting from burning, generally considered to be fluoranthene through benzo(g,h,i)perylene.

CONDENSATION
The process of changing from a vapor to a liquid.

DRY DEPOSITION
The deposition of particles during dry weather conditions. This can occur either by gravitational settling or as a results of turbulent mixing causing the particles to impact the deposition surface.

FUGITIVE DUST
Particulate matter or any visible air contaminant, other than uncombined water, that is not collected by a capture system and emitted by a stack, but is released to the atmosphere at the point of generation.

MASS BALANCE MODEL
Balance of incoming, outgoing, and resident chemicals.

MICROLAYER
The approximate 50μ-thick boundary layer at the sea-surface.

PRECIPITATION SCAVENGING
Collection of particles in the air by rain, snow, sleet, etc.

RAIN-OUT
Scavenging of aerosol components by processes taking place within clouds, such as the formation of condensation nuclei.

STRATIFICATION
The formation of layers with respect to buoyancy.

TRANSFER COEFFICIENTS
Factors which describe the rate at which transfers occur.

VAPOR EXCHANGE
Exchange of vapor principally between the air and water surfaces.

VOC
Volatile organic compound.

VOLATIZATION
Evaporation.

WET REMOVAL MECHANISM
Removal of particles from the atmosphere by both in-cloud and below-cloud processes.

XRF
Energy-dispersive x-ray fluorescence. A technique used for metals analysis.

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