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Monitoring of PCB and Hg Air Emissions in Sites Receiving Stabilized Harbor Sediment

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Executive Summary

Project Goals, Objectives, and Approach

The goal of this project was to assess the volatilization of gas phase polychlorinated biphenyls (PCBs) and mercury (Hg) from a landfill in Bayonne, New Jersey where stabilized dredged material (SDM) from the NY/NJ Harbor is being placed. This information was used to evaluate the potential impact of land-applied SDM to the ambient air quality of placement sites and adjacent areas. The specific objectives of the project were to determine the background ambient PCB and Hg concentrations in the air in Bayonne, NJ prior to and following the land application of SDM, and to estimate vertical fluxes and horizontal gradients of PCBs and Hg at the SDM landfill. Background concentrations of 59 PCB congeners or congener groups (total of 93 congeners quantified) and total gaseous Hg (TGM) were measured at the NJDEP air-monitoring trailer on the western side of the Bayonne peninsula near Newark Bay. Vertical fluxes of PCBs and Hg were estimated using the micrometeorological method with simultaneous measurements of vertical concentration gradients and atmospheric stability parameters above SDM. Horizontal gradients of PCBs were determined from measurements around the perimeter of the SDM landfill.

Field Sampling Operations

Ambient monitoring of PCBs at the NJDEP air-monitoring trailer on the western side of the Bayonne peninsula began in December 1999 and continued through November 2002. Ambient monitoring of total gaseous mercury (TGM) was carried out at the NJDEP trailer site from September 2001 to February 2003. Vertical fluxes and horizontal gradients of PCBs and Hg at the SDM landfill were estimated during six intensive sampling campaigns of one to three days duration conducted in July, August, and October 2001 and in May and November 2002. Sampling campaigns were divided into morning, afternoon, and occasional night sampling events. During sampling, chemical gradients and micrometeorological parameters were measured within the surface microlayer (approximately 10 m above the ground surface), which is that part of the atmospheric boundary layer over which the vertical fluxes of heat, water, and chemicals are constant with height. Sampling was conducted at the SDM landfill in the presence of recently deposited, un-stabilized dredged material (August 1, 2001), SDM that had been in place for up to three weeks (July 17-20, 2001, August 29-30, 2001), and recently placed SDM (October 23-25, 2001, May 6-8, 2002, November 13-15, 2002). PCB samplers were run for 4 h during each sampling event while TGM was sampled continuously and analyzed automatically on site in five-minute intervals.

Gaseous PCB Concentrations in Bayonne, NJ and at the SDM Landfill

Ambient concentrations of the sum of all measured PCB congeners (ΣPCBs) in the gas phase in Bayonne, NJ as measured at the NJDEP trailer averaged 1.7 ng m^{-3}, which is higher than the North American continental average background concentration (~0.3 ng m^{-3}), but similar to average ΣPCB concentrations measured in Jersey City, NJ and other large urban and industrial areas such as Chicago, IL and Baltimore, MD. Gas phase ΣPCB concentrations at the trailer and sediment application sites

followed a seasonal pattern that is likely due to temperature-dependent land-air exchange processes. Consequently, the average concentrations of ΣPCBs followed the order July (23^{o}C) > Oct (20^{o}C) > Nov (10^{o}C) and May (8^{o}C). The highest concentrations of gaseous ΣPCBs measured at the NJDEP trailer site occurred during NE winds, while the lowest were observed when the winds were out of the west. Thus, potential sources of PCBs to Bayonne from the northeast including Bayonne itself, the Hudson River, and New York City are greater than sources from the west such as Newark Bay. During E/SE winds, when the SDM landfill was upwind of the NJDEP trailer, gas phase PCB concentrations at the trailer were lower than average values.

Gaseous Mercury Concentrations in Bayonne, NJ and at the SDM Landfill

The annual average concentration of TGM in Bayonne (2.2 ng m^{-3}) was slightly higher than the range of average global background levels (1.5 to 2.0 ng m^{-3}; Slemr and Langer, 1992). Monthly averaged TGM concentrations at the NJDEP trailer in Bayonne ranged from 1.8 ng m^{-3} to 3.3 ng m^{-3} and were significantly correlated with air temperature ($r^2 = 0.57$; $p < 0.05$). Thus, TGM concentrations were generally lower and less variable in the winter than in the summer. Throughout the monitoring period, spikes of elevated TGM (>4 ng m^{3} up to 54 ng m^{-3}) lasting fifteen minutes to a few hours were observed. These spikes occurred primarily between midnight and 5 am. No relationship between the occurrence of these spikes and meteorological conditions has been found. These spikes are not addressed in this report, but have been used to calculate average TGM concentrations at in Bayonne. Because these spikes were of short duration (≤1 h) and represented less than 2% of the total number of measurements, their effect on monthly or annual average TGM concentrations was negligible.

TGM concentrations measured at the Bayonne landfill were consistently higher than those measured at the background site on the Western shore of Bayonne (Table 2). The average TGM concentration measured at the SDM landfill (3.2 ng m^{-3}, sampled 3 m above the surface), was significantly higher ($p < 0.05$) than the average background concentration measured at the NJDEP trailer or in New Brunswick, NJ on days that bracketed the SDM landfill sampling campaigns (1.8 ng m^{-3}).

Sediment – Air Fluxes of PCBs from SDM

The estimation of sediment-air PCB fluxes from SDM by the micrometeorological approach requires the measurement of concentration gradients within the surface microlayer. The results of this project demonstrate that gas phase PCB gradients can be measured within 3.5 m above the surface of SDM. Positive vertical fluxes (sediment-to-air) of ΣPCBs were observed during 16 of 20 sampling periods. These fluxes ranged from 72 to 15,000 ng m^{-2} h^{-1} and averaged 2050 ng m^{-2} h^{-1}. Nighttime PCB fluxes were an order of magnitude lower than daytime fluxes. Lower molecular weight di-, tri- and tetra-chlorinated PCBs dominated the vertical flux from SDM. Thus the volatilization of PCBs was dominated by the flux of higher vapor pressure, lower K_{ow}, less bioaccumulative and toxic PCB congeners. Temperature and atmospheric stability had significant effects on vertical PCB fluxes. Fluxes were positively related to temperature and thus highest in August and October and lowest in November and May. At night, the surface microlayer became increasingly stable resulting in decreases in both water vapor and PCB fluxes. During the day, as near-ground wind speeds and vertical convective air movement increased, PCB fluxes increased. The vertical flux of ΣPCBs decreased significantly as SDM aged over 5 d. Thus, emissions of PCBs from SDM are expected to be highest during the placement of fresh SDM and to decrease within a day or two thereafter.

Sediment – Air Fluxes of Hg from SDM

Among paired measurements of TGM at two heights above the surface at the SDM landfill, 86% (97 out of 113) of all gradients recorded were significant and indicative of net (positive or negative) sediment-air Hg fluxes. Positive sediment – air fluxes of TGM were observed in 14 out of 15 sampling periods. Sediment-air fluxes of Hg fluxes ranged from 17 to 1043 ng m^{-2} h^{-1} and averaged 312 ng m^{-2} h^{-1}. A single nighttime Hg flux estimate for May 7, 2002 was less than 3% of the average daytime fluxes observed in during the May 2002 campaign. Sediment – air Hg fluxes measured at the SDM landfill often exceeded those expected based on a reported relationship between soil Hg content and Hg flux. Thus the predicted flux for SDM with a Hg content of 3 ug g^{-1} (80 ng m^{-2} h^{-1}) was exceeded during 60% of the sampling events.

Summary of Findings and Conclusions

Gas phase concentrations of PCBs and Hg in Bayonne and at the SDM landfill were typical of urban environments, but orders of magnitude lower than regulatory safety limits. Vertical gas-phase concentration gradients of PCBs and Hg measured at the SDM landfill were consistent with net sediment to air volatilization fluxes. Net land-air fluxes of PCBs and Hg were quantified at the sediment application site and found to be generally positive during the day, but low to negative at night. These flux rates are highly variable and dependent on atmospheric conditions as well as the condition of the SDM. The gross contribution of SDM to the masses of PCBs and Hg in the air above the SDM landfill and to the atmosphere of Bayonne and adjacent environs is estimated to be minimal.

Our findings suggest that the SDM landfill is a relatively weak source of PCBs, that PCBs volatilized from the SDM landfill are rapidly scavenged by aerosols or deposited as they are carried west, that wind vectors alone cannot accurately account for the local atmospheric dynamics in this region, or that some combination of these and other factors are operating locally. Regardless of the mechanism, the present results demonstrate that the city of Bayonne, NJ, as represented by the NJDEP trailer air monitoring station, is impacted to a greater extent by PCB sources from areas other than the SDM site and suggest that the SDM landfill is not the primary source of PCBs to the city of Bayonne.

The average concentration of ΣPCBs at the SDM landfill was nearly twice as high as that at the NJDEP trailer, but there were sampling periods (6 of 29) when the concentrations at the trailer were greater than each of the three perimeter concentrations measured at the sediment application site. Higher downwind than upwind concentrations of ΣPCBs around the perimeter of the SDM landfill site were observed in only 5 out of 29 cases which suggests that SDM is not the only or dominant source of PCBs to the air above the landfill and that other offsite sources may be important. The PCB air concentrations measured directly above the SDM (3 – 14 ng m^{-3}) as it cures are relatively high compared to background values measured in the region (1 – 3 ng m^{-3}), but they are two orders of magnitude below the NIOSH recommended exposure limit of 1 μg m^{-3} and five orders of magnitude lower than the OSHA permissible exposure limits of 0.5 to 1.0 mg m^{-3}.

Similarly, by using Hg flux estimates from the SDM landfill and background Hg concentrations measured at the NJDEP trailer, the contribution of Hg from the placement of SDM to the air in Bayonne was estimated. This analysis showed that the contribution of Hg emissions from the SDM

landfill was only about 5% and 0.4% of the total TGM in the boundary layer of Bayonne in the summer and winter, respectively. Moreover, all TGM concentrations measured at the SDM landfill and the NJDEP trailer during this project were well below chronic effects limits for total gaseous mercury (200 ng m^{-3}, Agency for Toxic Substances and Disease Registry-CDC; 300 ng m^{-3}, EPA).

In conclusion:

- PCB concentrations measured in the city of Bayonne are similar to those in other large urban and industrial areas in the U.S.
- PCB and Hg concentrations were elevated in the air above the SDM landfill relative to background concentrations in Bayonne, but are *orders of magnitude* below potentially adverse human exposure limits.
- Significant positive vertical concentration gradients of gas-phase PCBs and Hg were observed during most sampling events at the SDM landfill.
- Net sediment-air fluxes of PCBs and Hg at the sediment application site were found to be generally positive during the day, but low to negative at night.
- Vertical fluxes of PCBs and Hg were highly variable and dependent on atmospheric conditions as well as the age and condition of the SDM.
- The city of Bayonne is impacted to a greater extent by PCB sources from areas other than the SDM site.
- The emissions of Hg from SDM are estimated to contribute <5% of this contaminant to the air of Bayonne and adjacent areas.

Recommendations for Further Study

1. Controlled laboratory studies of the volatilization of Hg and PCBs from SDM are needed to understand the variability of contaminant fluxes observed in the field and to study the importance of SDM properties such as water and cement content, grain size, and temperature on the sediment side resistance to volatilization.

2. An analysis of aerosol phase PCBs and Hg is needed to understand the phase transitions, transport, and deposition fate of these contaminants.

3. Fine scale modeling of the local atmosphere is needed to predict the transport and impact of contaminants emitted from SDM landfills and, with back trajectory dispersion models, to determine the source(s) of high background concentrations of PCBs and Hg in the NY/NJ metro area including the large spikes of TGM observed at the NJDEP trailer.

4. Laboratory and field studies of the emissions of Hg and PCBs from native (untreated), tidally exposed estuarine sediments are needed to quantify this potentially important part of the cycles of these contaminants.

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1.0 INTRODUCTION

The disposal of sediments that have been removed from navigation channels by maintenance dredging has become a significant problem for many ports and harbors. In New York Harbor maintenance dredging produces an annual volume of about $3x10^6$ m^3 of dredged material (Weinstein and Douglas, 2002). The annual maintenance dredging of all ports in the United States yields over $3x10^8$ m^3 of dredged material. Much of this material is contaminated and in recent years has been ruled unsuitable for ocean disposal. One alternative to ocean disposal is to use dredged materials, stabilized with cement or lime, as fill at construction or coastal restoration sites. The present study was conducted on a 50 ha site in Bayonne, New Jersey, USA (Fig. 1) where the use of stabilized dredged material (SDM) as a semi-impervious cap was permitted. This site, which is operated by the OENJ Cherokee Corporation, was a former town landfill and brownfield that was closed to dumping in 1983. It is estimated that this site will be able to accept 4.5 million cubic yards of SDM as structural fill at $29 per cubic yard.

Figure 1. Regional Map of the New York/New Jersey Harbor Estuary.

The dredged material at the Bayonne site comes from maintenance dredging operations in New York Harbor, primarily from the channels and berthing areas for container ships such as those in Newark Bay. These dredged sediments contain many types of contaminants including metals, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls (PCBs). An evaluation of the emissions of volatile pollutants, specifically PCBs and mercury (Hg) is included in the dredge disposal permit at the Bayonne landfill site. The average PCB concentration in the sediments of New York Harbor exceeds 40 ppb on a dry weight basis (Ho et al., 2000). This value exceeds the concentration for toxic effects of PCBs in marine organisms. Among large East Coast urban estuaries, the lower NY/NJ Harbor Estuary has some of the highest concentrations of Hg in surface sediments (EPA, 1997).

At the OENJ Bayonne landfill site, dredged sediments are mixed with cement prior to placement and the resulting SDM contains 12% cement by weight. This processing of harbor sediments and their

subsequent placement on land could lead to the volatilization of gas phase PCBs and Hg. Enhanced gaseous PCB and Hg release from dredged sediments may occur during stabilization, drying, and compaction due to heat build up, or the chemical production of volatile forms of inorganic mercury including Hg° and $HgCl_{2(g)}$. The primary form of Hg in estuarine sediments is oxidized Hg(II) bound in sulfide solids or adsorbed to organic-rich mineral phases, with monomethylmercury (CH_3Hg) accounting for < 2% of the total (Mason and Lawrence, 1999). Sediment-bound Hg may become volatile upon exposure to sunlight as a result of the photochemical reduction of Hg(II) to Hg°. Quantifying the emissions of PCBs and Hg from native, processed, and land-applied sediments is an important part of the evaluation of the environmental impacts of various uses of dredge materials and our understanding of PCB and Hg cycles in urban harbors.

The objectives of this project were to determine background ambient gas phase PCB and Hg concentrations in Bayonne, NJ prior to and following the land application of SDM and to estimate vertical fluxes and horizontal gradients of PCBs and Hg at the SDM landfill. Vertical PCB and Hg fluxes above SDM were estimated using a micrometeorological approach that combined the Aerodynamic Gradient Method, previously used to measure land-air pesticide fluxes (Majewski et al., 1991) and the Eddy Correlation Method to provide turbulent correction parameters. Mean wind speed, temperature, water vapor, and PCB and Hg concentrations were measured at two elevations above the ground as required by the Aerodynamic Gradient Method. Simultaneous measurements of the vertical turbulent flux of momentum, sensible heat, and latent heat at an intermediate height were also collected to provide realistic turbulent correction parameters by the Eddy Correlation approach. The vertical fluxes of PCBs and Hg were calculated using the Thornthwaite-Holtzmann equation (Thornthwaite et al., 1939) modified to account for non-adiabatic conditions. The underlying theory for these methods is provided in the next section. This is followed by results, discussion and conclusions.

2.0 ESTIMATION OF VERTICAL ENERGY AND MASS FLUXES

2.1 Aerodynamic Gradient and Eddy Correlation Theory

Most natural flows are turbulent as opposed to laminar. In laminar flow, agitation of fluid particles is of a molecular nature and, hence, at submicroscopic scales. On the macroscopic, observational scales laminar flow appears to be one in which particles are constrained to move in parallel paths due to viscosity. Laminar flows are, in essence, predictable given knowledge of the molecular properties of the fluid. In contrast, turbulent flows are characterized by random fluctuations in particle velocities, and contain a random field of embedded vortices or eddies. Exchange processes in turbulent flows are substantially enhanced relative to laminar flows. In particular, the flux of momentum, characterized by the stress in the fluid is of concern. The momentum per unit mass in the horizontal, x, direction is simply the fluid velocity component in the x direction, u. The flux of x-component momentum in an orthogonal direction, say in the vertical, z, direction is the shear stress, τ. In laminar flows the shear stress τ is given by:

$$\tau = \mu \frac{\partial u}{\partial z}$$

where μ is the coefficient of dynamic viscosity and is solely a property of the fluid. For turbulent flow, an early study by Boussinesq (1877) proposed that this shear stress would be:

$$\tau = \varepsilon \frac{\partial u}{\partial z} \tag{1}$$

where $\partial u / \partial z$ is the vertical gradient in mean velocity and ε is an eddy viscosity several orders of magnitude greater than μ and except very close to boundaries it is a function of the flow and not of the fluid properties.

The modern approach to turbulent flow began with the investigations of Reynolds (1895) who introduced the idea of decomposing the instantaneous velocity into a deterministic mean part and a randomly fluctuation, i.e.,

$$u = \bar{u} + u' \tag{2}$$

where $\bar{u}$ is the average velocity and u' is the fluctuation. Reynolds' work showed that the sear stress, τ, can be written as:

$$\tau = -\rho \overline{u'_x u'_z} \tag{3}$$

where ρ is the fluid density, and $\overline{u'_x u'_z}$ is the time average covariance of the turbulent fluctuations in horizontal and vertical velocities. Taylor (1921) demonstrated that there is a diffusive action in the lower atmosphere that is clearly stronger than could be attributed to molecular diffusion. He proceeded to derive an "eddy diffusivity" which was independent of the item that was being diffused. Independently of Taylor, Prandtl (1926) related the turbulent fluctuations to the general flow by suggesting that small fluid parcels are transported by turbulence a mean distance, l, from regions of one velocity to regions of another and in doing so suffer changes in their general velocities of motion. The distance l, was termed the mixing length, and Prandtl stated that the change in velocity over the length l is proportional to the velocities in each direction:

$$\tau = -\rho \overline{u'_x u'_z} = \rho l^2 \left(\frac{du}{dz} \right)^2 \tag{4}$$

This expression can then be combined with equation (1) to get an expression for ε, the eddy viscosity:

$$\varepsilon = \rho l^2 \left(\frac{du}{dz} \right) \tag{5}$$

von Karmen (1921) related the results of Prandtl to the actual flow profile near a wall using the relation l = κz. In this expression l is Prandtl's mixing length, z is the height, and κ is a constant. This constant was found experimentally to have a value of 0.4, and is known as von Karmen's constant. Using the previous relation and substituting into Prandtl's equation for shear stress, an expression for the logarithmic distribution of wind speed can be reached:

$$\frac{\partial u}{\partial z} = \frac{\sqrt{\tau/\rho}}{\kappa z} \tag{6}$$

Instead of shear stress it is convenient to introduce u_*, the friction velocity, where $u_* = \sqrt{\tau/\rho}$. The mixing length and eddy viscosity concepts were developed in the study of turbulent shear stress. These concepts may be readily extended to predictions for evaporative and sensible heat loss. Thornthwaite and Holzmann (1938) were the first to explore the application of these ideas to evaporative flux from land. Following Schmidt (1925) the vapor flux in the turbulent boundary layer is expressed as:

$$E = -A\left(dq/dh\right) \tag{7}$$

where A is the Austausch (mixing) coefficient developed by Schmidt, and dq/dh is the vapor concentration gradient. The research of Prandtl and von Karman led to an expression for the Austausch coefficient using the concepts of mixing length and shear stress. This led to the following equation for the evaporative flux:

$$E = \frac{\kappa \rho u_* (q_1 - q_2)}{\ln \frac{z_2}{z_1}} \tag{8}$$

where q_1, and q_2 are specific humidity values at the heights z_1 and z_2 respectively with z_2 above z_1. The friction velocity in this expression may be replaced by integrating the velocity profile equation between h_1 and h_2 to get:

$$u_2 - u_1 = \frac{u_*}{\kappa} \ln\left(z_2/z_1\right) \tag{9}$$

Substituting for u_* yields

$$E = \frac{\kappa^2 \rho (q_1 - q_2)(u_1 - u_2)}{\left[\ln\left(z_2/z_1\right)\right]^2} \tag{10}$$

This is the Thornthwaite Holzmann equation and it can be used provided there are adiabatic conditions in the atmosphere. An exactly analogous approach can be undertaken to obtain the flux of sensible heat, H, from observations at two elevations of the temperature and velocity, i.e.

$$H = \frac{\kappa^2 \rho C_p (T_1 - T_2)(u_1 - u_2)}{\left[\ln\left(h_2 / h_1\right)\right]^2} \tag{11}$$

where C_p is the specific heat of the fluid at constant pressure.

When there is stable vertical density stratification, such as at night, or unstable vertical density stratification such as hot days with low wind the atmosphere cannot be modeled with these equations. The first evidence of departure from adiabatic profiles was given by Pasquill (1945, 1948). He conducted a large scale experiment and collected data that clearly demonstrated that under certain conditions, the profiles of wind speed, heat, and water vapor were stretched or contracted depending on the atmospheric stability. Richardson (1920) proposed a method for classifying the atmosphere as a compressible environment.

$$Ri = \frac{g}{T} \frac{\partial\theta / \partial z}{\left(\partial u / \partial z\right)^2} \tag{12}$$

where g is the acceleration due to gravity, T is the absolute temperature, and θ is the potential temperature. Three cases are given for this classification scheme; (1) if Ri < 0 stratification is unstable and the energy of turbulence is increased, (2) if Ri > 0 stratification is stable thus hindering the development of turbulence, and (3) Ri = 0 stratification is neutral and does not affect the formation of turbulence. Another measure of stability is L, the Monin Obukov length scale, given by (Obukov, 1946).

$$L = \frac{\rho C_p u_*^{\,3} \theta}{\kappa g H} \tag{13}$$

where H is the directly measured value of the sensible heat flux. This can be modified to account for the effects of water vapor by replacing H with (H+0.07Le). The term z/L can then be used a classification scheme similar to that for the Richardson Number. Monin and Obukov (1954) used similarity theory to derive expressions for the profiles of wind speed, temperature, and moisture content of the air and take into account the possibility of non-adiabatic conditions. These equations are as follows:

$$\frac{\partial u}{\partial z} = \frac{u_*}{\kappa z} \phi_M \tag{14a}$$

$$\frac{\partial \theta}{\partial z} = \frac{H}{\rho C_p \kappa u_* z} \phi_H \tag{14b}$$

$$\frac{\partial \rho_e}{\partial z} = \frac{Le}{\lambda \kappa u_* z} \phi_W \tag{14c}$$

where u_* is the friction velocity, κ is von Karman's constant, ρ is the air density, C_p is the specific heat of the air at constant pressure, H is the sensible heat flux, Le is the Latent heat flux, ρ_e is the vapor density, and λ is the latent heat of vaporization. The values ϕ_M, ϕ_H, and ϕ_W represent atmospheric

stability correction factors for momentum, heat, and water vapor, they represent the departure of the atmosphere from adiabatic conditions. For unstable vertical density stratification the values for ϕ become less than one while for stable stratification they become greater than one. These values can be solved for directly, or estimated empirically as either a function of Ri or z/L.

Values of the atmospheric stability correction factors can be determined using measurements from an aerodynamic gradient system that measures wind speed, temperature, and water vapor concentration at two heights, and an eddy correlation system that directly measures u_*, and the sensible and latent heat fluxes. These data can then be used to estimate the atmospheric stability correction factors via two methods: (1) assume that the value of the correction factor is constant over the measurement interval, or (2) take an average value of the factor over the interval.

The first case assumes that the atmospheric stability correction factor is constant over the measured interval. The benefit of this assumption is that the mathematics involved are simple and the error involved in making this assumption is relatively small. The main drawback to this assumption is that the factors are a function of either Ri or z/L, both of which are a function of height. The following equations are used to determine the values for ϕ_M , ϕ_H , and ϕ_W :

$$\phi_M = \frac{(u_2 - u_1)}{\kappa u_* \ln(z_2/z_1)} \tag{15a}$$

$$\phi_H = \frac{\rho C_p \kappa u_* (\theta_2 - \theta_1)}{H \ln(z_2/z_1)} \tag{15a}$$

$$\phi_W = \frac{\lambda \kappa u_* (\rho_{e2} - \rho_{e1})}{Le \ln(z_2/z_1)} \tag{15a}$$

These values make the assumption that ϕ_M , ϕ_H , and ϕ_W are not a function of the height of measurement. Otherwise integration of the equations presented in the previous section would yield very different results.

The second case takes an average value of atmospheric stability correction factor by comparing the measured profile to a theoretical profile over the interval from the two measurement heights. This method is based on two assumptions: (1) There is a logarithmic distribution of velocity, temperature, and moisture content over the distance between the ground and the highest point of measurement, and (2) that u*, H, and Le are all constant over the same distance. The second assumption is commonly made for the turbulent boundary layer of the atmosphere. The equation for the logarithmic boundary layer under adiabatic conditions is:

$$\frac{\partial u}{\partial z} = \frac{u_{*_A}}{\kappa z} \tag{16}$$

Where the u_{*A} is the frictional velocity under adiabatic conditions. This equation can be modified to account for non-adiabatic conditions.

$$\frac{\partial u}{\partial z} = \frac{u_{*N}}{\kappa z}\phi_M \tag{17}$$

Where the u_{*N} is the frictional velocity under non-adiabatic conditions. The wind speed gradients in both equations are equal because the represent a value measured in the field. When the second equation is divided into the first a relation between the u_* values is determined.

$$\phi_M = \frac{u_{*A}}{u_{*N}} \tag{18}$$

This quantity can readily be determined using the eddy correlation system to directly measure the value of u_{*N}, and the aerodynamic gradient measurements entered into the equation for the logarithmic boundary layer under adiabatic conditions to determine the value of u_{*A}. The value determined for ϕ_M will be the mean value over the distance between the two sensor arms of the aerodynamic gradient system. Using this method it is also possible to determine the values for ϕ_H and ϕ_W, although both include the term ϕ_M.

$$\phi_H = \frac{H_A}{H_N \phi_M} \tag{19}$$

$$\phi_W = \frac{\rho_{eA}}{\rho_{eN} \phi_M} \tag{20}$$

Much research has been performed to generate values for the atmospheric stability coefficients. The stability coefficients have to be determined for both stable and unstable conditions, many researchers have done so, and in the two following tables their results are summarized.

Table 1. Empirical values for ϕ 's under unstable conditions.

Authors	Comments	Heat	Water Vapor	Momentum
Swinbank (1968)	Using κ=0.4, u* observed from drag coefficient -0.1>z/L>-2	$\phi_H = 0.227\left(-z/L\right)^{-0.44}$		$\phi_M = 0.613\left(-z/L\right)^{-0.20}$
Webb (1970)	Profiles only, no direct flux measurement z/L>-0.03	$\phi_H = 1 + 4.5\left(z/L\right)$	$\phi_W = 1 + 4.5\left(z/L\right)$	$\phi_M = 1 + 4.5\left(z/L\right)$
Dyer and Hicks (1970)	Using κ=0.41, Comparison of direct eddy fluxes and profiles 0>z/L>-1	$\phi_H = \left(1 - 16\left(z/L\right)\right)^{-1/2}$	$\phi_W = \left(1 - 16\left(z/L\right)\right)^{-1/2}$	$\phi_M = \left(1 - 16\left(z/L\right)\right)^{-1/4}$
Businger *et al.* (1971)	Using κ=0.41, Comparison of direct eddy fluxes and profiles z/L>-2	$\phi_H = 0.74\left(1 - 9\left(z/L\right)\right)^{-1/}$		$\phi_M = \left(1 - 15\left(z/L\right)\right)^{-1/4}$
Pruitt *et al.* (1973)	Using κ=0.42, Richardson Number used for stability measure		$\phi_W = 0.885\left(1 - 22Ri\right)^{-0.4}$	$\phi_M = \left(1 - 16\left(Ri\right)\right)^{-1/3}$

Table 2. Empirical values for ϕ 's under stable conditions.

Authors	Comments	Heat	Water Vapor	Momentum
Webb (1970)	Profiles only, no direct flux measurement z/L>-0.03	$\phi_H = 1 + 5.2\left(z/L\right)$	$\phi_W = 1 + 5.2\left(z/L\right)$	$\phi_M = 1 + 5.2\left(z/L\right)$
Businger *et al.* (1971)	Using κ=0.41, Comparison of direct eddy fluxes and profiles z/L>-2	$\phi_H = 0.74 + 4.7\left(z/L\right)$		$\phi_M = 0.74 + 4.7\left(z/L\right)$
Pruitt *et al.* (1973)	Using κ=0.42, Richardson Number used for stability measure		$\phi_W = 0.885\left(1 + 34Ri\right)^{0.40}$	$\phi_M = \left(1 + 16\left(Ri\right)\right)^{1/3}$

2.2 Chemical Contaminant Flux Estimation

The methods used for estimating the flux of contaminants from atmospheric measurements require knowledge of the gradient of contaminant concentrations in the measurement area as well as the atmospheric conditions. In order to use the atmospheric stability correction factors presented in the previous section to calculate contaminant flux estimates an assumption must be made. This assumption requires that the atmospheric stability function for contaminants, ϕ_C, is equal to ϕ_W. An equation for the profile of contaminants can be created in a manner similar to that for momentum, sensible, and latent heat.

$$\frac{\partial C}{\partial z} = \frac{F_c}{\kappa u_* z}\phi_C \tag{21}$$

If the first method for calculating atmospheric stability correction factors is used for the calculation of fluxes, the profile equation for contaminants can be integrated between heights z_2 and z_1 to yield:

$$C_1 - C_2 = \left[\frac{F_c}{\kappa u_*}\ln\left(z_2/z_1\right)\right]\phi_C \tag{22}$$

If we use the equation for (u_2-u_1) to eliminate the quantity ku_* in this second equation for concentration differences then it can be found that:

$$F_C = \frac{(u_2 - u_1)(C_1 - C_2)\kappa^2}{\left[\ln\left(z_2 / z_1\right)\right]^2 \phi_C \phi_M} \tag{23}$$

This is the Thornthwaite-Holzmann Equation.

Substituting the velocity profile (Eq. 9) into Eq. 23 yields and alternative expression for the chemical flux:

$$F_C = \frac{u_* \kappa (C_1 - C_2)}{\ln\left(z_2 / z_1\right) \phi_C} \tag{24}$$

Since, in the present observation, the friction velocity is directly measured this last equation may be used directly to find F_C.

The second method for calculating atmospheric stability correction factors will use the same initial equation while assuming that $\phi_C = 1$, thus adiabatic conditions are present. From this equation a value for the adiabatic flux, F_{CA}, is determined. Since values for ϕ_M and ϕ_C have been previously determined it is possible to estimate the flux of contaminants with the following equation:

$$F_{CN} = \frac{F_{CA}}{\phi_M \phi_C} \tag{25}$$

These two methods have been used in the determination of fluxes for the present study.

3.0 INSTRUMENTATION AND METHODS

3.1 Micrometeorological Systems

Micrometeorological data were collected in order to determine the vertical flux of PCBs. This was carried out using two micrometeorological systems purchased from Campbell Scientific of Logan, Utah, USA (www.campbellsci.com). The first, the Aerodynamic Gradient system, simultaneously measured temperature, vapor pressure, and wind speed at two heights, approximately one and three meters above the ground surface. The temperatures were measured with chromel-constantan thermocouples with a diameter of 74 μm. These thermocouples have a resolution of 0.006°C with 0.1 μV rms noise. The vapor pressures were measured by pumping air through a cooled mirror, dew point hygrometer (Model Dew-10, General Eastern Corp., Watertown, MA). Air is drawn from both heights continuously through inverted Teflon filters (Pore size 1 μm). The filters remove any dust or liquid water from the air stream. The hygrometer is equipped with a solenoid value that switches the air flow through the sensor between the two intakes for two minute intervals. The first minute of the interval is used to clear the air from the previous interval, while the second is used to collect the actual readings. The air is drawn at a flow rate of 0.4 l min^{-1} with 2 l mixing chambers to give a 5 min time constant. The Dew-10 has a resolution of approximately ±0.01 kPa. Wind speeds were measured using

R. M. Young 03001-5 Wind Sentries. These included a cup anemometer and a directional wind vane. The anemometer has a range of 0 to 50 m sec^{-1} with a threshold value of 0.5 m sec^{-1}. All measurements taken with the Aerodynamic Gradient system were averaged over twenty min intervals. The Aerodynamic Gradient system (Figure 2), as well as the PCB air samplers, are described in further detail in section 3.3 of this report.

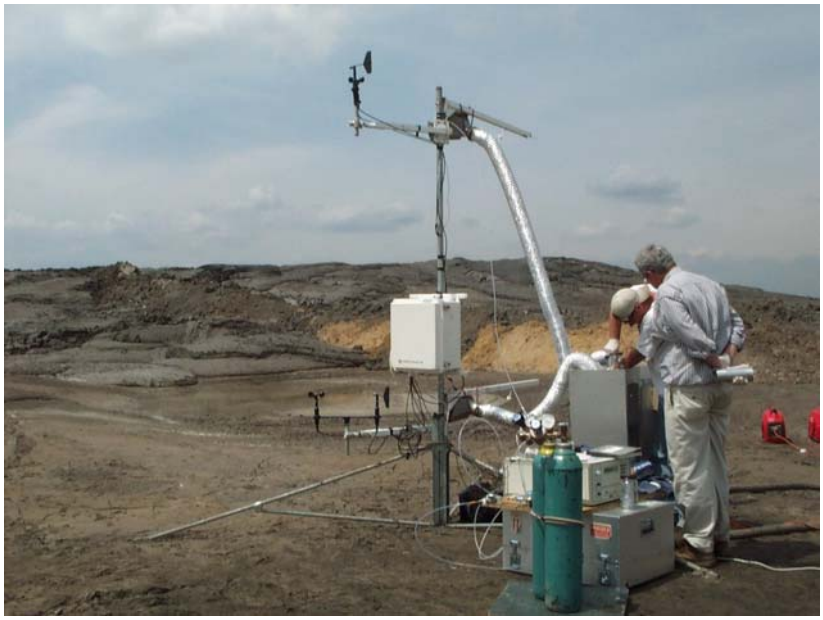

Figure 2. Aerodynamic Gradient System.

The second system, the Eddy Correlation system (Figure 3), included quick response instruments capable of measurements at 10 hertz in order to resolve the turbulent fluctuations in vertical velocity, w', horizontal velocity, u', temperature, θ', and specific humidity, q', in the near surface atmosphere. These measurements were processed and averaged to give 5-min averages of friction velocity and latent and sensible heat fluxes. The Eddy Covariance system consists of three sensors, the CSAT3 is a 3-D Sonic Anemometer that can sample at 60 Hertz, with noise in the horizontal directions of 1 mm sec^{-1}, 0.5 mm sec^{-1} in the vertical, and at 0.002 ^{o}C for the sonic temperature measurement. The range of wind speed measurement is ±65.535 m sec^{-1}. The fluctuations in the moisture content of the air are measured using a KH2O Ultraviolet Krypton Hygrometer capable of measuring at rates up to 100 Hertz. The system also includes a FW05 fine wire thermocouple (0.0013 cm) that measures very accurately at high sampling rates and is not affected by solar radiation.

3.2 Meteorological Station

A standard 10 m high meteorological tower (UT30 Weather Station) was employed to measure atmospheric conditions. These included temperature, wind speed and direction, pressure, humidity, and rainfall. The temperature and relative humidity were measured using a HMP45C Temperature and Relative Humidity Probe with a Platinum Resistance Temperature Detector and a Vaisala HUMICAP

180 capacitive relative humidity sensor. The temperature sensor is accurate to within ±0.4°C over the operating range of the sensor (-40°C to +60°C). The relative humidity sensor is accurate to within ±3%. The wind speed and direction were measured with a Young 05103 Wind Monitor. Wind speed from 0 to 60 m sec^{-1} can be measured with an accuracy of ±0.3 m sec^{-1} with a threshold value of 1 m sec^{-1}. The wind direction is measured accurately to within ±3°. The barometric pressure was measured with a CS105 Barometric Pressure Sensor which measures barometric pressure over 600 to 1060 mBar range with an accuracy of ±0.5 mBar @ +20ºC. Finally the rainfall was measured using a TE525WS Tipping Bucket Rain Gage. The bucket Tips at 0.03 mm increments and is accurate to ±1% at rate of up to 2.5 cm h^{-1}.

Figure 3. Eddy Correlation System.

3.2 Gas Phase PCB Sampling

Gas-phase PCB samples were collected using high-volume air samplers (Tisch Environmental, Village of Cleves, OH) operated at a calibrated airflow rate of ~800 l min^{-1}. Gaseous PCB samples were collected over four hour sampling periods on solvent-cleaned polyurethane foam plugs (PUF) from air that had passed through pre-combusted quartz fiber filters (QFF). The two high-volume samplers used to measure vertical PCB concentration gradients above SDM were modified to sample air at the two heights of the micrometeorological sensors. This was accomplished using flexible aluminum duct. The high-volume samplers consist of a vacuum pump and a manometer to measure the air flow rate through the sampler. The sampler's manometers were calibrated prior to and following each sampling event to ensure that flow measurements were accurate. Manometer calibration was carried out using a Tisch Adjustable Orifice Calibrator at five known air flow rates that were chosen to bracket field sampling flow rates. A linear regression was then used to determine the actual flow rate in the field. Calibrations run with an $r^2 < 0.98$ were rejected and the calibration was repeated.

3.4 Total Gaseous Hg Sampling

Total gaseous mercury was measured continuously in ambient air using a Tekran Model 2357A Mercury Vapor Analyzer (Tekran Inc., Toronto, Canada). Air was sampled at a flow rate of 1.5 l min^{-1} for a period of five-min during which time total gaseous mercury is concentrated by amalgamation onto one of two gold traps. At the Bayonne landfill, vertical TGM concentration gradients were determined from two five-min air samples collected at each of two heights above the SDM using the Synchronized Two-Port Sampler (Tekran, Model 1110) thereby reducing the potential for cartridge bias.

3.5 Field Work

Background ambient monitoring of atmospheric PCBs commenced on 8 December 1999 at the NJDEP air-sampling trailer located in Bayonne, NJ adjacent to Newark Bay (Figure 4). Twenty-four hour integrated air samples were collected at this site every 12 days for a total of 30 air samples.

Intensive sampling campaigns at the SDM landfill in Bayonne, NJ were carried out during four days in July 2001, three days in August 2001, three days in October 2001, three days in May 2002, and three days in November 2002. During these intensive sampling campaigns, air samples were collected at the NJDEP trailer on the west side of the Bayonne Peninsula for background PCB and Hg concentrations and above recently placed stabilized sediment and the SDM application site in Bayonne for the assessment of vertical fluxes (Figure 4). Additional PCB samples were collected at sites on the perimeter of the SDM application site in Bayonne to assess horizontal gradients. At the start of each

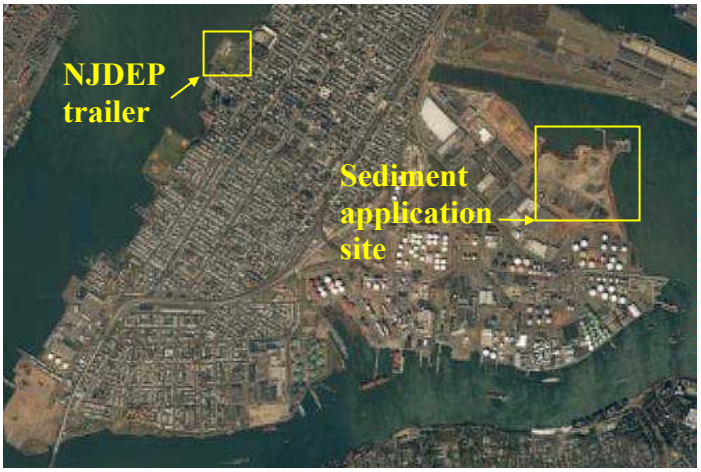

Figure 4. Aerial view of the Bayonne peninsula showing the sediment application site and the NJDEP air monitoring trailer where background concentrations of PCBs and Hg were measured.

sampling campaign, OENJ personnel were consulted to identify an appropriate site for the vertical flux measurements and every effort was made to place the sampling apparatus on top of recently placed SDM. Sampling was conducted over SDM under three conditions: On 1 August 2001, a sample was taken over recently laid, un-treated dredged material; on 29-30 August 2001, samples were taken over SDM that had been in place for three weeks; and on 23-25 October 2001, 6-8 May 2002, and 13-15

November, 2002, samples were taken over recently placed SDM. Weather conditions as well as forecasts for the following days were also taken into account in order to ensure that air would pass over freshly placed dredge prior to contact with sampling equipment. The micrometeorological systems were assembled and run on DC power from 12 volt batteries and once started, were allowed to collect data continuously for the length of the sampling campaign, unless there was a rain event.

For the vertical gradient measurements, air sample intakes for PCB and Hg samplers were placed downwind of the micrometeorological systems and the intakes attached to the upper and lower sampling bars. The samplers were powered by 1 kW portable generators, placed approximately 15 m downwind of the sampling location. PUF sampling media was brought to the site at the start of each day. Prior to being brought to the site, all PUFs were placed in glass sleeves in the lab and wrapped in aluminum foil. In this manner, they were easily placed in the sampler and the amount of time they were exposed was reduced. PCB samplers were run for 4 h during each sampling event; the flow rate was recorded at the beginning of the 4 h periods and periodically during each interval. At the conclusion of the 4 h interval, the samples were removed and labeled and the elapsed time was recorded to determine the total flow. Sampling campaigns were 3 to 4 days and encompassed day and night-time sampling. At the end of each day the samples were brought back to the laboratory, where they were removed from the sample holders and placed in extraction cells.

3.6 Chemical Analyses

Gas phase PCBs

The vertical gradient PUF samples were extracted using a Dionex ASE 300 Accelerated Solvent Extractor using dichloromethane. The extractions were done at 100 ºC and at 1500 psi. The samples were then concentrated using a Rotary Evaporator. The concentrated extract requires a clean-up step prior to analysis. This was done using Supelclean LC-Florisil SPE Tubes. The samples were passed though the Florisil, which is then rinsed with hexane to ensure that none of the sample is retained in the Florisil. The elution is then concentrated with nitrogen.

Perimeter and background (NJDEP trailer) PUF samples were spiked with a surrogate standard and extracted in Soxhlet apparatus for 24 h in petroleum ether. The sample extracts were concentrated using rotary evaporation (Büchi Model RotoEvaporator111) to ~2 ml and the solvent switched to hexane. The extracts were transferred to 12 ml amber vials and blown-down with a nitrogen-evaporator (Organomation Associates 111) under a steady stream of purified N_2 gas to ~0.5 ml.

The samples were then fractionated on a 3% water deactivated alumina column (Brockman neutral activity 1- mesh size: 60-325). The first elution using 12ml of hexane was captured in centrifuge vials which were then concentrated by a gentle stream of purified N_2 gas and transferred to 2ml vials. Copper granules were ‘activated’ with a 1 N solution of HCl and placed into the sample vials prior to injection into the gas chromatograph-electron capture detector (GC-ECD) to remove any sulfur chromatographic interferences resulting from the high sulfur content of the sediment.

Congener-specific quantification of PCBs was performed by GC-ECD using a 60 m, 5% diphenyl-dimethylpolysiloxane column (DB-5: 60m, 0.32 mm ID, 0.25 mm film thickness). Hydrogen was used as the carrier gas and a P5 mixture (5%-CH_4, 95% Ar) was used as the make-up gas.

Quality assurance and quality control were determined using laboratory blanks and field blanks. Laboratory blanks are used to assess the potential for contamination of samples in the laboratory during handling and processing. PCB masses in the laboratory blanks (n = 19 laboratory blanks) were low relative to the masses in the samples accounting for from 0.1 to 3 % of the total PCB mass in PUF samples. Therefore, a correction for laboratory contamination was unwarranted. Field blanks, used to determine PCB detection limits, consisted of PUFs placed into the samplers with no air flow. The method detection limits, defined as the mass plus three times the standard deviation of the mass in the site-specific field blank ranged from 9.1 pg (PCB congeners 137+176+130) to 1030 pg (congeners 8+5) and from 8.3 (PCB congeners 137+176+130) to 1080 pg (PCB congeners 81+87) for gas phase PUFs at the NJDEP trailer site and the sediment application site, respectively. Average PUF field blank masses accounted for 1.5 % and 2.9 % of the total sample masses for the NJDEP trailer site and the sediment application site, respectively. Average PUF field blank masses accounted for from 0.3 to 7% of the total sample masses.

Total gaseous Hg

Trapped Hg collected with the Tekran 2537A was automatically quantified in the field by cold vapor atomic fluorescence spectrometry (CV-AFS) following thermal desorption (Schroeder et al., 1995). Alternating sample collection and analysis on the Tekran's two gold traps allowed for continuous sample analysis. The significance of the vertical TGM concentration gradients was evaluated using the percent gradient (PG) method (Kim and Kim, 1999). In this method, the percent difference of the vertical concentration gradient (percent gradient) is compared with the analytical uncertainty. Analytical uncertainty was evaluated as the coefficient of variation (standard deviation divided by mean x 100) of replicate measurements over a 30 min period at the NJDEP trailer site (n = 6) and was found to be 1.3 %. Vertical gradients whose percent difference values were greater than twice the analytical uncertainty (2 x 1.3 % or 2.6 %) were considered significant and used to estimate positive or negative fluxes. Gradients whose percent difference values were less than the analytical uncertainty were assigned vertical fluxes of zero. The percent gradient was evaluated according to the following equation:

$$\text{Percent gradient} = \frac{|TGM_{lower} - TGM_{upper}|}{TGM_{lower}} \times 100 \qquad (26)$$

5.0 RESULTS

5.1 Gas Phase PCB Concentrations in Bayonne, NJ and at the SDM Landfill

For the period of December 1999 – November 2000, background gas phase ΣPCB concentrations measured at the NJDEP trailer in Bayonne ranged from 0.27 to 3.7 ng m^{-3} and averaged 1.8 ng m^{-3} (Figure 5). Gas phase PCB concentrations varied seasonally with the highest concentrations occurring in the summer and fall and the lowest in the winter and spring. Although concentrations differed seasonally, the relative PCB congener profiles were statistically similar among all four months (winter vs. spring: r^2=0.88, p<0.001; winter vs. summer: r^2=0.80, p<0.001; winter vs. fall: r^2=0.85, p<0.001; spring vs. summer: r^2=0.83, p<0.001; spring vs. fall: r^2=0.73, p<0.001; summer vs. fall: r^2=0.92,

p<0.001). The highest individual ΣPCBs concentrations occurred under predominantly northeast winds from over the city of Bayonne and the lowest ΣPCB concentrations occurred when winds were out of the west across Newark Bay.

Average PCB concentrations measured around the perimeter of the sediment application site were 1.5 to 2-fold higher than Bayonne background concentrations measured at the NJDEP trailer site (Figure 6). Average ΣPCB concentrations during the July 2001 campaign were 7128 pg m^{-3} and 3945 pg m^{-3} at the perimeter of the sediment application site and the Bayonne trailer site, respectively. For the October 2001 campaign, average ΣPCB concentrations were 2857 and 1284 pg m^{-3}, respectively. For the May 2002 campaign, average ΣPCB concentrations were 1604 and 947 pg m^{-3}, respectively. For the November 2002 campaign, average ΣPCB concentrations were 1644 and 881 pg m^{-3}, respectively.

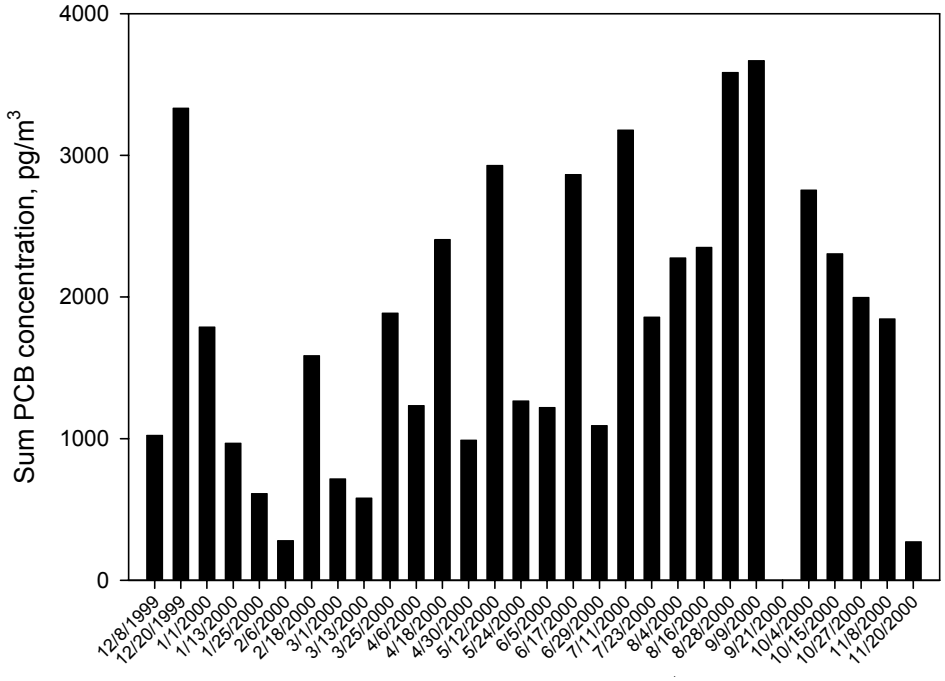

Figure 5. Gas phase ΣPCB concentrations measured at the NJDEP Bayonne trailer site for the year of Dec 1999 – Nov 2000.

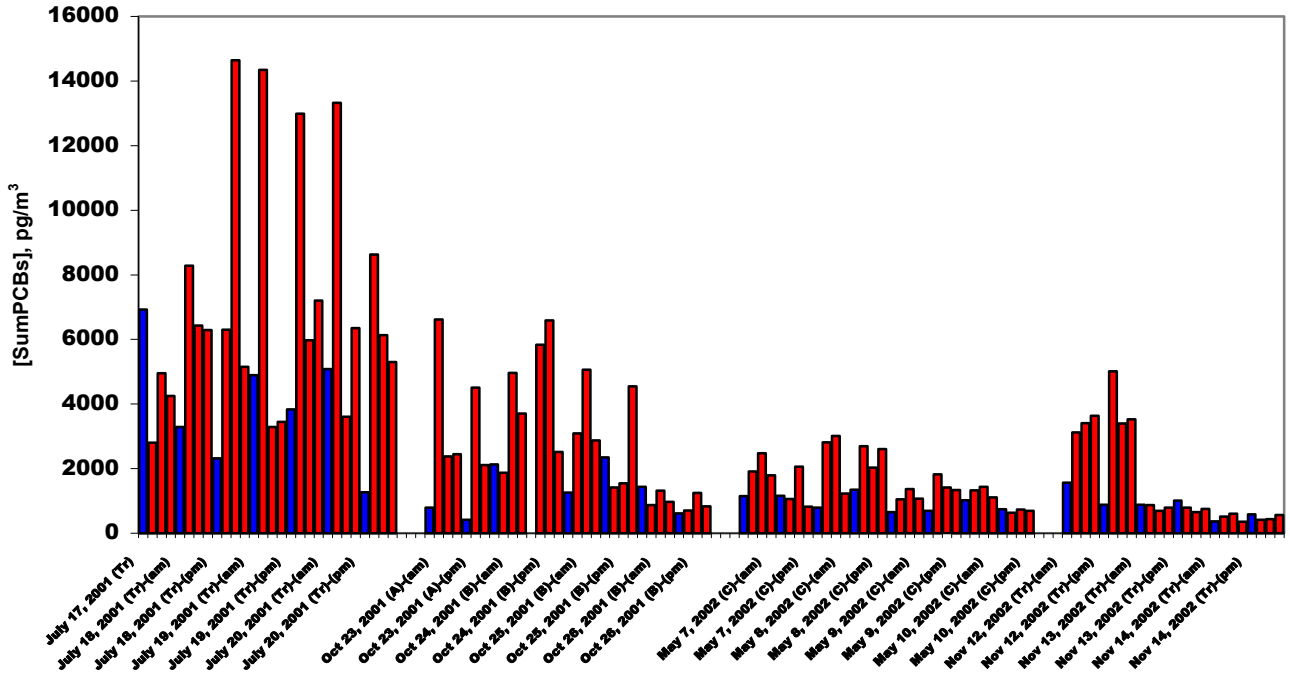

Figure 6. Concentrations of gas phase PCBs measured at the trailer site (blue) and at the perimeter of the sediment application site (red).

5.2 Total Gaseous Hg Concentrations in Bayonne, NJ and at the SDM Landfill

The average concentration of total gaseous mercury (TGM) measured at the NJDEP trailer in Bayonne, NJ for the period of September 2001 to February 2003 was 2.2 ng m^{-3}, a value consistent with background levels for the Northern Hemisphere (Slemr and Langer, 1992). Average monthly Hg vapor concentrations ranged from 1.69 ng m^{-3} (January 2003) to 3.34 ng m^{-3} (June 2002) and the range and variability of TGM concentrations was generally lower in the winter than in the summer (Table 3; Figure 7). However, throughout the monitoring period, "spikes" of elevated Hg that lasted for fifteen minutes to a few hours and occurred primarily between the hours of midnight and 0500 were observed at the NJDEP trailer. The highest concentration among these spikes (54 ng m^{-3}) was recorded on 30 June 2002 (Figure 8). No relationship between the occurrence of these spikes and meteorological conditions has been found. Average total gaseous Hg concentrations were significantly higher ($p < 0.01$) at the sediment application site than at either the Bayonne or New Brunswick background sites (Figure 9). The average background TGM concentration for samples collected on the days before and after intensive field campaigns at the SDM landfill was 1.8 ng m^{-3} compared with an average of 3.2 ng m^{-3} measured at the landfill.

Table 3. Monthly average total gaseous mercury (TGM) concentrations at the NJDEP trailer site in Bayonne, NJ.

	TGM (ng m^{-3})			
Month	**Average**	**Min**	**Max**	**n**
February 2002	2.15	1.38	5.89	0
March 2002	2.02	1.46	18.62	4804
April 2002	2.19	1.62	11.82	1858
May 2002	2.31	1.15	34.62	2344
June 2002	3.34	1.28	53.86	5017
July 2002	2.70	1.46	21.67	2699
October 2002	1.75	0.51	20.74	6604
November 2002	1.82	0.53	27.93	3147
January 2003	1.69	0.98	18.01	3279
February 2003	1.96	1.55	6.47	969

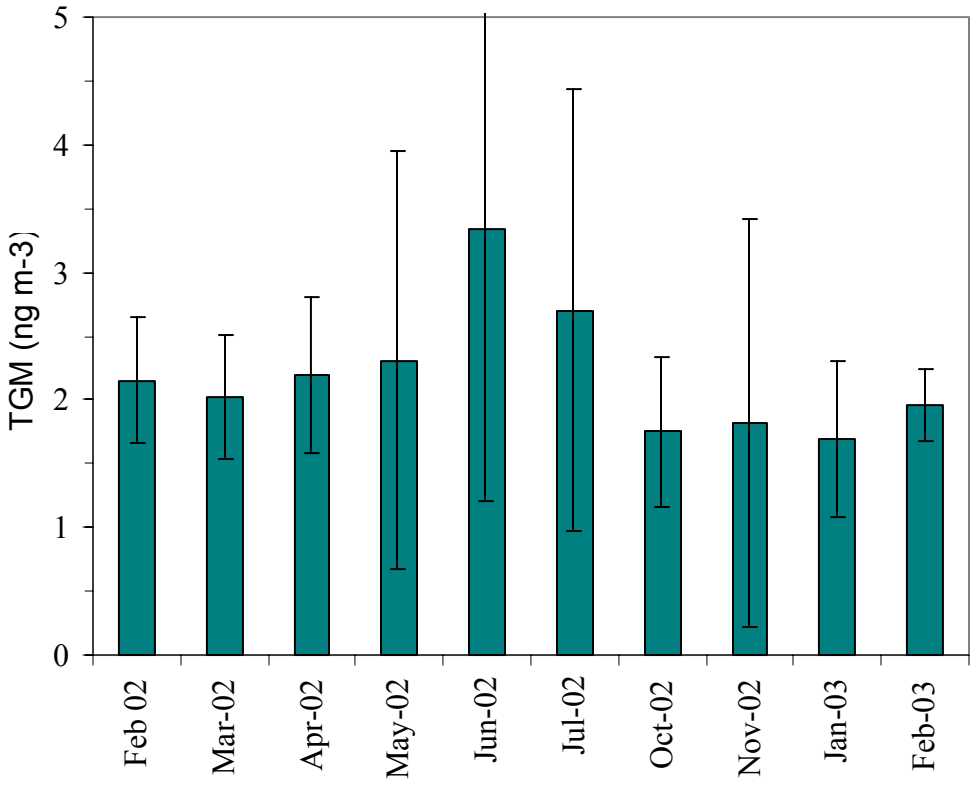

Figure 7. Monthly average total gaseous mercury concentrations at the NJDEP trailer site in Bayonne, NJ for the period February 2002 – February 2003.

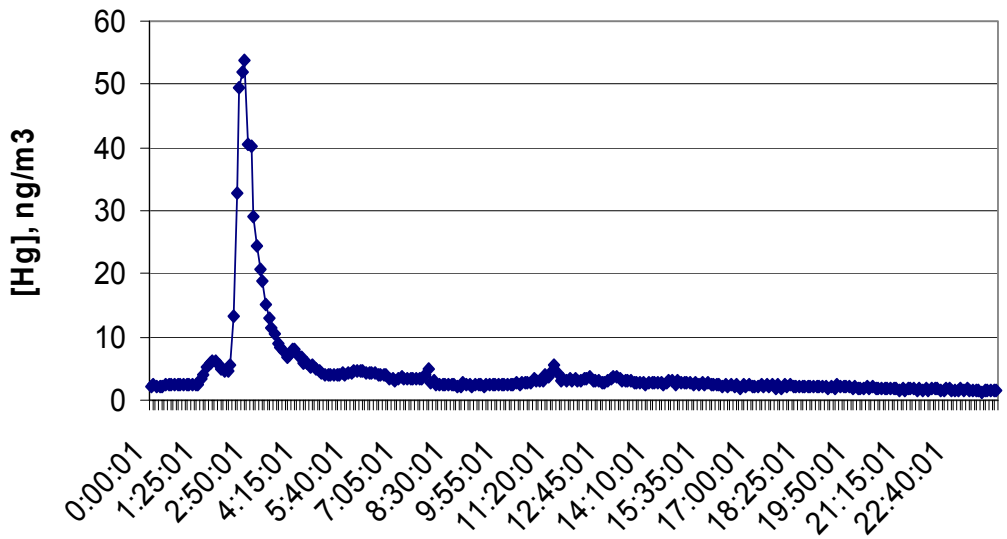

Figure 8. Total gaseous mercury concentrations at the NJDEP trailer site in Bayonne, NJ on 30 June 2002.

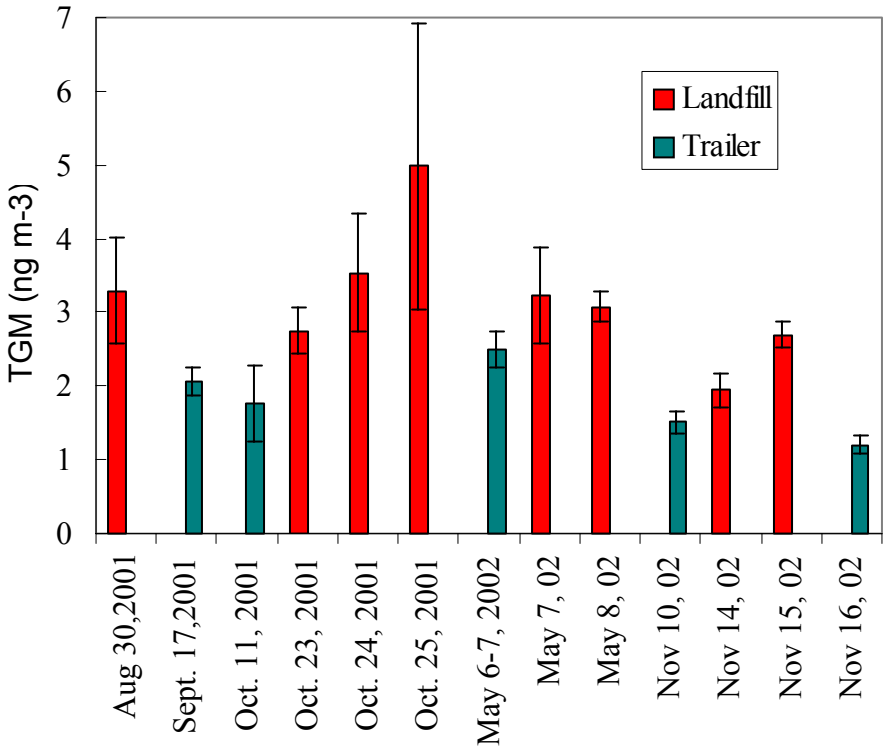

Figure 9. Average total gaseous mercury (TGM) concentrations at the SDM landfill and the NJDEP trailer during intensive field campaign.

5.3 Summary of Vertical Fluxes of PCBs and Hg at the SDM landfill

Micrometeorological estimates of sediment-air fluxes of gas phase PCBs and Hg from SDM are summarized in Tables 4 and 5. Positive vertical fluxes (sediment-to-air) were observed during 16 of 20 sampling periods for ΣPCBs and in 14 of 15 sampling periods for Hg. Negative fluxes do not necessarily indicate net absorption of the contaminants by SDM; they may be the result of variable atmospheric conditions during those sampling periods that resulted in inverted concentration gradients (lower near the SDM surface). Vertical PCB fluxes ranged from 72 to 15,000 ng m^{-2} h^{-1} and were highest in during the May 2002 campaign (Table 4). Nighttime PCB fluxes were an order of magnitude lower than daytime fluxes. Sediment-air fluxes of Hg fluxes ranged from 17 to 1043 ng m^{-2} h^{-1} and, like the PCB fluxes, were highest in May 2002 (Table 4). The percent difference in vertical TGM gradients measured at the SDM landfill site ranged from 0.3% to 32.3% (Appendix 6). With an analytical uncertainty of 2.6% in the difference between paired measurements, 86% (97 out of 113) of all gradients recorded were significant and indicative of net (positive or negative) sediment-air Hg fluxes. The single nighttime Hg flux estimate for 7 May 2002 was less than 3% of the average daytime fluxes observed in during the May 2002 campaign.

Table 4. Sediment-air fluxes of gas phase PCBs and meteorological parameters at the SDM landfill in Bayonne.

Date	Local Time	Wind speed (m s^{-1})	Temp (^{0}C)	Vertical gradient (ng m^{-3})	Flux (ng m^{-2} h^{-1})
08/01/01	1030-1245	2.0	28	0.62	201
	1245-1441	3.0	29	0.62	134
08/29/01	2225-0210	2.2	21	-0.49	-47
08/30/01	1030-1430	4.7	29	-5.07	-1944
10/23/01	1020-1400	4.3	32	-0.42	-106
	1430-1807	6.7	27	3.51	1276
10/24/01	1020-1419	2.2	26	8.53	2205
	2010-2330	3.7	22	1.56	326
10/25/01	0800-1200	3.3	28	3.72	1366
05/06/02	1230-1530	3.4	24	6.38	14871
	1530-1830	4.2	21	2.12	4207
05/07/02	0930-1230	2.4	23	1.82	1987
	1300-1600	3.4	26	2.37	2332
	2000-2315	0.9	21	1.05	72
05/08/02	0930-1230	4.3	19	0.97	2877
11/13/02	1537-1930	5.6	9	0.24	76
11/14/02	0815-1130	3.3	7	0.71	492
	1200-1500	2.7	13	0.48	260
	1630-1945	3.7	12	-0.08	-17
11/15/02	0830-1130	4.2	11	0.24	74

Table 5. Sediment-air fluxes of gas phase Hg and meteorological parameters at the SDM landfill in Bayonne.

Date	Local Time	Wind speed ($m\ s^{-1}$)	Temp (^0C)	Average vertical gradient ($ng\ m^{-3}$)	Flux ($ng\ m^{-2}\ h^{-1}$)
8/30/01	1310 - 1436	3.6	25	0.42	187
10/23/01	1100 - 1200	3.9	19	0.23	30
	1320 - 1330	4.3	19	0.46	139
10/24/01	1235 - 1555	2.6	29	0.78	156
10/25/01	1110 - 1120	7.6	26	2.11	559
	1445 - 1455	8.0	26	0.84	310
5/07/02	1045 - 1200	1.9	21	0.91	1043
	1205 - 1455	3.6	24	0.32	314
	2030 - 2305	1.3	24	0.29	19
5/08/02	0955 - 1210	4.6	20	0.45	966
	1330 - 1600	5.1	19	0.26	552
11/14/02	1000 - 1150	3.8	11	0.05	34
	1210 - 1635	3.1	13	0.03	17
11/15/02	0920 - 1150	3.8	13	-0.04	-13
	1210 - 1400	3.8	15	0.11	41

5.4 17-20 July 2001 Sampling Campaign

Background and Perimeter Gas-Phase PCBs

In July 2001, samples for gas-phase PCBs were taken simultaneously around the perimeter of the SDM landfill and the NJDEP trailer site. The three high-volume air samplers were labelled A, B and C. Station A was located adjacent to the front entrance security gate, station B was located about 9 m from the meteorological tower, and station C was located near the pug mill on the Hudson River side of the site (see Figure 20 below). A total of 34 (28 samples plus 6 field blanks) air samples were taken during this campaign. Samples were taken in the morning (0900 – 1300) and in the afternoon (1300 – 1700) on each day at both sites. ΣPCB (n= 93 congeners) concentrations ranged from ~1200 to 7000 pg m^{-3} at the trailer site and ~3000 to 15000 pg m^{-3} at the SDM landfill perimeter sites during the July sampling campaign (Figure 6). Vertical PCB and Hg concentration gradients were not measured during this campaign.

5.5 1 August 2001 Sampling Campaign

SDM landfill site conditions

During the 1 August 2001 sampling campaign, vertical PCB fluxes were measured on an access road leading from the pug mill along the waterfront on the eastern side of the SDM landfill site (Figure 10). The wind was from the southwest. Directly adjacent to the experimental set-up and up-wind was a lagoon of one-day old un-stabilized dredged material. The weather conditions at the site are summarized in Figure 11. The sampling interval was from 1040 to 1440 PM. During the first three hours of sampling, the wind was blowing across the dredged material. In final hour the wind direction changed such that it was blowing off the water and there was a pronounced change in the observations.

Figure 10. Bayonne landfill site conditions, 1 August 2001.

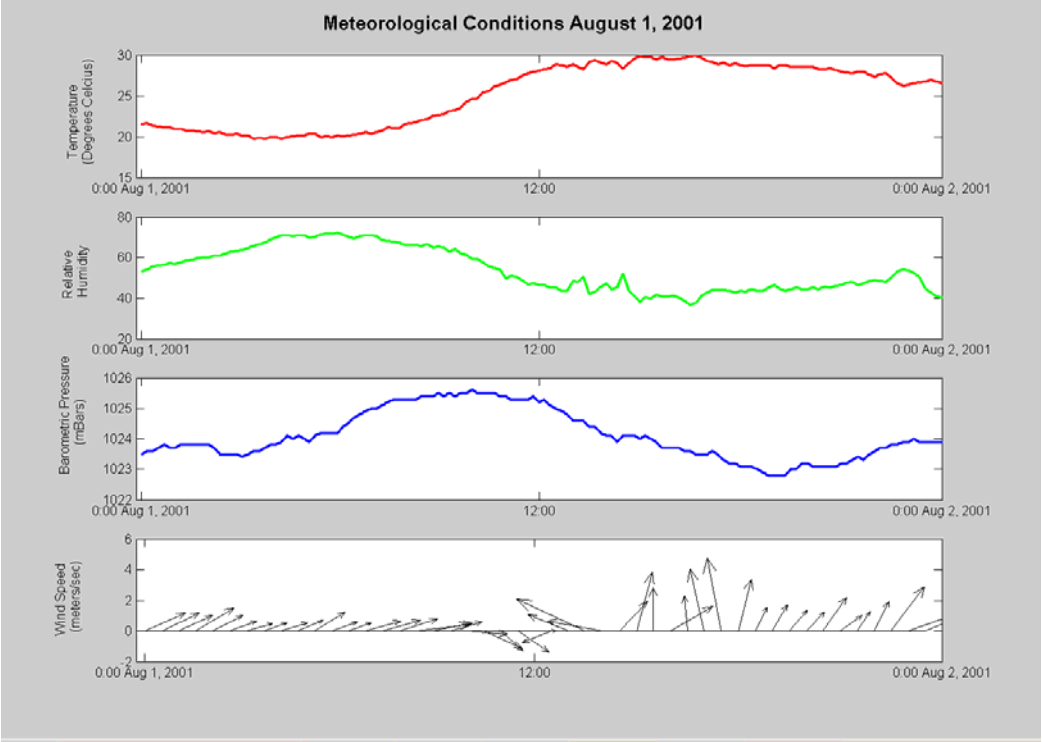

Figure 11. Meteorological conditions at the Bayonne landfill site, 1 August 2001.

The change in conditions also had an impact on the micrometeorological observations. The wind speed gradient in the last two hours dropped from 0.3 to 0.1 m s^{-1} over the two meter elevation difference, while the u_* values were only slightly changed. The temperature gradient in the last two hours decreased from > 1 ^{0}C to < 0.2 ^{0}C over the 2 m elevation difference, while the Latent Heat Flux increased from 250 to 500 watts m^{-2}. The Sensible Heat Flux remained nearly constant through out the sampling interval with values ranging from 100 to 160 watts m^{-2} (Figure 12). These changes indicate a shift from stable conditions to unstable conditions that would facilitate the flux of PCB from the drying sediment. Vapor pressure data obtained on this date were found to be incorrect due to a calibration problem. Subsequent discussion with the manufacturer uncovered the problem, which was corrected for the remainder of the sampling campaign. Average values of ϕ_M and ϕ_H were found to be 0.704 and 0.974 respectively. Due to the aforementioned problem with the vapor pressure data, the ϕ_H value was used in place of ϕ_W in the calculation of PCB flux. It has been shown in studies by Pruitt et al. (1973), that for slight departures of atmospheric stability from a neutral condition, that ϕ_W has approximately the same value as ϕ_H.

Vertical PCB Fluxes

The ΣPCB concentrations at 1.03 m and 3.04 m above the surface were 13.2 ng m^{-3} and 12.5 ng m^{-3}, respectively. The congener distribution on August 1 was greatly skewed toward the lower molecular weight PCBs (Appendix 8, Figure 1). This pattern was repeated for most of the samples taken at the site during this project.

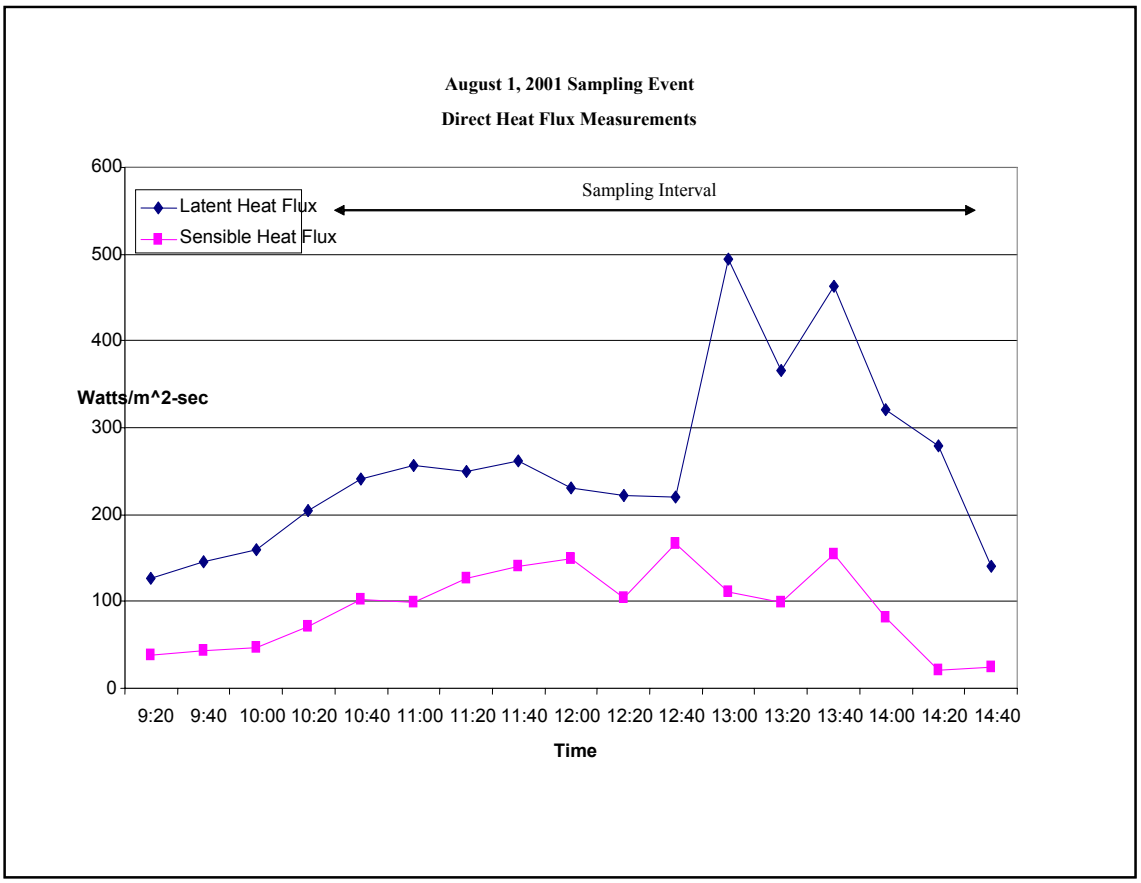

Figure 12. Latent and sensible heat fluxes at the Bayonne landfill sampling site, 1 August 2001.

Although the gradient of ΣPCB concentrations at the two heights would appear to denote a flux into the ground, if the various PCB homologues are evaluated separately a different picture emerges. For example, since only the lower molecular weight congeners will volatilize, then it seems reasonable to assume that some subset of the lighter PCB congeners will dominate the sediment-air flux. Estimates of the vertical fluxes for each PCB homologue group are presented for the August and October 2001 sampling campaigns in Figure 13.

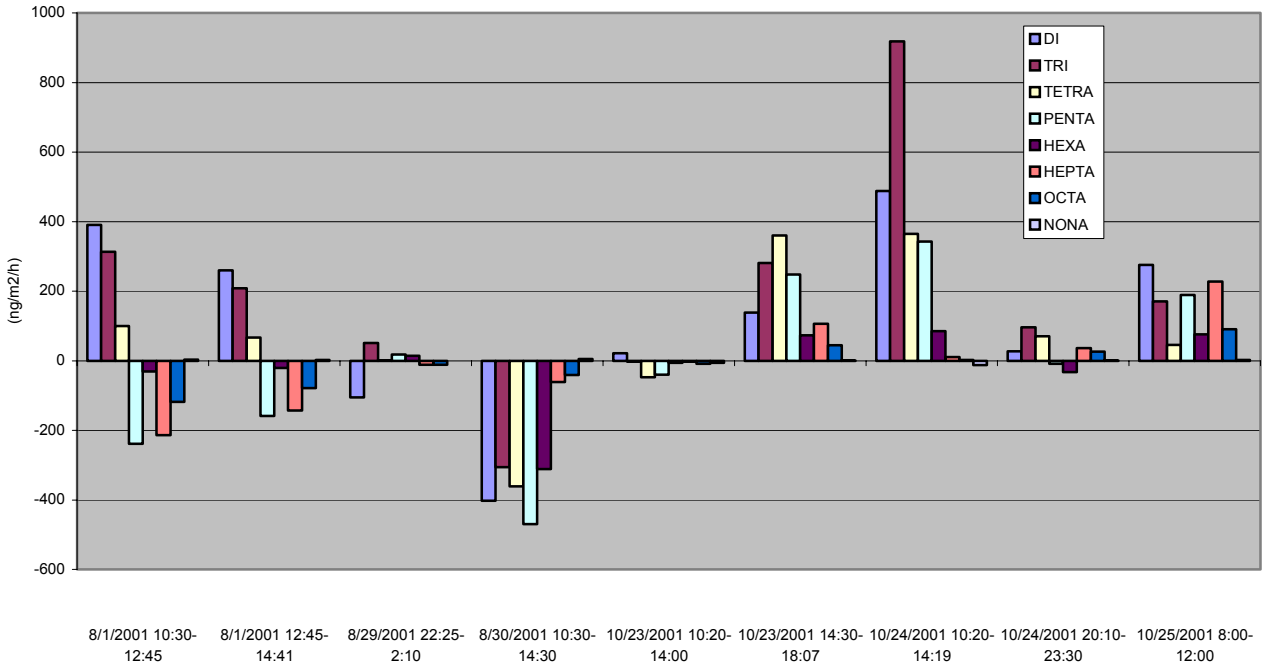

Figure 13. PCB homologue flux rates at the Bayonne landfill, 1 August 2001.

5.6 29-30 August 2001 Sampling Campaign

SDM Landfill Site Conditions

Although dredge material was not being delivered on site during sampling, the experimental set up was erected on recently spread stabilized dredge material. The material had been stabilized three weeks prior, however it was dug back up and spread in the two days prior to sampling. The wind was from the Northwest. The Eddy Correlation System, Bowen Ratio System, and air samplers were set up and run for approximately four hours at three separate time intervals. Sampling occurred during the day on the 29th and 30th, and overnight on the 29th. Due to equipment failure, PCB concentrations were not determined during the daytime on August 29th. The site conditions for the two sampling intervals are shown in Figures 14 and 15. The weather conditions are summarized in Figure 16.

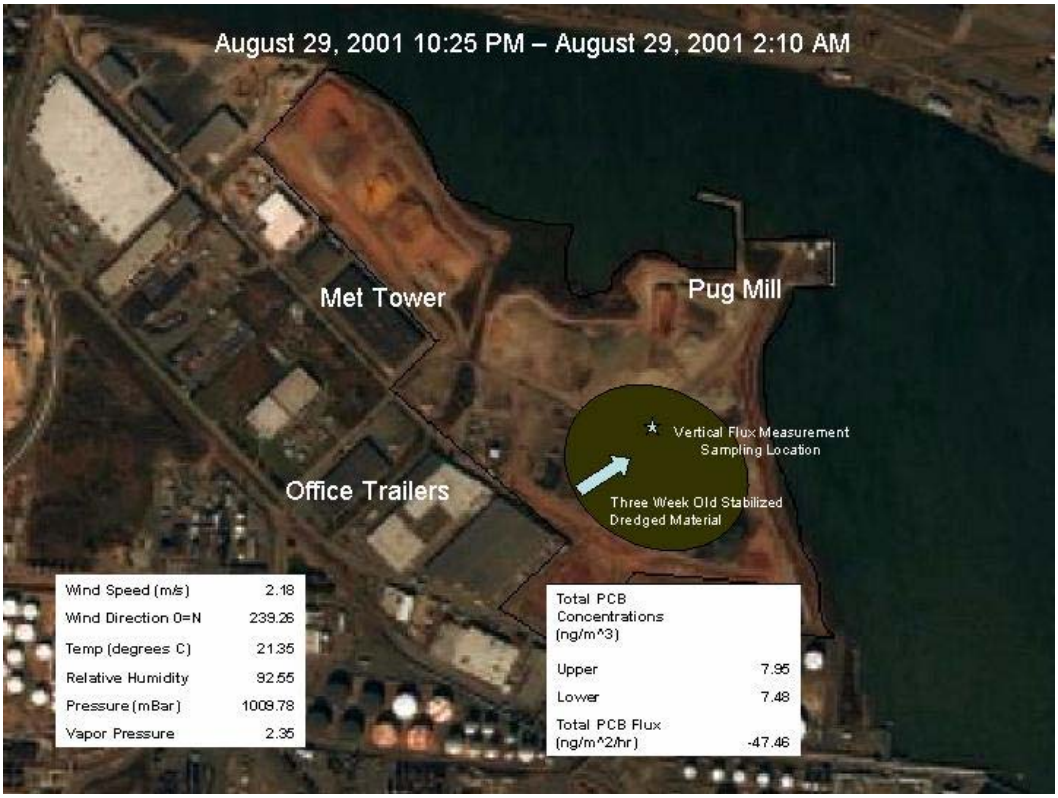

Figure 14. Bayonne landfill site conditions, 29-30 August 2001.

Figure 15. Bayonne landfill site conditions, 30 August 2001.

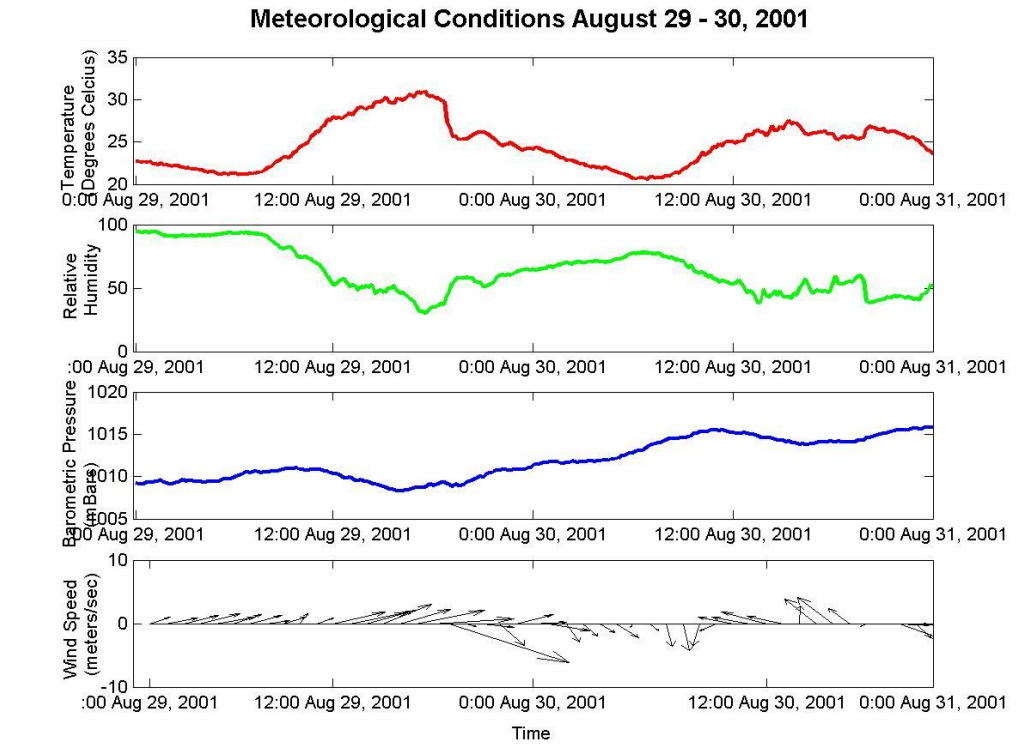

Figure 16. Meteorological conditions at the Bayonne landfill site, 29-30 August 2001.

All system worked well during this deployment including the vapor pressure measurements at two heights. After extensive consultation with personnel at Campbell Scientific the problems with the calibration procedure for the cooled mirror hygrometer in the Bowen Ratio System were completely resolved. During this deployment there were no apparent problems with the vapor pressure measurements.

Measurements of sensible heat flux were made for the three sampling intervals. On 29 August, these revealed a positive heat flux during the day of the order of 130 watts m^{-2}, while during the night sampling a negative heat flux (into the ground) of the order of –10 watts m^{-2} was found. During August 29th, a positive heat flux of the order of 120 watts m^{-2} was found. During these same consecutive sampling times the latent heat flux values were 200 watts m^{-2}, 34 watts m^{-2} and 100 watts m^{-2} respectively. The heat flux measurements for the nighttime sampling interval are shown in Figure 17.

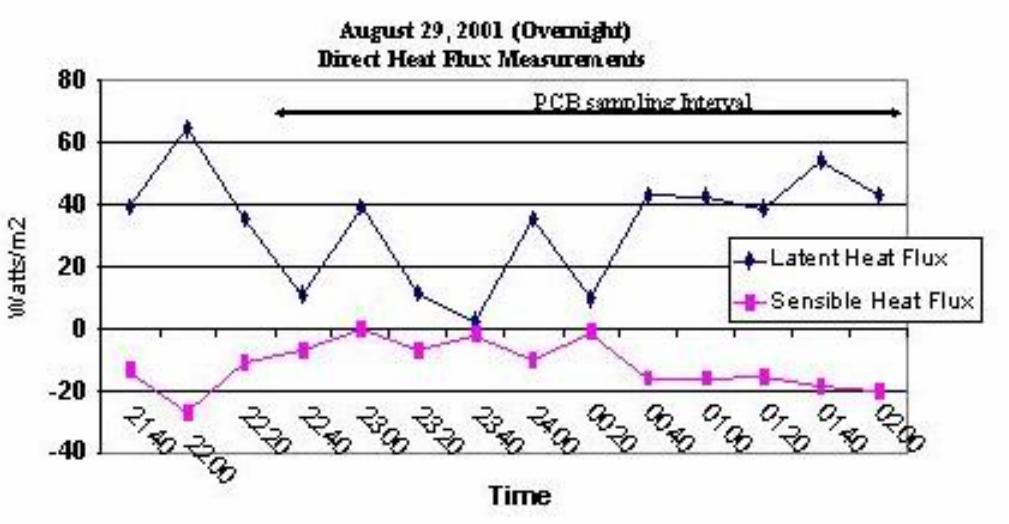

Figure 17. Nighttime latent and sensible heat flux measurements at the Bayonne landfill site, 29 August 2001.

The decrease in daytime latent heat flux in combination with the high sensible heat flux relative to the latent heat flux from 29-30 August may be attributed to the drying of the amended dredge material. This drying was apparent from the white crust observed during day two forming on the surface. Figure 18 is a plot of the heat flux measurements during 30 August.

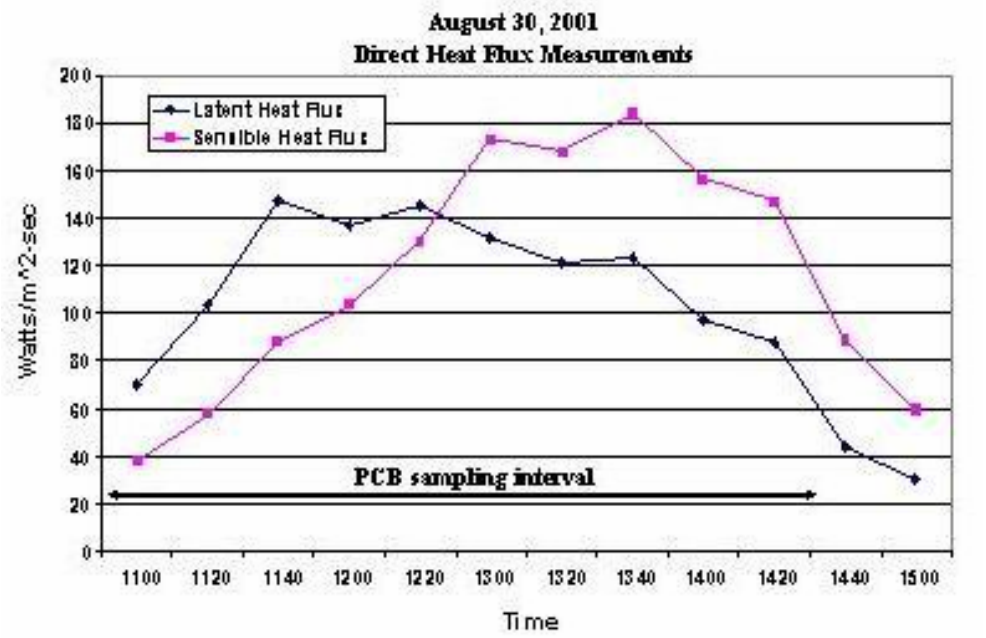

Figure 18. Latent and sensible heat flux measurements at the Bayonne landfill site, 30 August 2001.

Atmospheric stability coefficients were determined using our flux-gradient equations. The daytime value for ϕ_M was 0.54 and the value for ϕ_W was 1.19. This indicates conditions where the atmosphere is slightly stable with respect to the latent heat, but is very unstable with respect to momentum. This could be a result of the drying of the SDM. During the overnight interval the atmosphere was stable with values for ϕ_M and ϕ_W of 1.34 and 1.91 respectively.

Vertical PCB Fluxes

PCB concentrations measured above three-week old SDM during the overnight sampling interval on 29 August were very similar at the two heights with values of 7.95 and 7.46 ng m^{-3} for the upper and lower heights, respectively. The congener distribution of PCBs in these samples (Appendix 8, Figure 2) shows that the vast majority of the airborne PCBs have low molecular weight. It also shows a gradient out of the ground for those low molecular weight PCB congeners; however the opposite is true for the higher weight congeners. The small gradients in both directions, along with a relatively stable nighttime atmosphere led to small flux estimates. The total flux was estimated to be -47 ng m^{-2} h^{-1}, however, there were concentration gradients both into and out of the ground and fluxes in both directions depending on the molecular weight.

On 30 August, very high PCB concentrations were measured and there was a large gradient from the upper intake to the lower intake (19 and 14 ng m^{-3} for the upper and lower intakes, respectively). This gradient is found to be consistent over homologues (Appendix 8, Figure 3). The large gradient of PCB concentrations into the ground results in a PCB flux estimate of -1944 ng m^{-2} h^{-1}. The elevated PCB concentrations observed on this day may have been the result of the advection of PCBs to the site from an upwind source. SDM may not necessarily have been absorbing PCBs, but this is strong evidence that PCBs were not volatilizing from the site on 30 August.

Total Gaseous Mercury Fluxes

Positive vertical gradients in TGM concentrations were observed above the SDM on 30 August with average TGM concentrations of 4.1 ng m^{-3} and 3.3 ng m^{-3} for the lower (0.8 m) and upper heights (3 m), respectively. Paired measurements used in flux estimates had an average gradient of 0.42 ng m^{-3} and yielded an average net flux of Hg out of the SDM of 187 ng m^{-2} h^{-1} (Table 5).

5.7 23-25 October 2001 Sampling Campaign

Background and Perimeter Gas-Phase PCBs

Samples were taken in the morning (0900 – 1300 hours) and in the afternoon (1300 – 1700 hours) on each day at the perimeter of the sediment application and the trailer site for a total of 34 air samples (30 samples plus 4 field blanks). ΣPCB (n= 93 congeners) concentrations ranged from ~400 to 2000 pg m^{-3} at the trailer site and ~700 to 7000 pg m^{-3} at the perimeter of the sediment application site over the October sampling campaign.

During the first sampling interval (23 October 2001, 1020 – 1400 hours) the wind was blowing over a SDM lagoon that was just starting to be filled during this time period. The perimeter PCB concentration measurements for this interval show that there were greater concentrations measured

near the Office Trailers which were downwind of the large SDM lagoon in the center of the site than near the Pug Mill, which was upwind of the site. The conditions during the second sampling interval on 23 October 2001 (1430 – 1807 hours) were similar to those of the earlier sampling interval in that wind blew from the ocean and it was overcast and cool. Neither of the perimeter samples was representative of air blowing over the SDM. On 24 October 2001, the wind was directly over the fresh dredge, and much slower than the previous day. PCB concentrations collected during this interval on the perimeter show an increase in the concentrations leaving the site. The samples collected on the evening of 24 October 2001 were taken while the wind was blowing in off the ocean. It was blowing over both SDM lagoons for part of this interval. Perimeter samples were not taken during this time interval. The wind during 25 October was blowing in off the ocean. The perimeter samples show greater PCB concentrations in air that has traveled over the site than in air that has not.

SDM Landfill Site Conditions

Vertical gradients in PCB and Hg concentrations were collected over five sampling events during this campaign. The micrometeorological systems and air samplers were setup on the eastern side of the site between two lagoons where SDM was being dumped continuously during the campaign. The sampling location can be seen in Figures 19 – 23; these show the site conditions during each of the five sampling intervals as well as perimeter PCB concentrations during four of the five intervals. During the three-day interval, meteorological conditions at the site varied. This included wind direction which varied from over the two different SDM lagoons and areas of the site with no SDM. The resulting flux estimates reflect the variability of the meteorological conditions.

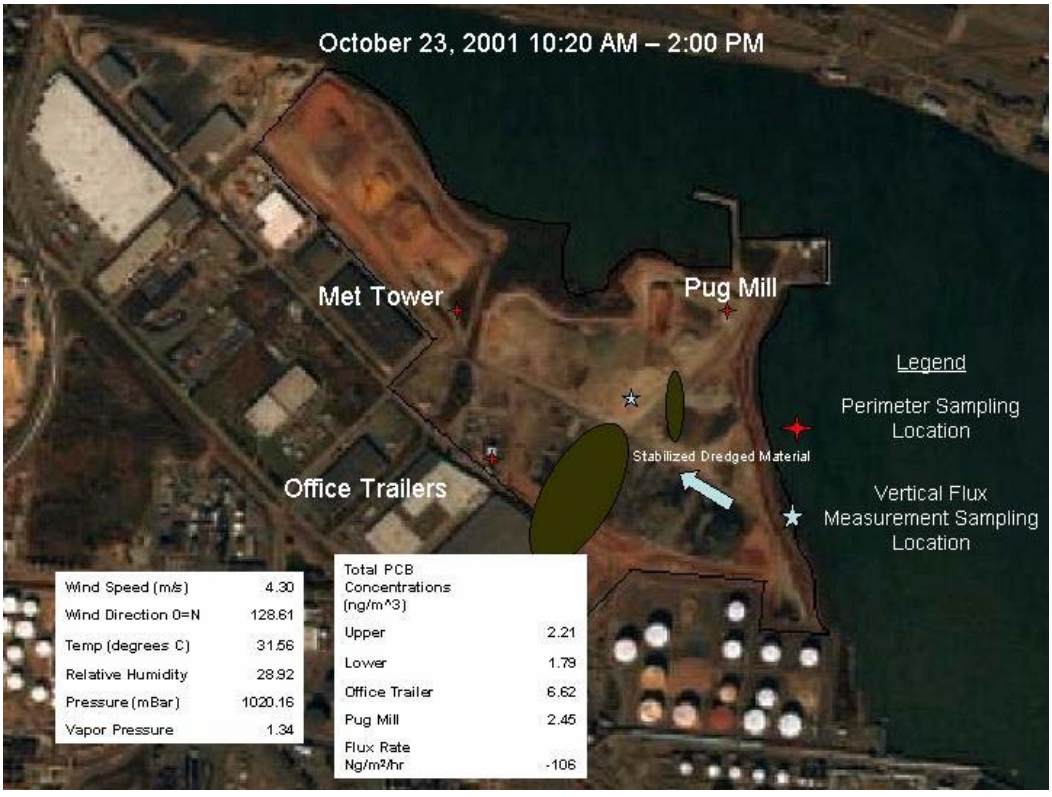

Figure 19. Bayonne landfill site conditions, 23 October 23 2001, 1020 – 1400 hours.

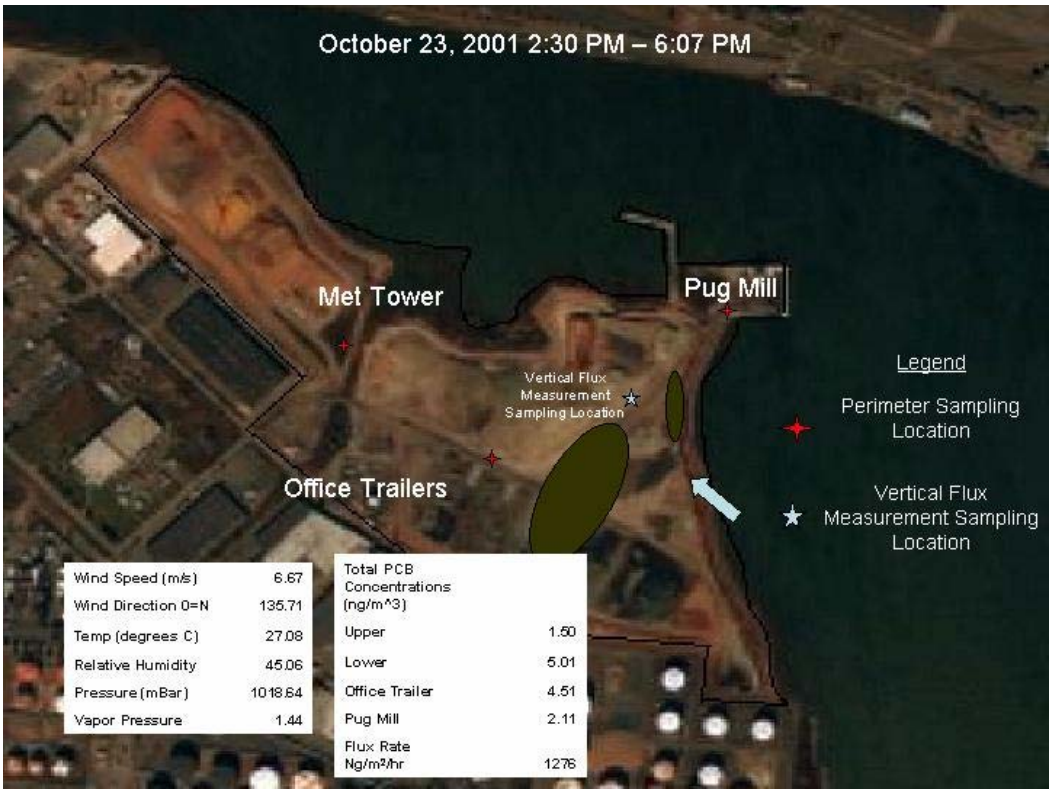

Figure 20. Bayonne landfill site conditions, 23 October 2001, 1430 – 1807 hours.

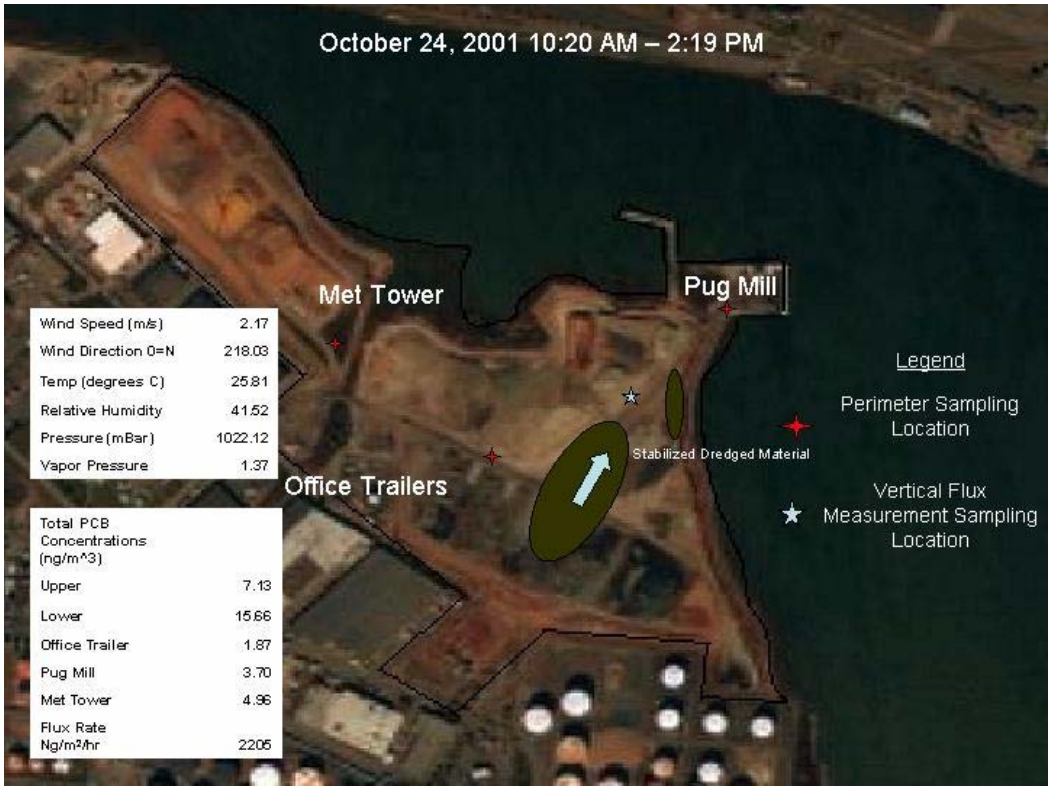

Figure 21. Bayonne landfill site conditions, 24 October 2001, 1020 - 1419 hours.

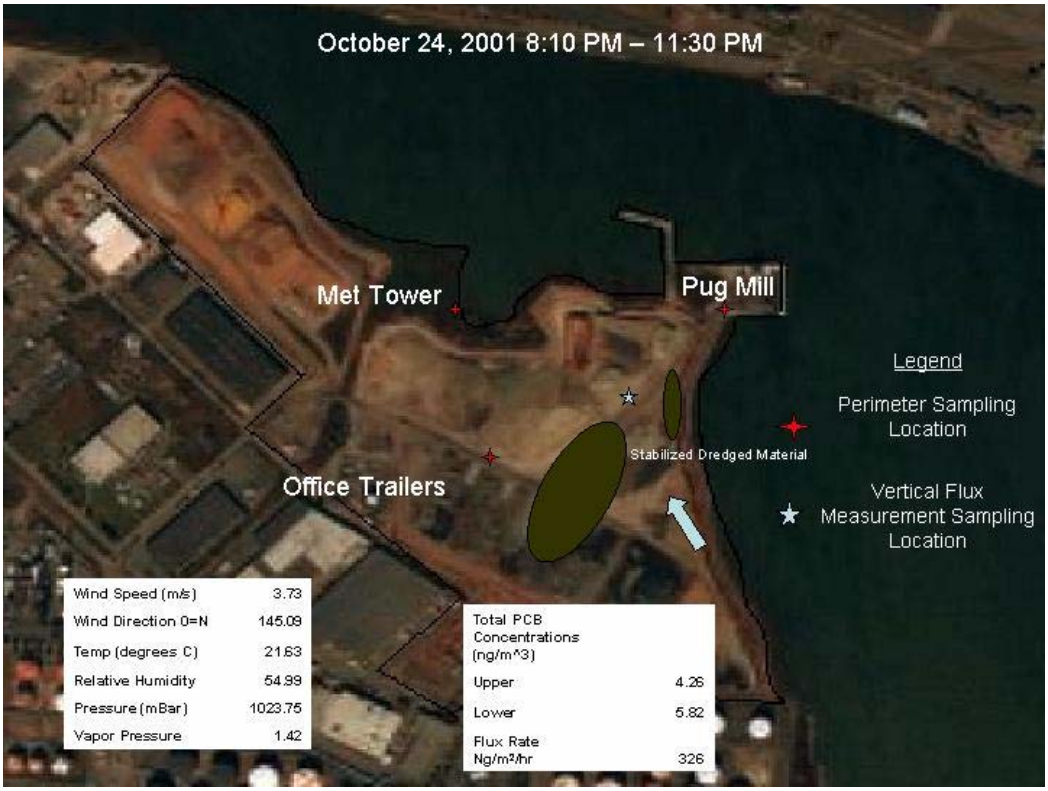

Figure 22. Bayonne landfill site conditions, 24 October 2001, 0810 – 1130 hours.

Figure 23. Bayonne landfill site conditions, 25 October 2001, 0800 – 1200 hours.

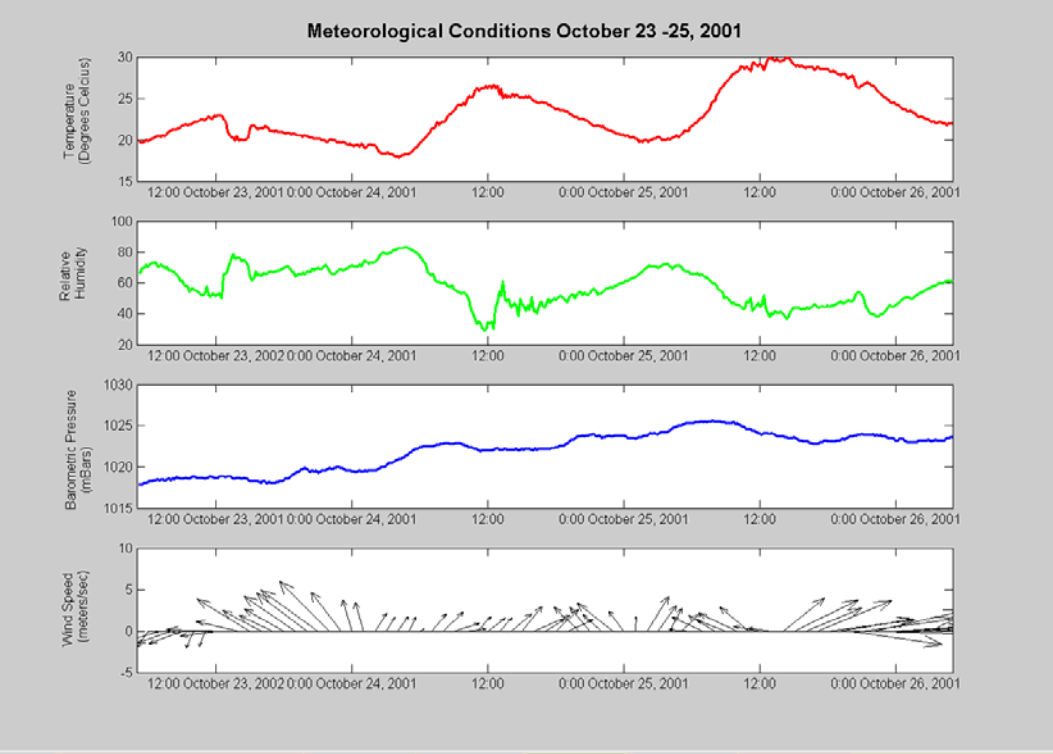

Figure 24. Bayonne landfill meteorological conditions, 23 -25 October 2001.

The meteorological conditions for the sampling interval are presented in Figure 24. The weather during the October sampling campaign changed over the three days. It began on a cool overcast day. High pressure moved in as time went on and the cloud cover cleared and the temperature rose.

Vertical PCB Fluxes

The observed PCB fluxes are closely linked to the latent and sensible heat flux values in magnitude and direction. However, the latent heat flux appears to have a greater effect (Figure 25). It is observed that there are relatively high latent and sensible heat flux values during the day and very small or negative values at night; this is due to the solar radiation heating up the ground surface.

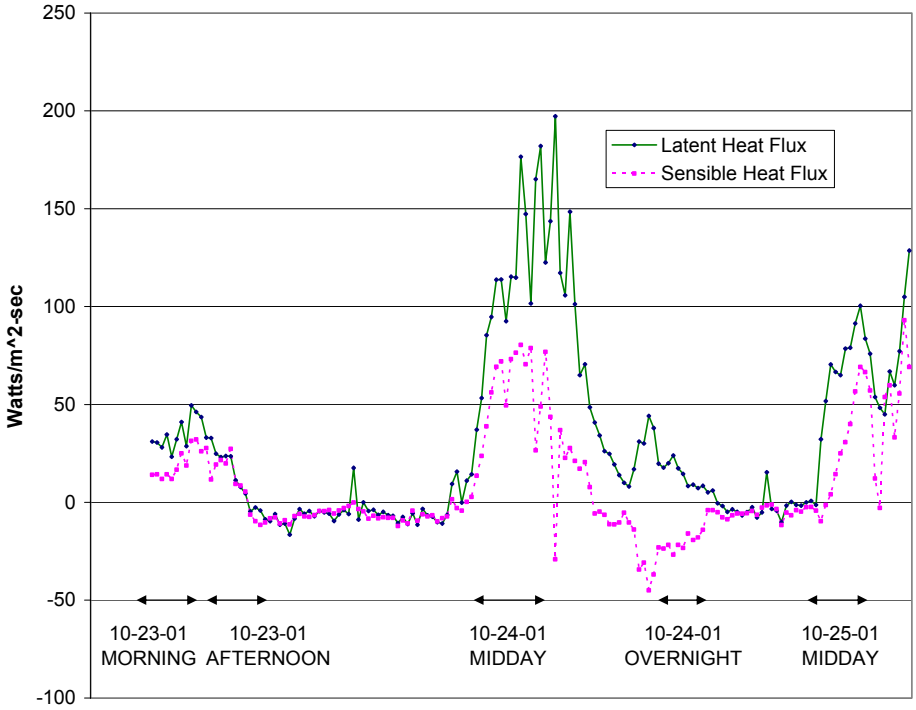

Figure 25. Observed fluxes of sensible and latent heat during the October sampling campaign.

On 23 October 2001 it was overcast and the wind was off the water from the southeast. As a result of the presence of cooler, humid air and little sunlight, the sensible heat flux on this day was very small. These conditions combined to yield nearly neutral stability. The values for ϕ_M were 0.99 and 0.94, and the values for ϕ_W were 1.00 and 1.00 for the two sampling periods on 23 October, respectively. The ϕ_W value for the second sampling interval is 1.00 because a range of stabilities was observed as indicated by Richardson numbers of –0.03 to 0.01. During this sampling interval, the sun set, sensible and latent heat fluxes declined, and ϕ_W values varied from less than one to greater than one. The following two days the wind changed to southwest, the skies cleared, and relative humidity was lower, and as a result the atmosphere became unstable. The daytime sample on 24 October 2001 exhibited a less stable atmosphere, but the gradient in the moisture content was below the resolution of the cooled mirror hygrometer. As a result the value for ϕ_W used was that for the ϕ_H. For slight departures of atmospheric stability from a neutral condition, ϕ_W has approximately the same value as ϕ_H (Pruitt et al., 1973). The final two intervals included a nighttime sample and a sample on 25 October 2001. The nighttime sampling interval was atypical in that the temperature inversion eroded as the winds changed from southwest to southeast (from over the bay). In Figure 25, there is a small spike of latent heat flux during the sampling campaign, indicating a certain amount of instability with respect to the moisture content. Because measured values could not be determined during the nighttime sampling event, fluxes were estimated using ϕ values of 1.0.

PCB concentrations were measured during the five intervals and in each case, except the morning sample on 23 October, exhibited a gradient out of the ground. The samples for the morning sampling interval on 23 October, exhibited a gradient out of the ground only for the lowest molecular weight

congeners. The congener distributions for the five sampling intervals are presented in Appendix 8, Figures 4 through 8.

The concentrations measured during this interval were very low in comparison to those measured later in the campaign. As a result, this interval had the lowest flux estimate for the sampling campaign. Although the concentrations were small there was a pronounced gradient from the lower sampling intake to the upper intake. The gradient was present for all the congeners regardless of molecular weight. This distribution still showed that the highest concentrations observed were for the lowest molecular weight congener, but there were relatively high concentrations of congeners with chlorination numbers of three and four.

The PCB concentrations collected during this sampling interval were much higher than the previous day's. There was a distinct gradient in the magnitude of concentrations from the lower intake to the upper intake. The congener distribution showed much higher concentrations for the low molecular weight congeners.

The nighttime samples collected on 24 October 2001 are very similar in magnitude; however a small gradient can be seen between the lower intake and the upper intake. The congener distribution shows higher concentrations for the low molecular weight congeners. There was a spike that represents three co-eluting peaks 56+60+89, this was at first assumed to be an analytical error, however it was also present in the subsequent sampling interval.

The final sampling event of the campaign resulted in the highest flux rates and there was a consistent gradient in the PCB concentrations collected at the site. The large peak for congener 56+60+89 was present again, and there was also a spike in the area of the heaviest congeners corresponding to PCB congener 180.

Total Gaseous Mercury Fluxes

During the October sampling campaign, the average TGM concentration measured at the lower height rose from 3.1 ng m^{-3} on the morning of 23 October 2001 to 7.3 ng m^{-3} on the afternoon of 25 October 2001. Over the three day campaign, the observed vertical TGM concentration gradient increased from 0.23 ng m^{-3} on 23 October, to 0.78 ng m^{-3} on the 24th, and 2.1 ng m^{-3} on the morning of 25 October (Table 5). Following the change in wind direction, the vertical gradient in TGM concentration dropped to 0.84 ng m^{-3} in the afternoon of 25 October. The vertical flux of TGM from SDM was 30 ng m^{-2} h^{-1} on the morning of 23 October and increased to 139 and 156 ng m^{-2} h^{-1} on the afternoons of 23 and 24 October, respectively (Table 5). On 25 October, the vertical TGM flux increased to 559 ng m^{-2} h^{-1}in the morning and 310 ng m^{-2} h^{-1} in the afternoon.

5.8 6-8 May 2002 Sampling Campaign

Background and Perimeter Gas-Phase PCBs

PCB samples were also collected in the morning (0900 – 1300 hours) and in the afternoon (1300 – 1700 hours) on each day at the perimeter of the sediment application site and at the trailer for a total of 39 air samples (32 samples plus 7 field blanks). The 3 high-volume air samplers were labeled A, B

and C. Station A was located west of the SDM along the western perimeter of the landfill, station B was located about 30 feet from the meteorological tower, and station C was located NW of the SDM near the perimeter of the landfill (see Fig. 26). ΣPCB (n= 93 congeners) concentrations ranged from ~600 to 1300 pg m^{-3} at the trailer site and ~600 to 3000 pg m^{-3} at the perimeter of the sediment application site over the sampling campaign.

SDM Landfill Site Conditions

The May 2002 sampling campaign was conducted directly on top of freshly placed SDM. The SDM had developed a solid surface layer and was strong enough to support sampling equipment, however at one foot below the surface, the sediment had apparently not yet cured. The sampling equipment was placed downwind of approximately 100 m of exposed, freshly laid SDM. Placement of SDM in the area of study ceased on the first day of the sampling campaign. During the campaign, the SDM dried and developed a white crust. Sampling took place on the western side of the site and the wind blew over the SDM for the duration of the sampling campaign with the exception of the final interval when the wind changed and blew from the northeast. At that time, the sampling equipment was moved as far as possible to the southwest. After moving the equipment, it was downwind of approximately 25 m of SDM.

Figure 26 shows the site conditions during the early afternoon sampling interval on 6 May when the highest estimated PCB fluxes were observed. During this sampling interval the wind was blowing from the southwest directly over SDM placed just prior to the sampling interval.

Site conditions during the late afternoon/evening sampling interval on 6 May are shown in Figure 27. The weather conditions were similar to the early afternoon, except that the there was a slight temperature drop toward evening.

On the second day of sampling the wind was variable, and it was hot and sunny. The wind was blowing directly over the SDM. Figures 28 and 29 show the conditions at the site on 7 May 2002.

Figure 26. Bayonne landfill site conditions, 6 May 2002, 1230 – 1530 hours.

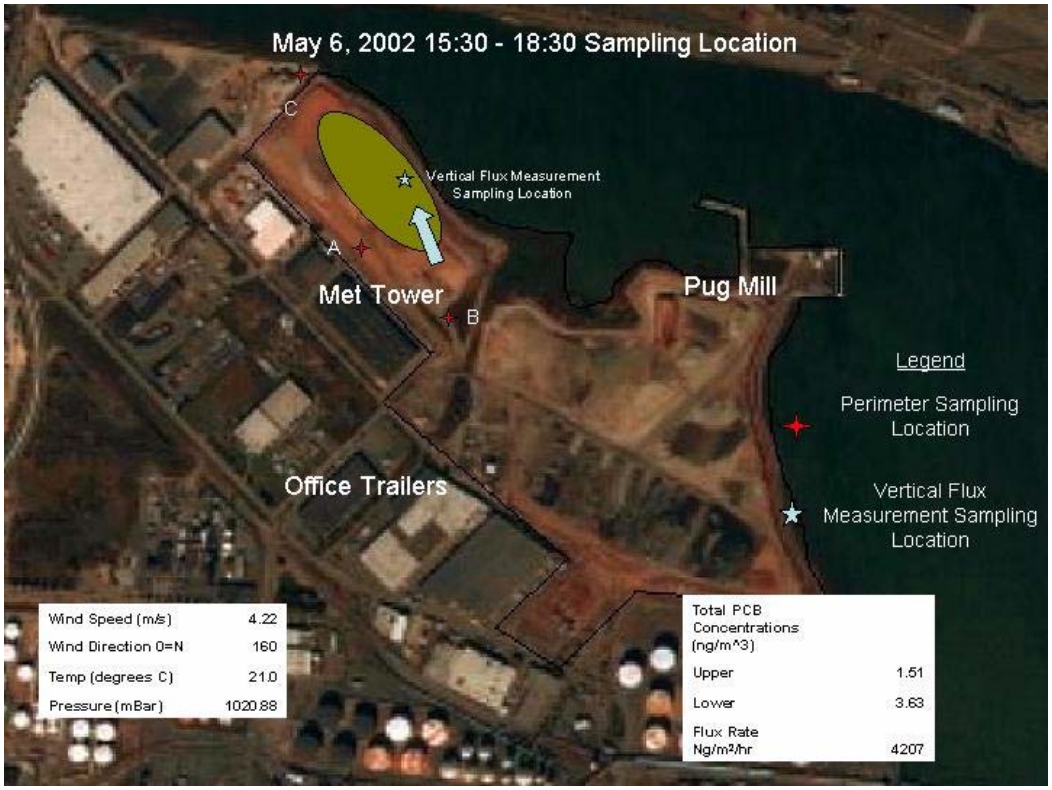

Figure 27. Bayonne landfill site conditions, 6 May 2002, 1530 – 1830 hours.

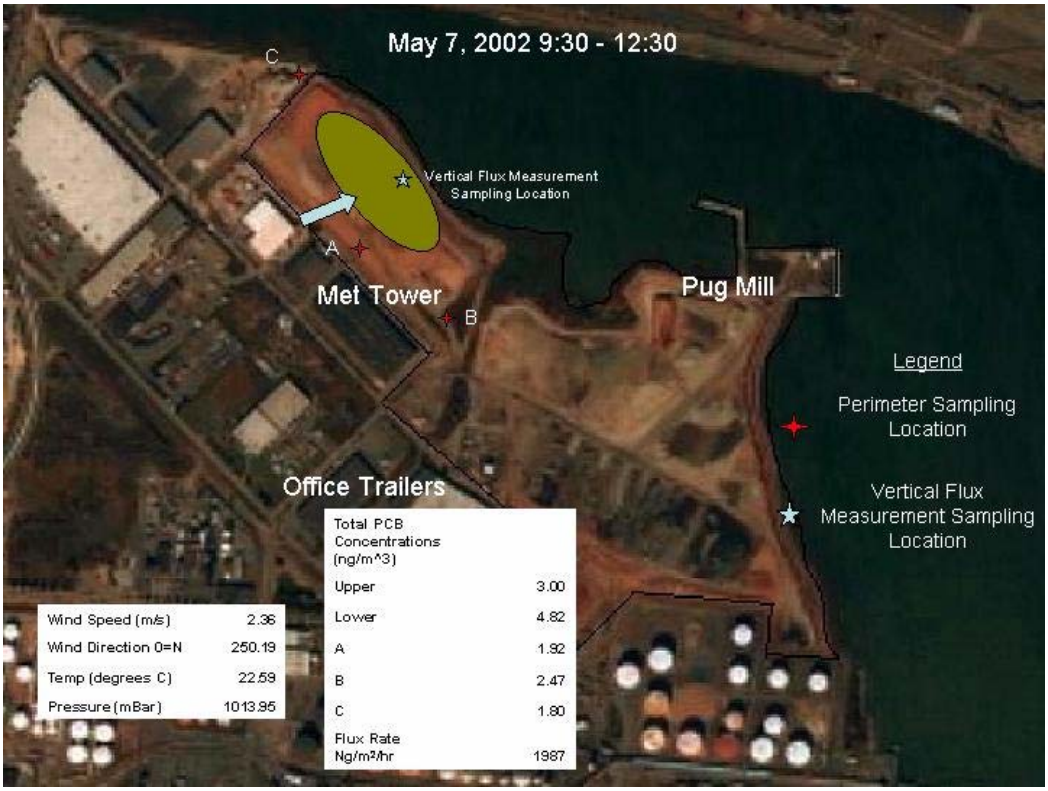

Figure 28. Bayonne landfill site conditions, 7 May 2002, 0930 – 1230 hours.

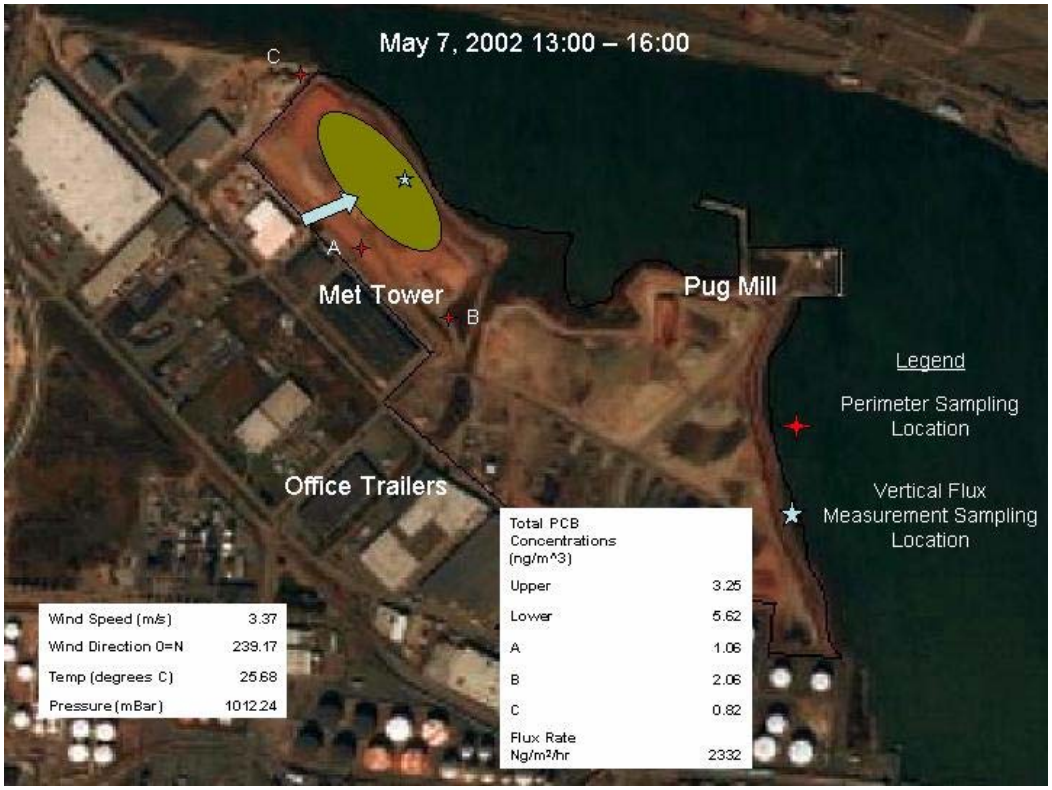

Figure 29. Bayonne landfill site conditions, 7 May 2002, 1300 – 1600 hours.

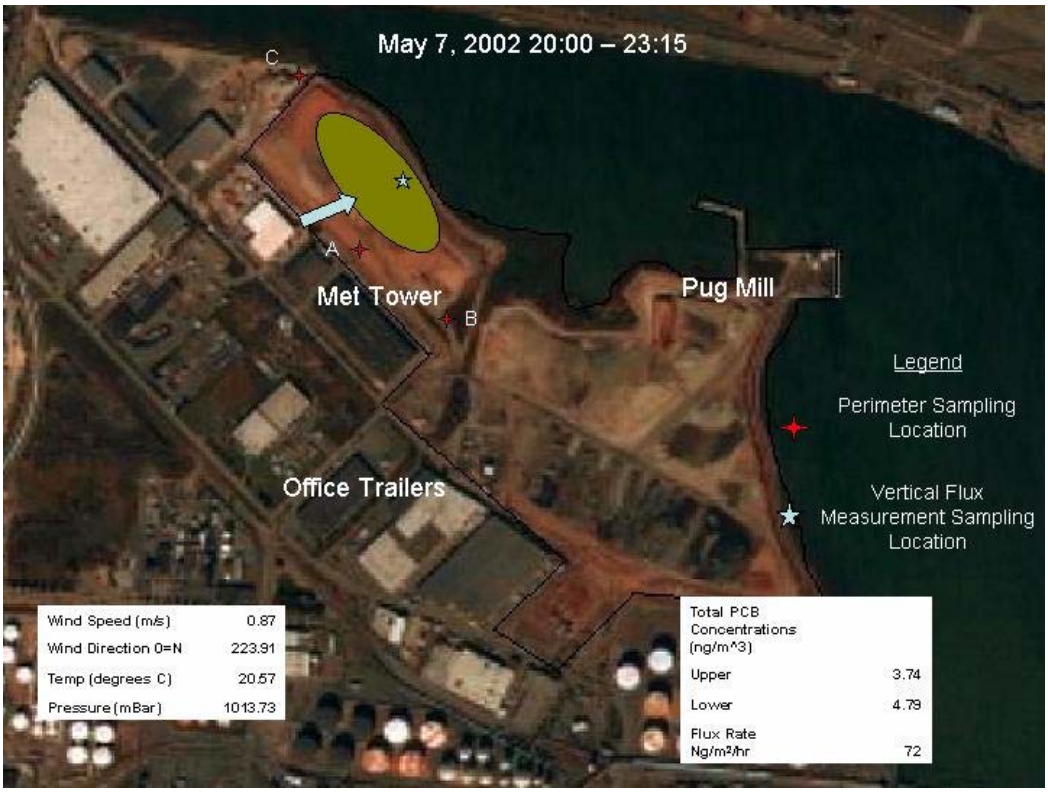

Figure 30. Bayonne landfill site conditions, 7 May 2002, 2000 – 2315 hours.

During the overnight sampling on 7 May 2002 the wind died down and it was cool. The condition atop the SDM differed greatly from the surrounding area. The air over the SDM was extremely humid and warm, while the air about 30 m to the north the air was cooler and drier. Figure 30 shows the conditions at the site during the nighttime sampling interval on 7 May 2002.

On the final day of the sampling campaign the wind changed and blew out of the northeast. The sampling equipment was moved to increase the amount of SDM over which the wind was blowing. The Site conditions are shown in Figure 31.

Figure 31. Bayonne landfill site conditions, 8 May 2002, 0930 – 1230 hours.

The meteorological data collected during the May sampling campaign is presented in Figure 32. Due to a malfunction with the on-site meteorological tower, weather data for the site was lost. However, meteorological data was retrieved from the National Oceanic and Atmospheric Administration (NOAA) site located at Bergen Point, NY (see Appendix 9). This site is on Staten Island and located approximately 3.2 km (2 miles) southwest of the site. The site identification information can be accesses at: http://co-ops.nos.noaa.gov/data_res.html.

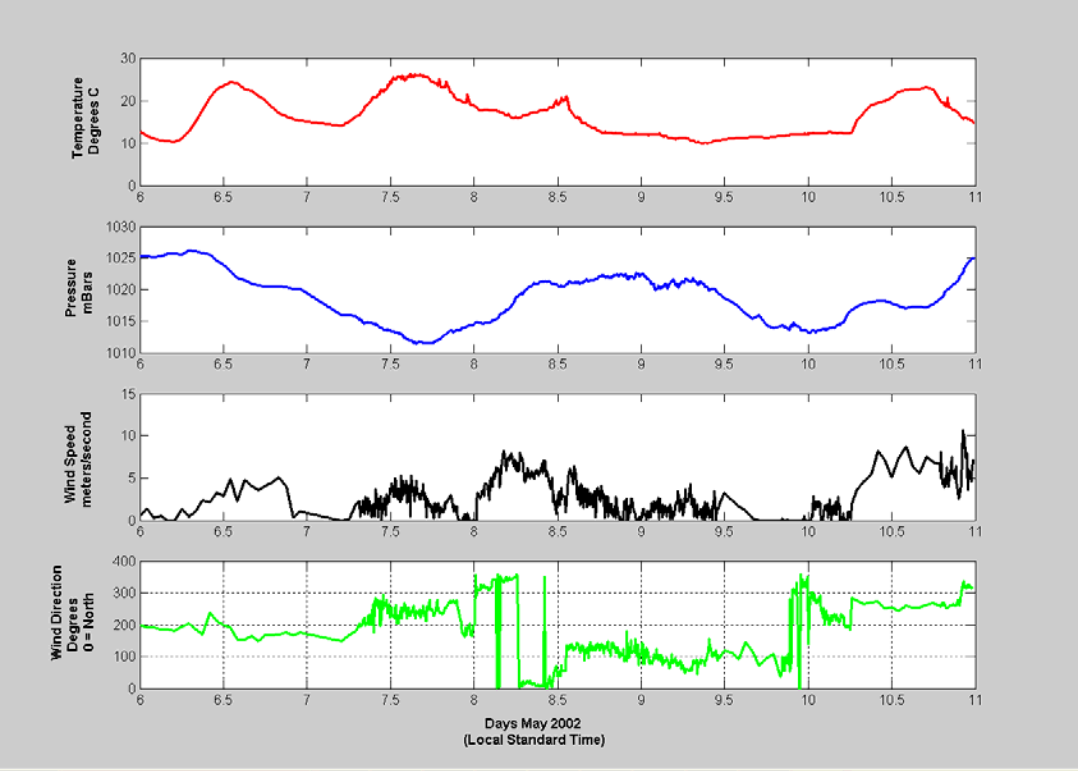

Figure 32. Bayonne landfill meteorological conditions, 6-10 May 2002.

Figure 33 shows the observed heat fluxes during May 2002 sampling campaign. It can be seen that during the first sampling interval there is a very large latent heat flux corresponding to the drying of the SDM. During the sampling interval on 8 May there were large heat fluxes observed however by this point the surface of the SDM had dried, this can be seen by the fact that the sensible and latent heat fluxes had very similar values. The atmospheric stability coefficients for these intervals were similar for all of the intervals with the exception of the overnight sample. The daytime values for ϕ_M averaged 1.04 with a standard deviation of 0.22 and the values for ϕ_W averaged 0.25 with a standard deviation of 0.04. This denotes conditions where the atmosphere is relatively neutral with respect to the momentum, but is very unstable with respect to latent heat. During the overnight interval, the atmosphere became very stable and measured values of ϕ_M and ϕ_W were both much greater than those that inhibit fluxes of momentum and latent heat.

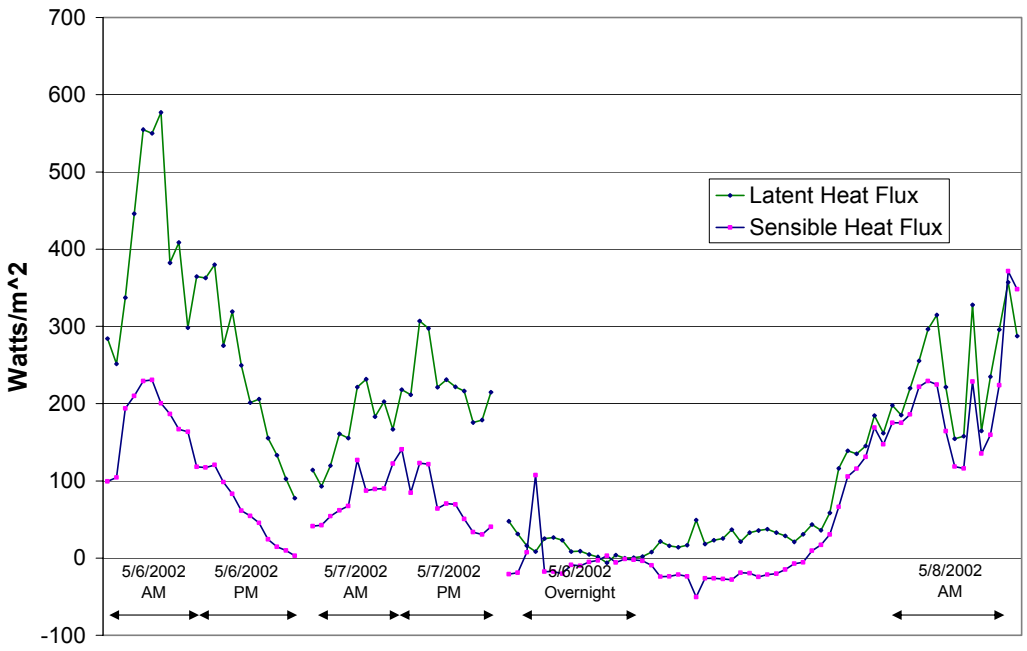

Figure 33. Observed fluxes of sensible and latent heat during the May sampling campaign.

Vertical PCB Fluxes

PCB concentrations were measured during all six sampling intervals and they all yielded positive vertical gradients out of the ground. ΣPCB concentrations ranged from 1 to 9.5 ng m^{-3} and the distribution of PCB congeners in each sample followed the same pattern presented earlier in which low molecular weight PCBs were present in much higher concentrations than high molecular weight congeners (Appendix 8, Figs. 9-14). As a result, the vertical fluxes of PCBs were dominated by the di-, tri-, and tetrachlorinated PCBs during the May campaign (Fig. 34).

SDM samples for moisture content and PCB analysis were collected during the May sampling campaign. The SDM was found to have high moisture content and very high PCB concentrations. The samples were taken from the fresh dredged material about 15 cm below the surface. Total PCB concentrations were 21 and 31 ppb. The distribution of PCB congeners in the SDM differed greatly from the PCB air concentrations (Appendix 8, Fig. 15). The PCB congeners present in the highest abundance in the SDM were in the middle of the molecular weight range for PCBs corresponding to chlorination numbers of three, four, and five.

The PCB flux estimates decreased over time during the May 2002 campaign. During this three-day period, the flux of ΣPCBs decreased from approximately 15,000 ng m^{-2} h^{-1} to approximately 2900 ng m^{-2} h^{-1} (Table 4) following a decreasing trend in PCB concentrations above the SDM. Atmospheric conditions also changed, thus influencing the PCB flux estimates. Most notably during the 7 May overnight sampling interval the PCB flux appears to approach zero, this is due to a stable atmosphere that restricted vertical fluxes.

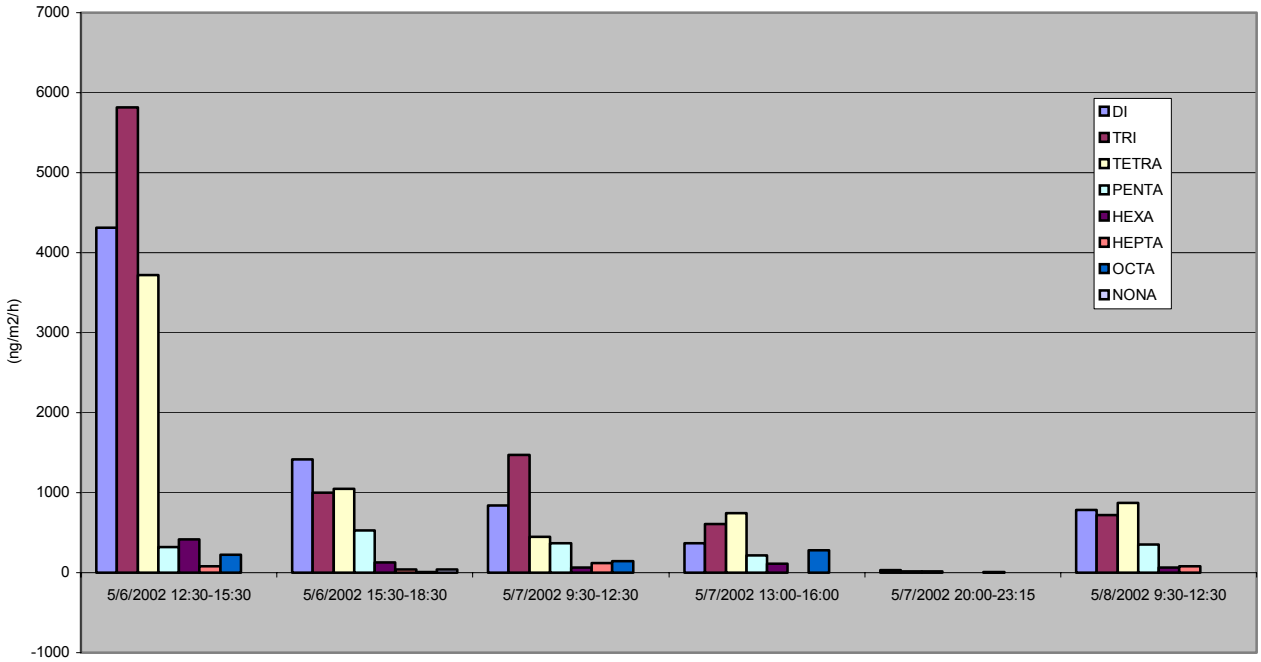

Figure 34. Estimated PCB flux values for the May 2002 sampling campaign (grouped by homologue).

Total Gaseous Mercury Fluxes

In May 2002, average TGM concentrations measured at the lower height ranged from 3.3 to 4.4 ng m^{-3} and at the upper height ranged from 3.1 to 3.5 ng m^{-3}. The vertical TGM concentration gradient was greatest on the morning of 7 May (0.91 ng m^{-3}) and decreased to 0.32 ng m^{-3} during the day (Table 5). On 7 May, the sediment-air flux was estimated to be 1043 ng m^{-2} h^{-1} during the morning and 314 ng m^{-2} h^{-1} in the afternoon. During the nighttime sampling period of 7 May (2030 and 2300 hours), a large decrease in the sediment-air TGM flux was observed. Along with a large increase in atmospheric stability, the vertical TGM flux decreased to 19 ng m^{-2} h^{-1} even though the average vertical gradient was still 0.29 ng m^{-3}. The following day brought higher wind speeds and vertical fluxes of 966 and 552 ng m^{-2} h^{-1} in the morning and afternoon, respectively (Table 5).

5.9 13-15 November 2002 Sampling Campaign

Background and Perimeter Gas-Phase PCBs

Samples were collected in the morning (0900 – 1300 hours) and in the afternoon (1300 – 1700 hours) on each day at the perimeter of the sediment application site and the Bayonne trailer for a total of 28 air samples (24 air samples plus 4 field blanks). The 3 high-volume air samplers were labeled A, B and C. Station A was located about 30 feet from the meteorological tower, station B was located SW of the SDM along the western perimeter of the landfill, and station C was located SE of the SDM near the oil tank field (see Figure 35). ΣPCB (n= 93 congeners) concentrations ranged from ~400 to 1600

pg m^{-3} at the trailer site and ~400 to 5000 pg m^{-3} at the sediment application site over the sampling campaign.

SDM Landfill Site conditions

Sampling occurred for three days in November 2002 (Figures 35 to 39). During the sampling campaign, observations over 4 h were made during five intervals: the afternoon of the 13th, the morning, the afternoon, and the evening of the 14th and the morning of the 15th. The sampling

Figure 35. Bayonne landfill site conditions, 13 November 2002, 1537 – 1930 hours.

Figure 36. Bayonne landfill site conditions, 14 November 2002, 0815 – 1130 hours.

Figure 37. Bayonne landfill site conditions, 14 November 2002, 1200 – 1500 hours.

Figure 38. Bayonne landfill site conditions, 14 November 2002, 1630 – 1945 hours.

Figure 39. Bayonne landfill site conditions, 15 November 2002, 0830 – 1130 hours.

equipment was set up on the south end of the site directly on top of recently placed SDM. During the campaign, SDM was continuously placed to the west of the sampling site. Initially the wind was from the northwest directly over a large expanse of SDM, however the wind changed to the southwest and reduced the distance over SDM that the wind was blowing to approximately 30 m.

The weather during the sampling campaign was cold, rainy, and overcast. The heat fluxes monitored during the sampling campaign are small relative to previous sampling campaigns. This is due to the colder temperatures and lack of sunlight. During our sampling campaigns we have made every effort to remain either down wind or directly on top of the SDM, however wind speed and direction are variable. During this time period the wind was initially blowing from the north and then turned to the southwest during the last day of the sampling campaign. Figure 40 shows the meteorological conditions at the site during the November 2002 sampling campaign.

Vertical PCB Fluxes

Daytime vertical PCB fluxes at the SDM landfill ranged from 74 to 492 ng m^{-2} h^{-1} during the November campaign (Table 4). A negative PCB concentration gradient was observed during the evening of 14 November (Table 4), indicating that the PCB flux had shut down overnight.

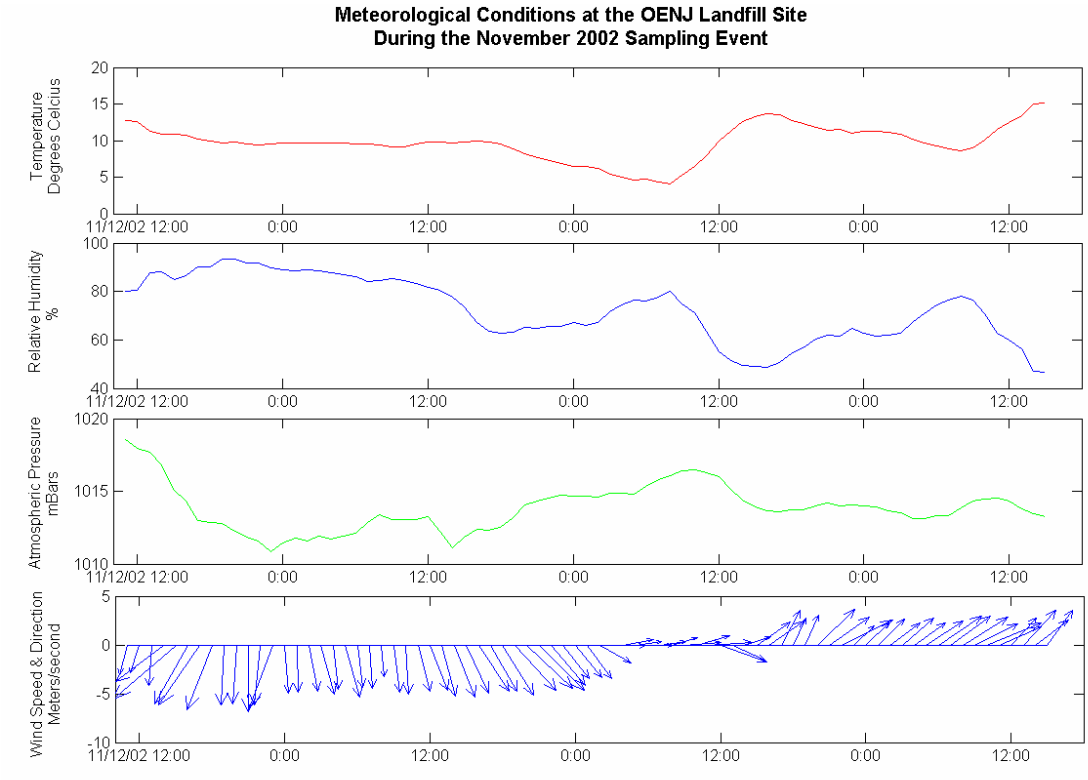

Figure 40. Bayonne landfill meteorological conditions, November 2002.

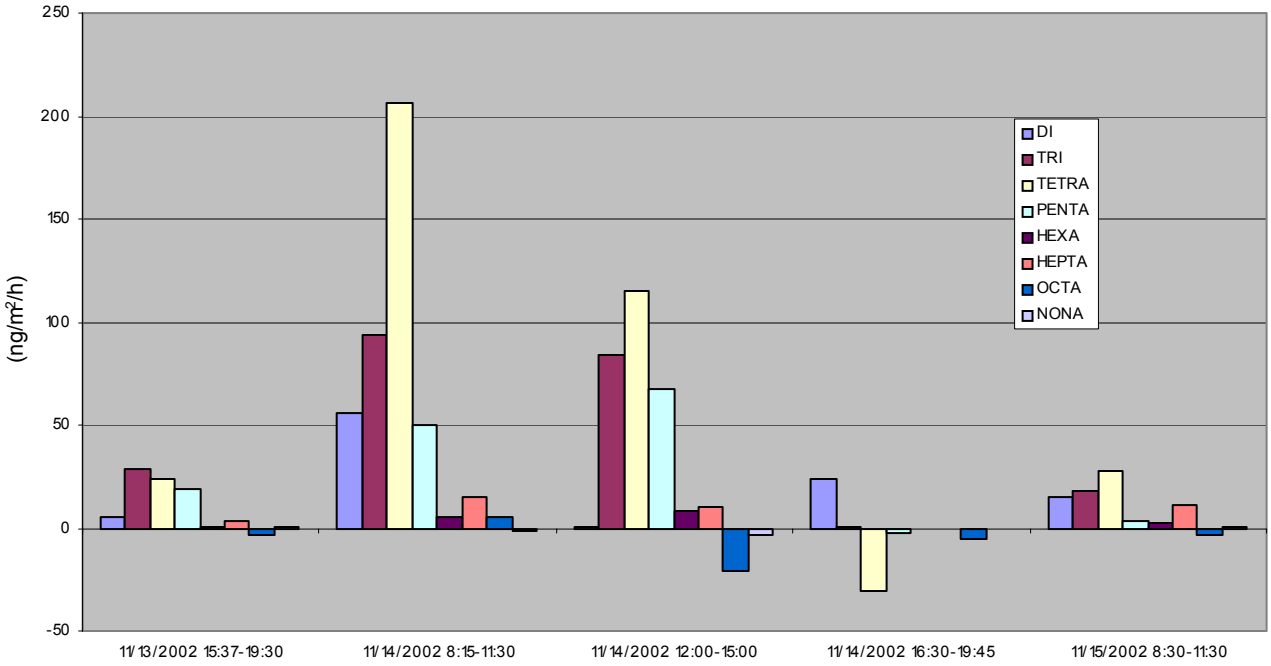

Figure 41. Estimated vertical fluxes of PCBs at the SDM landfill during the November 2002 sampling campaign (grouped by homologue).

Total Gaseous Mercury Fluxes

Vertical TGM concentration gradients ranged from -0.04 to 0.11 ng m^{-3} during the November 2002 sampling campaign (Table 5). Small chemical gradients and a nearly neutral surface microlayer resulted in low Hg fluxes during this campaign. On 14 November, very small vertical concentration gradients were detected (0.05 and 0.03 ng m^{-3}) resulting in estimated average vertical fluxes of 34 and 17 ng m^{-2} h^{-1} in the morning and afternoon, respectively (Table 5). On the morning of 15 November, a small negative concentration gradient was observed (-0.04 ng m^{-3}). In the afternoon of 15 November, a small net flux of Hg out of the sediment (41 ng m^{-2} h^{-1}) was estimated based on the observed positive vertical gradient of 0.11 ng m^{-3} (Table 5).

6.0 DISCUSSION

6.1 Micrometeorology

Stability correction factors for momentum (ϕ_M), heat (ϕ_H), and water (ϕ_W) were determined from *in situ* measurements in two ways. These two methods led to nearly identical values for the stability factors. As a consequence, all reported stability correction factors were determined using what will be referred to as the approximate integration method. For this method, the profile equations are integrated between the two measurement levels z_1 and z_2 in the following manner:

$$\int_{z_1}^{z_2}\frac{\partial u}{\partial z}dx = u(z_2)-u(z_1)=\int_{z_1}^{z_2}\frac{u_*}{\kappa z}\phi_M(z)dz=\phi_{Mest}\frac{u_*}{\kappa z}\ln\left(z_2/z_1\right) \tag{27}$$

$$\int_{z_1}^{z_2}\frac{\partial \theta}{\partial z}dx = \theta(z_2)-\theta(z_1)=\int_{z_1}^{z_2}\frac{H}{\kappa u_* \rho C_p}\phi_H(z)dz=\phi_{Hest}\frac{H}{\kappa u_* \rho C_p}\ln\left(z_2/z_1\right) \tag{28}$$

$$\int_{z_1}^{z_2}\frac{\partial \rho_e}{\partial z}dx = \rho_e(z_2)-\rho_e(z_1)=\int_{z_1}^{z_2}\frac{Le}{\kappa u_* \lambda}\phi_W(z)dz=\phi_{West}\frac{Le}{\kappa u_* \lambda}\ln\left(z_2/z_1\right) \tag{29}$$

The values for ϕ_{Mest}, ϕ_{Hest}, and ϕ_{West}, are found from these integrated equations. Focusing on just momentum, the stability factor ϕ_{Mest} is obtained from

$$\phi_{Mest}=\frac{u(z_2)-u(z_1)}{\left(u_*/\kappa\right)\ln\left(z_2/z_1\right)} \tag{30}$$

which can be evaluated from observations of $u(z_2)$, $u(z_1)$, and the frictional velocity u_*. The quantity ϕ_{Mest} was considered to be the average stability factor over the interval from z_2 to z_1. The other stability correction factors are found in a similar manner.

It is useful to determine the nature of the error in estimating the stability factors using this approximate integration method. To do this, the theoretical formulation for ϕ_M, as a function of z/L (see Section 2.1, Eq. 13) developed by Dyer and Hicks (1970) for unstable stratification and the theoretical formulation of Webb (1970) for stable stratification will be used. The approach will be to assume that the theoretical models are correct and then determine the difference between the actual average stability factor and that estimated from equation (4). The Dyer and Hicks (1970) model for unstable stratification is

$$\phi_M\left(z/L\right)=\left[1-16\left(z/L\right)\right]^{-1/4} \tag{31}$$

This formulation for ϕ_M can be simplified by expanding in a Taylor series about z/L = 0; i.e.

$$\phi_M\left(z/L\right)=\phi_M(z=0)+\left.\frac{\partial\phi}{\partial z}\right|_{z=0}\left(z/L\right)+\text{ higher order terms} \tag{32}$$

Substituting equation (5) into equation (6) the following approximation for ϕ_M is obtained:

$$\phi_M\left(z/L\right)=1+4\left(z/L\right)+\text{ higher order terms} \tag{33}$$

Retaining just the first two terms allows for the integration of the profile equation between z_2, and z_1 to obtain the "log + linear" profile equation for velocity:

$$u(z_2) - u(z_1) = \frac{u_*}{\kappa} \ln\left(z_2 / z_1\right) + \frac{4}{L}\frac{u_*}{\kappa}(z_2 - z_1) \tag{34}$$

The average value of ϕ_M over the interval from z_2 to z_1 is found as follows:

$$\phi_{Mavg} = \frac{1}{z_2 - z_1}\int_{z_1}^{z_2} \phi_M\left(z/L\right)dz \tag{35a}$$

$$\phi_{Mavg} = \frac{1}{z_2 - z_1}\int_{z_1}^{z_2} \left[1 + 4\left(z/L\right)\right]dz \tag{35b}$$

$$\phi_{Mavg} = 1 + \frac{4}{2L}\frac{\left(z_2^{\,2} - z_1^{\,2}\right)}{z_2 - z_1} \tag{35c}$$

$$\phi_{Mavg} = 1 + \left(4/L\right)z_{avg} \tag{35d}$$

Combining equation (8) with equation (4) yield the following expression for ϕ_{Mest} i.e.,

$$\phi_{Mest} = \frac{\ln\left(z_2/z_1\right) + 4/L\,(z_2 - z_1)}{\ln\left(z_2/z_1\right)} \tag{36}$$

$$\phi_{Mest} = 1 + \frac{4/L\,(z_2 - z_1)}{\ln\left(z_2/z_1\right)} \tag{37}$$

Equations (9d) and (11) may be used to evaluate the assumed true value of ϕ_{Mavg} and to compare it with the values for ϕ_{Mest}. For the measurements at the landfill typical values for z_1, z_2 and u_* were 1 m, 3 m, and 2 m respectively. For values of L ranging from –10 to –100 the values for ϕ_{Mest} are given in Table 6.

Table 6. Stability correction factors for momentum.

L (m)	Z_{avg}/L	ϕ_{Mavg}	ϕ_{Mest}
-10	-0.200	0.20	0.27
-20	-0.100	0.60	0.54
-40	-0.050	0.80	0.82
-60	-0.033	0.87	0.88
-80	-0.025	0.90	0.91
-100	-0.020	0.92	0.93
-200	-0.010	0.96	0.96

For values of the magnitude of z/L less than 0.1. The error in the approximate integration method is less than 10% and for magnitudes less than 0.05 it is less than 3%.

The results are much the same using Webb's (1970) formulation for ϕ_M for stable stratification. This formulation is

$$\phi_M = 1 + 5.2\, z/L \quad \text{for L>0} \tag{38}$$

The use of this expression yields an average value of ϕ_M over the interval z_2 to z_1.

$$\phi_{Mavg} = 1 + \frac{5.2}{L} z_{avg} \tag{39}$$

The equation for calculating ϕ_{Mest} becomes

$$\phi_{Mest} = 1 + \frac{5.2/L\,(z_2 - z_1)}{\ln\left(z_2/z_1\right)} \tag{40}$$

For z_1= 1 m, z_2= 3 m, z_{avg}= 2 m, and for L= +40 m, the true coverage value of the stability factor is ϕ_{Mavg} = 1.26 and the value estimated from the approximate integration is ϕ_{Mest} = 1.24. Thus, for stable stratifications similar results are obtained for reasonably small values of z/L.

6.2 Background and Perimeter SDM Landfill PCB Concentrations

Background Concentrations of PCBs at the NJDEP Trailer in Bayonne

The sources of PCBs to Bayonne may include the city of Bayonne itself, adjacent Newark Bay, and surrounding urban/industrial areas. On the day of highest PCB concentration in Bayonne (9 September 2000), winds were coming primarily from the northeast, directly over the city of Bayonne toward the sampling station. The second highest ΣPCB concentration occurred on 28 August 2000, when winds came from the east, also from over the city of Bayonne. On the date of the lowest ΣPCB concentration (20 November 2000) winds were coming from the west over Newark Bay. The second lowest PCB concentration occurred on 6 February 2000 and again the winds were from the west. This simple analysis suggests that Newark Bay, which has been subject to historical PCB contamination and is located due west of the NJDEP trailer in Bayonne, is <u>not</u> the largest source of PCBs to the city of Bayonne. If Bayonne is under the influence of one dominant source-type for PCBs, then the PCB congener distributions should be similar regardless of the total PCB concentration. Regression of the congener profiles from 9 September 2000 and 20 November 2000 yielded an r^2 of 0.90 ($p < 0.001$) indicating that the two profiles were not statistically different from one another. Thus despite differences in PCB concentrations and wind directions between these samples, the PCB fingerprints indicate that they are influenced by the same source type or source process.

In order to gain perspective regarding the magnitude of the PCB concentrations measured at the NJDEP trailer in Bayonne, we have compared the concentrations of PCB congeners from Bayonne with those measured elsewhere in North America (Table 7). The average concentrations of PCB congeners were higher in Bayonne than at three New Jersey Atmospheric Deposition Network stations located in or near urban/industrial areas (Jersey City, New Brunswick, Sandy Hook). Most PCB congeners had higher concentrations at Bayonne than all of the other North American sites with the exception of Chicago, IL (Table 7). PCB concentrations measured at Bayonne show a striking contrast to those measured near the Arctic at Alert, Canada demonstrating the extent of PCB contamination in the NY/NJ metropolitan area.

A more detailed comparison of PCB concentrations is possible for Bayonne and Jersey City since on four occasions in December 1999 and January 2000 simultaneous samples were collected at these two sites (Figure 42). The Jersey City site at the Liberty Science Center is located 8 km northeast of the NJDEP trailer in Bayonne. On 8 December 1999, gas phase, congener-specific PCB concentrations at the two sites were virtually identical. However, for the next three sampling periods the concentrations differed by as much as a factor of 4 (Figure 42).

Table 7. Average gas phase concentrations of PCB congeners (pg m^{-3}) at the NJDEP trailer in Bayonne and at other sites in the United States and Canada.

PCB Concentration (pg m^{-3})	Bayonne, NJ (gas)	Jersey City, NJ (gas)	New Brunswick, NJ (gas)	Sandy Hook, NJ (gas)	Chesapeake Bay (gas)	Chicago, IL (gas)	Alert, Cananda (may-sept) (gas)	Egbert, Ontario Cananda (gas)
datasource	this study	a	a	a	b	c	d	e
18	109	76	39	34	20	191	5.1	6.6
16+32	106	84	46	30	25	204	0.80	8.8
28	82	58	28	20	63*	432*	1.3	16
52+43	102	56	31	31	16	96	1.8	16
41+71	33	22	9.1	9.6	19	111	0.30	2.3
66+95	105	75	43	38	33	303	1.6	6.5
101	52	27	16	14	6.8	51	0.89	6.4
87+81	27	13	8.1	6.6	3.7	29	0.27	2.0
110+77	51	25	17	14	7.9	91	0.65	4.0
149+123+107	22	10	5.9	5.2	7.1	29	0.90	2.8
153+132	22	10	5.4	5.2	10	71	0.77	3.2
163+138	26	9.9	6.0	5.0	4.4	43	0.47	2.8
187+182	3.5	2.6	2.0	2.1	2.3	7.8	0.39	1.7
174	2.7	1.7	0.90	0.70	1.8	4.9	0.14	0.92
180	3.3	2.1	1.2	1.0		44	0.55	1.1

a: Brunciak et al, 2000; b: Nelson et al, 1998; c: Simcik et al, 1998; d: Stern et al, 1997; e: Hoff et al, 1992; * includes PCB #31

To further quantify differences in congener profiles at the two sites, PCB congener concentrations at Bayonne and Jersey City were regressed against each other for each simultaneous sample (Fig. 43). The slope of the line relating PCB congener concentrations at the two sites for the December 8, 1999 samples is 0.92 indicating a nearly 1:1 relationship (Fig. 43). The regression of the December 8 data gives an r^2 of 0.77 ($p<0.01$), but if the two outlying congeners (out of 93) are removed, the r^2 improves to 0.94 ($p<0.01$). Regressions of PCB congener concentrations at the two sites for the other three simultaneous samples have slopes that deviate significantly from the 1:1 line (12/20/99 slope=0.24; 01/01/00 slope=0.70; 01/13/00 slope=0.34) reflecting higher PCB concentrations at Bayonne than in Jersey City. The congener-specific profiles for 20 December 1999 and 13 January 2000 are statistically similar (r^2=0.92, $p<0.01$ and r^2=0.94, $p<0.01$, respectively), indicating that although different concentrations of PCBs were measured at Bayonne and Jersey City on these days, the sources may be related.

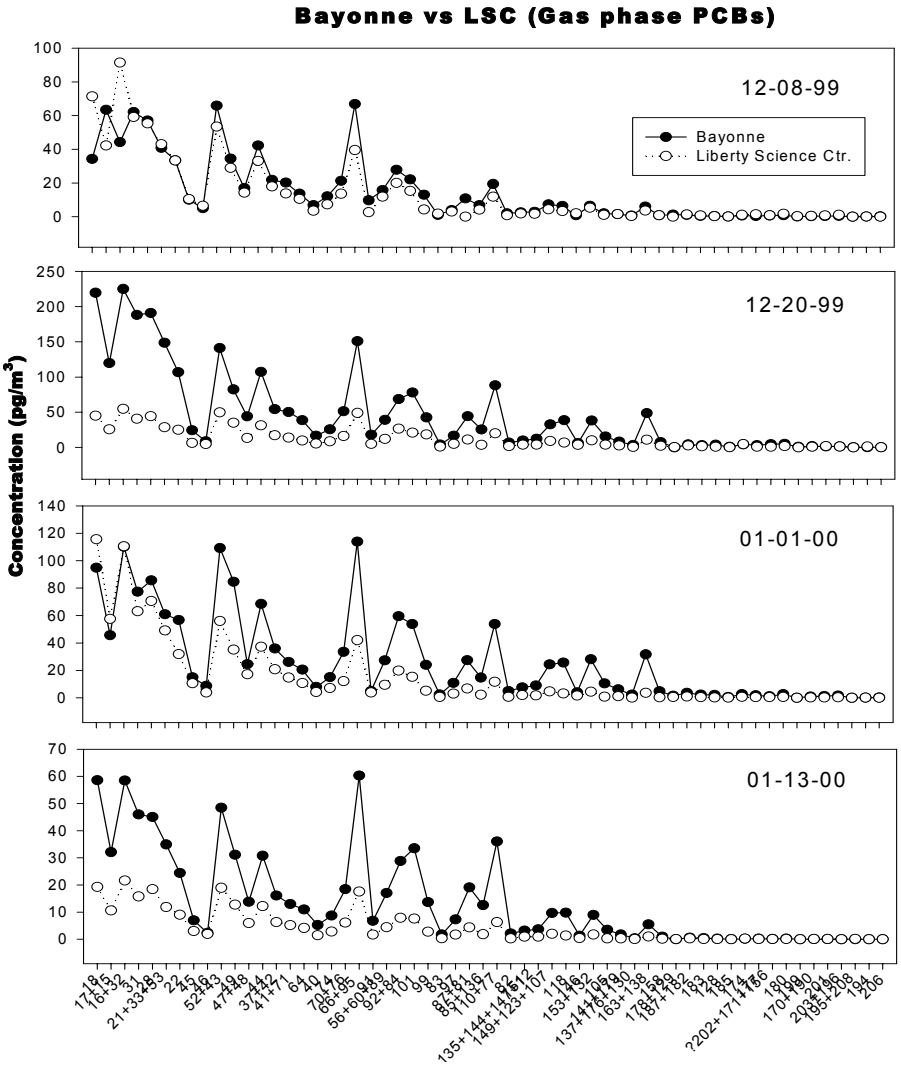

Figure 42. Comparison of congener-specific PCB concentrations for four simultaneous air samples collected in December 1999 and January 2000 at the NJDEP trailer in Bayonne and at the Liberty Science Center in Jersey City.

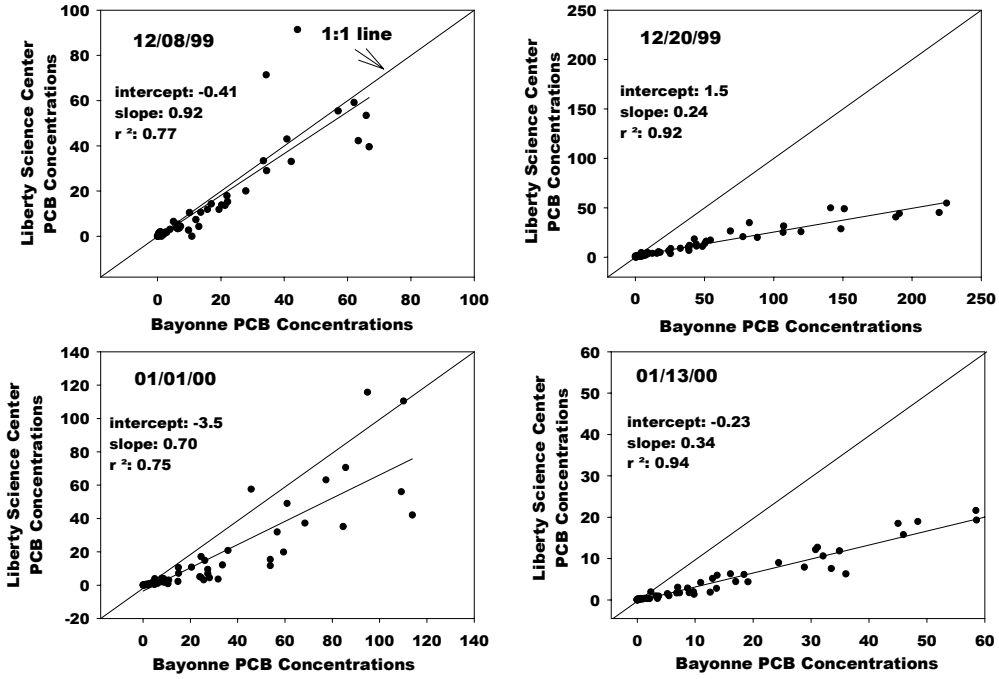

Figure 43. Correlations between gas phase PCB congener concentrations measured at the NJDEP trailer in Bayonne and at the Liberty Science Center in Jersey City for four simultaneous samples collected in December 1999 and January 2000.

The highest gas phase concentrations in Bayonne were measured in the summer when warm temperatures can lead to increased volatilization via air-surface exchange. In order to look more closely at the relationship between PCB concentrations and temperature, we employed an equilibrium model (Eq. 41) to predict how much of the variation in concentration can be explained by temperature alone:

$$\log[PCB]_{gasphase} = a + \frac{m}{T} \qquad (41)$$

In this case, we have divided the individual PCB congeners into their respective homologue groups. That is, we have summed all of the di-chlorinated biphenyls together, the tri-chlorinated together, etc. The PCB homologue groups with the strongest temperature-dependencies are the octa-chlorinated biphenyls (with T explaining 65% of the variability) and the tri-chlorinated biphenyls (with T explaining 58% of the variability) (Figure 44). If the r^2 values were all near 1, then air-surface exchange would be the only process controlling PCB concentrations in this area. This plot clearly demonstrates that other factors in addition to temperature affect gas phase PCB concentrations in Bayonne.

Figure 44. Clausius-Clapeyron-type plot of the log of the concentration of PCB homologue groups versus inverse temperature.

PCB Concentrations at the SDM landfill Before and after SDM Application, May 2001

A comparison of gas phase, congener-specific PCB concentrations in samples collected at the SDM landfill in Bayonne before and after the placement of SDM indicates that gas phase ΣPCB concentrations were found to be lower (1.5X) after the sediment was applied to the site at the end of May compared to the beginning of May (Figure 45). A regression between the relative congener profiles of the two samples gave an r^2 value of 0.55, indicating that the profiles are not statistically identical at the 95% confidence level and that these two samples were influenced by different PCB sources. Therefore, there appears to be a source of PCBs at the SDM landfill (possibly the SDM itself) on May 31st which is not seen at the site prior to SDM application or at the NJDEP trailer. The wind direction was not the same on the two sampling days in May at the sediment application site. On 1 May 2001 (pre-sediment application), winds came out of the SW at an average wind speed of 4.5 m s^{-1}; whereas on 31 May 2001 (post-sediment application) winds came from the NW at an average wind speed of 7.0 m s^{-1}. Wind direction does not explain the difference in ΣPCB concentrations on these two days since at the DEP trailer site, the lowest concentrations were measured under southwesterly winds. Wind speed may play a role with high winds resulting in greater dilution on 31 May. Thus although the volatilization of PCBs from SDM may add to observed concentrations at the SDM landfill, this signal will be affected by wind direction and speed and neighboring sources.

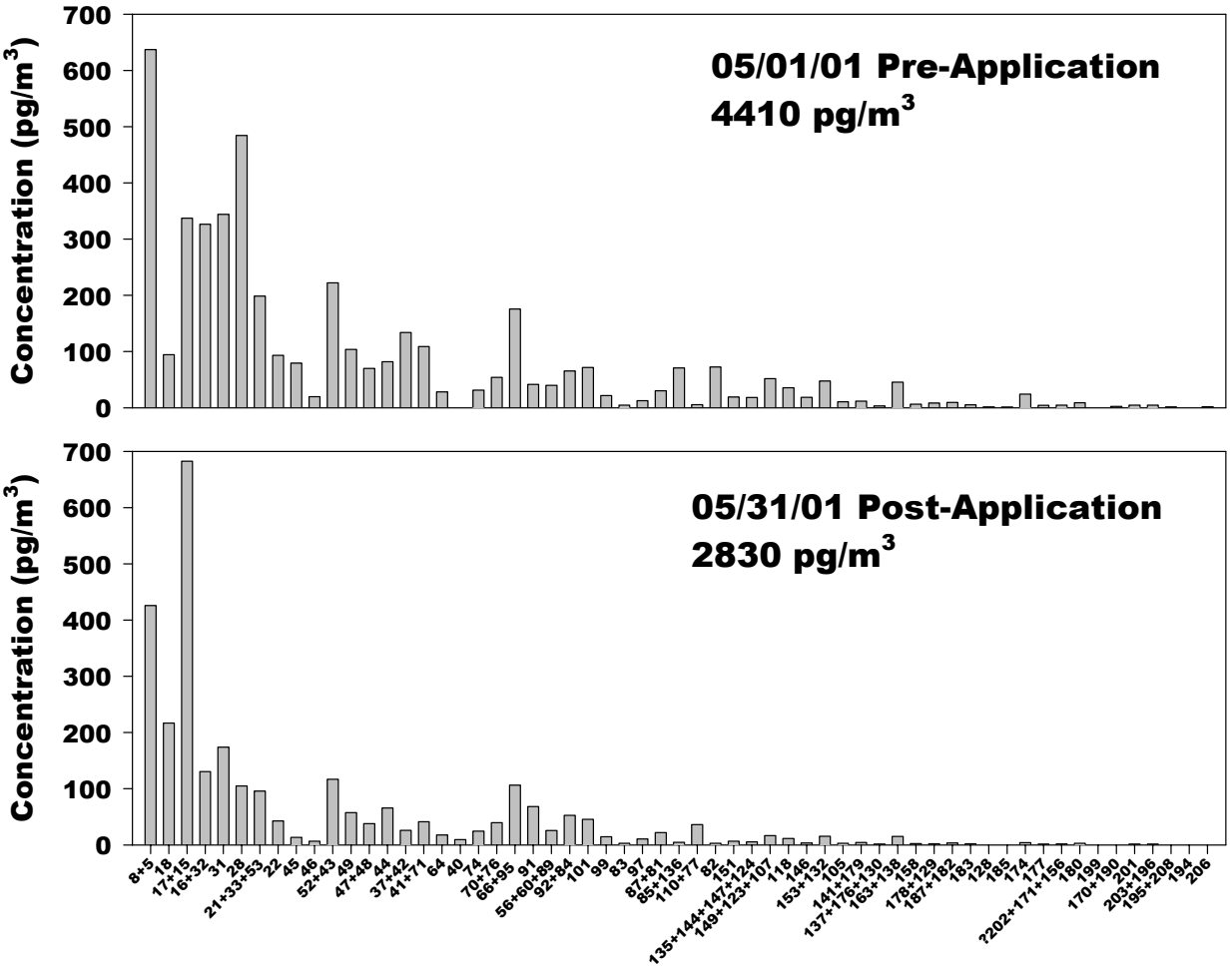

Figure 45. Congener-specific, gas phase PCB concentrations at the SDM landfill in Bayonne before (1 May 2001) and after (31 May 2001) SDM was applied.

The gas phase ΣPCB concentrations measured at the SDM landfill in May 2001 can be compared with those collected from December 1999 to November 2000 at the NJDEP trailer in Bayonne. The two samples taken at the sediment application site in May 2001 were both higher than the average concentration at the trailer and the concentration at the SDM landfill on 1 May was higher than the highest value observed at the trailer during the period prior to SDM application (see Figure 5).

Horizontal Gradients of PCBs at the SDM Landfill in Bayonne

July 2001 Campaign

An important aspect of this study involves interrogating the horizontal concentration gradients seen at the sediment application site under different wind regimes. During the July 2001 campaign, three high volume air samplers were deployed near the perimeters of the SDM application areas in the eastern

part of the site. The triangulation of the samplers allows for an assessment of upwind/downwind gradients under appropriate wind direction regimes (Table 8).

Table 8. Summary table of gas phase ΣPCB concentrations (pg m^{-3}) at the NJDEP trailer and the SDM landfill in Bayonne during the July 2001 intensive sampling campaign.

Σ PCB Concentration pg m^{-3} (Gas Phase) July 2001	**Bayonne Trailer**	**Sediment Site A**	**Sediment Site B**	**Sediment Site C**
17 July (All Day)	6925	2804	4958	4248
18 July (Morning)	3288	8278	6434	6289
18 July (Afternoon)	2322	6298	14647	5153
19 July (Morning)	4983	14350	3285	3445
19 July (Afternoon)	3838	12993	5971	7202
20 July (Morning)	5085	13326	3604	6354
20 July (Afternoon)	1265	8625	6132	5298

17 July 2001 all day: On this day, there were two dominant wind directions NE, and W,SW. The variability in wind direction does not allow for an assessment of upwind/ downwind gradients. As it appeared that wind direction at the site shifted from morning to afternoon, the decision was made to sample two times per day for all remaining samples for the study.

18 July 2001 morning: For this sampling period, winds were primarily from the E, such that site "C" (in grid H16) represented upwind conditions and sites "A" and "B" were downwind of the applied dredge material. ΣPCB concentration at the upwind site C was 6289 pg m^{-3} and the downwind concentrations were 6434 pg m^{-3} (site B) and 8278 pg m^{-3} (site A). The increase in ΣPCB concentrations was not greater than the 20% inherent uncertainty associated with the PCB measurements between sites C and B. There was, however, a significant increase in PCB concentrations from site C to site A.

18 July 2001 afternoon: For this sampling period, winds came from the SE, with both sites A and C acting as upwind sites and site B as the downwind site. Concentrations upwind (site C = 5153 pg m^{-3}, site A = 6298 pg m^{-3}) were as much as 2.5X lower than downwind (14647 pg m^{-3}), suggesting that the dredge material contributed to the atmospheric burden of PCBs onsite.

19 July 2001 morning: On the morning of July 19, 2001, strong winds were coming out of the NE. Site C "saw" PCB concentrations from off-site (3445 pg m^{-3}); whereas, site A saw concentrations coming from over the sediment application area (14647 pg m^{-3}). Site B also saw concentrations that arrived from off-site (3285 pg m^{-3}). This provided clear insight into the impact of PCB emissions on-site versus off-site showing that PCB volatilization on-site can be a significant contributor to atmospheric PCB concentrations.

19 July 2001 afternoon: For this sampling period, winds were still out of the NE, and concentrations at the two upwind sites, B (5971 pg m^{-3}) and C (7208 pg m^{-3}) were significantly lower than those measured downwind of the dredge material at site A (14350 pg m^{-3}). The perimeter sampling again supported the conclusion that the dredge material contributes to the air burden on-site.

20 July 2001 morning: Morning winds were out of the NE, and once again, the upwind sites had lower ΣPCB concentrations than sites downwind of the dredge material by at least a factor of 2. ΣPCB concentrations upwind at site C and site B were 6354 and 3604 pg m^{-3}, respectively. The ΣPCB concentration at the downwind site was 12993 pg m^{-3}.

20 July 2001 afternoon: For this sampling period, the winds shifted to the SE, thus sites C and A were upwind of the dredge material and site B was downwind. However, ΣPCB concentrations at the upwind site A (8625 pg m^{-3}) were higher than downwind at site B (6132 pg m^{-3}), suggesting that the dredge material was not the dominant source of PCBs to the air above the sediment application site. Off-site sources contributed more strongly to the burden during this sampling period.

Samples were also collected at the Bayonne trailer site, located across town to the northwest of the sediment application site (see Figure 4). This allowed us to investigate whether the Bayonne trailer site can "feel" the influence of the sediment application site. In order for the Bayonne trailer site to feel the direct influence of the sediment application site, there must be strong winds from the E/SE. Two sampling periods during the July 2001 intensive met this condition, 18 July in the afternoon and 20 July in the afternoon.

If the Bayonne NJDEP trailer site "feels" the influence of the sediment application site, then it would be expected that concentrations would be elevated at the trailer. Under E/SE winds on those two days, the trailer site had the lowest concentrations measured during the entire July 2001 campaign. The average ΣPCB concentration at the trailer site was 3945 pg m^{-3} during the July 2001 campaign and on the two E/SE wind regime days concentrations were 2322 and 1265 pg m^{-3}, thus the sediment application site is not the dominant source of PCBs to the city of Bayonne, NJ.

<u>October 2001 Campaign</u>

The sampler locations for the October 2001 campaign were the same as in the July 2001 campaign. A summary of the gas phase ΣPCB concentrations from the October 2001 intensive campaign are presented in Table 9.

October 23, 2001 (morning): Winds were consistently out of the SE, thus all the sites were downwind of the applied dredge material. The ΣPCB concentration at site A (6619 pg m^{-3}) was greater than that at site C (2446 pg m^{-3}). This observation was consistent with the fact that the primary area with the largest amount of dredge applied was SE of site A. Dredge was also applied SE of site C, though in a considerably smaller quantity. Because of sampling problems, an assessment using site B cannot be performed.

October 23, 2001 (afternoon): Winds were again out of the SE during this sampling period. The ΣPCB concentration at site A (4506 pg m^{-3}) was greater than that at site C (2113 pg m^{-3}), thus, as was

the case for the morning, the dredge material was a source of PCBs to the air on-site. Because of sampling problems, an assessment using site B cannot be performed.

October 24, 2001 (morning): The winds were predominantly out of the SW. Therefore, sites A and B were upwind of the applied dredge material and site C was downwind. The ΣPCB concentration was higher downwind at site C (3704 pg m^{-3}) than upwind at site A (1869 pg m^{-3}) consistent with the dredge acting as a source of PCBs to the site. However, site B, upwind of the applied dredge material, had the highest ΣPCB concentrations on-site (4959 pg m^{-3}) suggesting that PCB sources other than the dredge material are affecting concentrations on-site.

Table 9. Summary table of gas phase ΣPCB concentrations (pg m^{-3}) at the NJDEP trailer and the SDM landfill in Bayonne during the October 2001 sampling campaign. (Note: Only one full day sample was taken at Site B on 23 October).

Σ PCB Concentration pg m^{-3} (Gas Phase) October 2001	**Bayonne Trailer**	**Sediment Site A**	**Sediment Site B**	**Sediment Site C**
23 October (Morning)	791	6619	3278	2446
23 October (Afternoon)	418	4506	-	2113
24 October (Morning)	2125	1869	4959	3704
24 October (Afternoon)	-	5839	6591	2517
25 October (Morning)	1260	3091	5058	2875
25 October (Afternoon)	2344	1414	1542	-
26 October (Morning)	1436	872	1318	975
26 October (Afternoon)	614	704	1244	834

24 October 2001 (afternoon): For this sampling period, winds were out of the SE, as was the case on 23 October. The ΣPCB concentrations at sites A (5839 pg m^{-3}) and B (6591 pg m^{-3}) are not statistically different from one another, because they are within the 20% uncertainty bounds about the concentrations, although site A was closer than site B to the area where dredge was applied. Once again, site C had a lower ΣPCB concentration (2517 pg m^{-3}) than sites B and A.

25-26 October 2001 (morning and afternoon): The winds came out of the W for these 4 sampling periods, from over the city of Bayonne toward the sediment application site. Therefore, both sites A and B were upwind. However, site C was not directly downwind of the dredge material, not allowing for an upwind/downwind spatial assessment. Interestingly, ΣPCB concentrations at the site on 25 October in the afternoon through the end of the afternoon on 26 October, were the lowest measured during the campaign, ranging from ~700 to 1500 pg m^{-3}. This can likely be attributed to a dilution factor, because wind speeds were ~3X the average from the earlier sampling periods in the campaign. During the October 2001 campaign, E/SE wind occurred on 23 October, in the morning. Concentrations at the sediment application site were 6619 pg m^{-3} downwind of the applied sediment. The ΣPCB concentration across town at the NJDEP trailer was 791 pg m^{-3}, nearly 8X lower. It is apparent that although concentrations at the sediment application site are high, the concentrations are lower only a short distance downwind from the site.

May 2002 Campaign

The sampler locations for the May 2002 campaign were not the same as in the July and October 2001 campaigns (see Figure 26). A summary of the gas phase ΣPCB concentrations from the May 2002 intensive campaign is presented in Table 10.

Table 10. Summary table of gas phase ΣPCB concentrations (pg m^{-3}) at the NJDEP trailer and the SDM landfill in Bayonne during the May 2002 sampling campaign.

Σ PCB Concentration pg m^{-3} (Gas Phase) May 2001	**Bayonne Trailer**	**Sediment Site A**	**Sediment Site B**	**Sediment Site C**
7 May (Morning)	1147	1915	2473	1797
7 May (Afternoon)	1162	1056	1992	821
8 May (Morning)	796	2809	3013	1230
8 May (Afternoon)	1349	2691	2033	2602
9 May (Morning)	658	1048	1363	1074
9 May (Afternoon)	696	1826	1418	1339
10 May (Morning)	1023	1328	1436	1114
10 May (Afternoon)	744	638	728	695

7 May 2002 (morning): Winds were out of the W/SW such that all sites A, B, and C represented upwind concentrations or concentrations coming from off-site. Concentrations at sites A (1915 pg m^{-3}) and C (1797 pg m^{-3}) were not statistically different from one another (assuming an inherent 20% uncertainty around the PCB measurements). However, the ΣPCB concentration at site B was statistically higher (2473 pg m^{-3}).

7 May 2002 (afternoon): Under W winds, all sites were once again upwind of the applied dredge material. Similarly, site B, located adjacent to the Stevens Institute meteorological tower, had a higher ΣPCB concentration (1992 pg m^{-3}) than sites A (1056 pg m^{-3}) and site C (821 pg m^{-3}).

8 May 2002 (morning): During this sampling period, the winds came out of the NE. There was no statistical difference between concentrations at site B (3013 pg m^{-3}) and site A (2809 pg m^{-3}), although site A (and not site B) was downwind of the applied dredge material. Site C displayed a significantly lower ΣPCB concentration (1230 pg m^{-3}).

8 May 2002 (afternoon): Under SE winds, site B was located upwind of the dredge material and site C was downwind. However, concentrations were statistically similar at the upwind site B (2033 pg m^{-3}) and the downwind site C (2602 pg m^{-3}), indicating that the dredge material was contributing a negligible portion to the overall air burden above the sediment site.

9 May 2002 (morning): Once again, the site was affected by SE wind conditions. Identical to the conclusion drawn for May 8th (afternoon), concentrations were statistically similar at the upwind site B

(1363 pg m^{-3}) and the downwind site C (1074 pg m^{-3}), indicating that the dredge material was contributing minimally to the overall air burden above the sediment site.

9 May 2002 (afternoon): During this sampling period, there were once again SE winds. Thus, the same conclusion can be drawn for this sampling event as well. The dredge material was not contributing significantly to the air burden on-site. This conclusion was drawn, because the concentration at the upwind site B (1418 pg m^{-3}) was similar to that at the downwind site C (1339 pg m^{-3}).

10 May 2002 (morning): On this sampling period, winds shifted and came out of the W leaving all sites upwind of the applied dredge material. All sites had similar ΣPCB concentrations: site A (1328 pg m^{-3}), site B (1436 pg m^{-3}), and site C (1114 pg m^{-3}).

10 May 2002 (afternoon): Winds were out of the W and concentrations were statistically similar among the three sites: site A (638 pg m^{-3}), site B (728 pg m^{-3}), and site C (695 pg m^{-3}).

Under three sampling periods, conditions were ideal such that an assessment could be made regarding whether the NJDEP trailer site can "feel" the influence of the sediment application site: May 8 (afternoon), May 9 (morning), and May 9 (afternoon). The concentrations measured at the NJDEP trailer site on May 9 in the morning (658 pg m^{-3}) and in the afternoon (696 pg m^{-3}) were the two lowest ΣPCB concentrations measured at the site during the May campaign, indicating that the sediment site is not the dominant source of PCBs to the air near the NJDEP Bayonne trailer. However, for the May 8 afternoon sampling event, gas phase ΣPCB concentrations were the highest measured during the May campaign at the trailer (1349 pg m^{-3}).

November 2002 Campaign

The sampler locations for the November 2002 campaign were not the same as in any of the previous campaigns (see Fig. 35). A summary of the gas phase ΣPCB concentrations from the November 2002 intensive campaign is presented in Table 11.

Table 11. Summary table of gas phase ΣPCB concentrations (pg m^{-3}) at the NJDEP trailer and the SDM landfill in Bayonne during the November 2002 sampling campaign.

Σ PCB Concentration pg m^{-3} (Gas Phase) November 2002	**Bayonne Trailer**	**Sediment Site A**	**Sediment Site B**	**Sediment Site C**
12 November (Morning)	1568	3118	3411	3638
12 November (Afternoon)	883	5009	3395	3530
13 November (Morning)	878	869	697	793
13 November (Afternoon)	1010	797	656	753
14 November (Morning)	362	517	600	361
14 November (Afternoon)	586	421	461	564

12 November 2002 (morning): During this sampling period, winds came out of the NE. The upwind Site A saw PCBs from off-site; whereas, site B was downwind of the dredge sediment. ΣPCB concentrations were similar at all three sites: A (3118 pg m^{-3}), B (3411 pg m^{-3}), and C (3638 pg m^{-3}), indicating that the application of dredge sediment was not the controlling factor in PCB concentrations on-site.

12 November 2002 (afternoon): During this sampling period, winds came out of the NE. The upwind Site A saw PCBs from off-site; whereas, site B was downwind of the dredge sediment. However, ΣPCB concentrations were similar at these two sites: B (3398 pg m^{-3}), and C (3530 pg m^{-3}). Site A, the site upwind of the applied sediment, had a significantly larger gas phase ΣPCB concentration (5009 pg m^{-3}).

13 November 2002 (morning): Winds were derived from the N/NW over this sampling event. Site A would therefore represent the upwind site, and site C the downwind site. However, the ΣPCB concentrations at all three sites were statistically similar (within the 20% uncertainty surrounding the PCB measurements): Site A (869 pg m^{-3}), Site B (697 pg m^{-3}), and Site C (793 pg m^{-3}). Thus, there was no apparent upwind/downwind gradient and the applied sediment did not contribute significantly to the over-site air.

13 November 2002 (afternoon): Winds were once again from the N/NW over this sampling period. Site A would therefore represent the upwind site, and sites C the downwind site. However, the ΣPCB concentrations at all three sites were again statistically similar (within the 20% uncertainty surrounding the PCB measurements): Site A (797 pg m^{-3}), Site B (656 pg m^{-3}), and Site C (753 pg m^{-3}). Thus, there was no apparent upwind/downwind gradient and the applied sediment did not contribute significantly to the over-site air.

14 November 2002 (morning): On this sampling period, the winds came from the W and all sites were therefore upwind of the dredge material. ΣPCB concentrations were similar at sites A (517 pg/m^3) and B (600 pg/m^3), but lower at site C (361 pg/m^3).

14 November 2002 (afternoon): Under SW winds, all three sites were also upwind of the dredge material. Sites A (421 pg m^{-3}) and B (461 pg m^{-3}) were similar in magnitude, but site C displayed a higher ΣPCB concentration (564 pg m^{-3}).

Unfortunately, during the November intensive campaign, there were no SE wind conditions that would allow for an assessment of the impact of the dredge sediments on atmospheric PCB concentrations at the NJDEP trailer site.

Summary

Average concentrations at the sediment application site were found to be ~1.5-2X higher than those measured at the Bayonne trailer (Figure 6). Average ΣPCB concentrations during the July 2001 campaign were 7128 pg m^{-3} and 3945 pg m^{-3} at the sediment application site and the Bayonne trailer site, respectively. For the October 2001 campaign, average ΣPCB concentrations were 2857 and 1284 pg m^{-3} at the two sites, respectively. Average ΣPCB concentrations for the May 2002 campaign were 1604 at the SDM landfill and 947 pg m^{-3} at the NJDEP trailer. For the November 2002 campaign,

average ΣPCB concentrations were 1644 and 881 pg m^{-3}, at the SDM landfill and trailer sites, respectively. Average ΣPCB concentrations during the intensive field campaigns were highest during the warmest seasonal campaigns, July 2001 (average temperature: 23°C) and October 2001 (average temperature 20°C). ΣPCB concentrations were lowest during the two coolest seasonal campaigns, May 2002 (average temperature: 8°C) and November 2002 (average temperature: 10°C).

Average ambient PCB concentrations in the city of Bayonne can be compared before and after the application of SDM. The average annual concentration of ΣPCB at the Bayonne trailer for the year prior to the application of SDM (December 1999 – November 2000) was 1711 pg m^{-3}. This value is similar to the average annual concentration of ΣPCB (1764 pg m^{-3}) for the period over which SDM was being applied. This value was estimated as the average of the ΣPCB concentrations measured at the trailer during the intensive campaigns, which include all four seasons.

In Figure 46, ΣPCB concentrations at the trailer site and SDM application site are compared with data from other studies. ΣPCB concentrations at the Bayonne trailer and the SDM application site are of similar magnitude to those from other urban/industrial sites such as Baltimore, MD, Chicago, IL, and Jersey City, NJ. Concentrations at both the trailer site and the sediment application site are significantly higher than those measured at "rural" sites which are near continental background concentrations of ~300 pg m^{-3}.

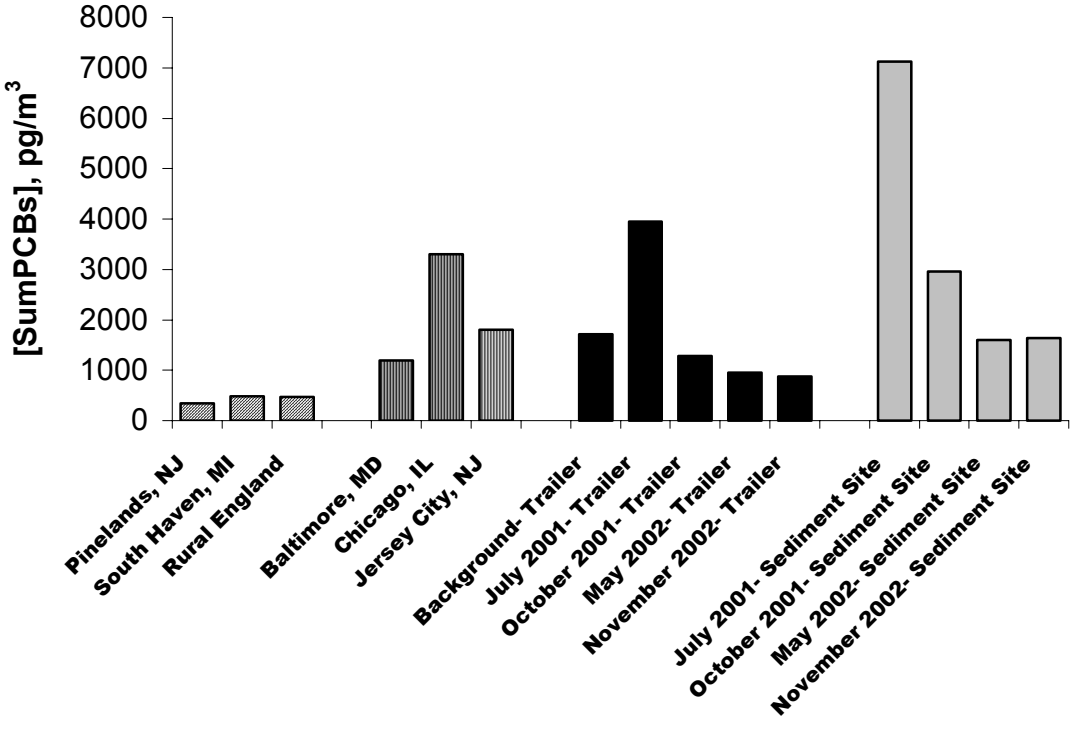

Figure 46. Comparison of gas phase ΣPCB concentrations (pg m^{-3}) from this study to other studies:

Pinelands: NJADN data (Van Ry et al, *ES&T,* 2002), Jersey City: NJADN data (Totten et al., *ES&T*, in review), South Haven/Chicago: (Simcik et al, *ES&T*, 1997), Baltimore: (Offenberg et al, *J.AWMA*, 1999), Rural England: (Lee and Jones, *ES&T*, 1999).

6.3 Vertical PCB Fluxes at the SDM Landfill

The determination of the flux of PCB's has been based on theoretical considerations of exchange processes in a turbulent boundary layer. A fundamental assumption underlying the theory is that the flow is in steady state or nearly so. During intervals of changing wind conditions the vertical distributions of velocity, temperature and water vapor will undergo an adjustment toward a new equilibrium. During such intervals of change it is entirely possible that one measure of stability, say the Richardson Number, Ri, may indicate unstable conditions (temperature decreasing with height above the ground) while another measure such as z/L simultaneously indicates a stable stratification because the heat flux is negative on/into the ground. For the 19 PCB vertical gradient measurement intervals just three cases occurred where the sampling interval average values of Ri and z/L had opposite signs - August 1, 2001, last 2 hours; October 24, 2001 evening and October 25, 2001 morning. In each of these cases, the wind had shifted during the sampling interval significantly in direction leading to a lack of equilibrium conditions in the lower atmosphere. Thus, the estimates for the vertical flux of PCB's for these three intervals must be considered with caution.

One measure of the reasonableness of the observations at the landfill is to compare the values of the stability correction factors for momentum exchange, ϕ_M, calculated from the present measurements with values obtained in other studies. In Figure 47, the presently calculated values for ϕ_M are plotted against values of z/L. Also shown on this figure are the empirically-based equations for this dependence developed in five other studies. The results from the presently reported observations were taken from selected intervals in which the wind conditions were reasonably steady. There is considerable scatter in the data similar to most micrometeorological observational studies, but there is substantial agreement with the theoretical dependence of ϕ_M on z/L.

For a few sampling intervals the values of the stability factors were in marked disagreement with expectations. For example, for the late afternoon sampling on November 14, 2002, the atmosphere was unquestionably stable with Ri and z/L both greater than zero. The stability factor for momentum was, surprisingly, significantly <1 while the factor for sensible heat was >1 as expected. The reasons for this are obscure but there was a significant shift in wind direction during this interval.

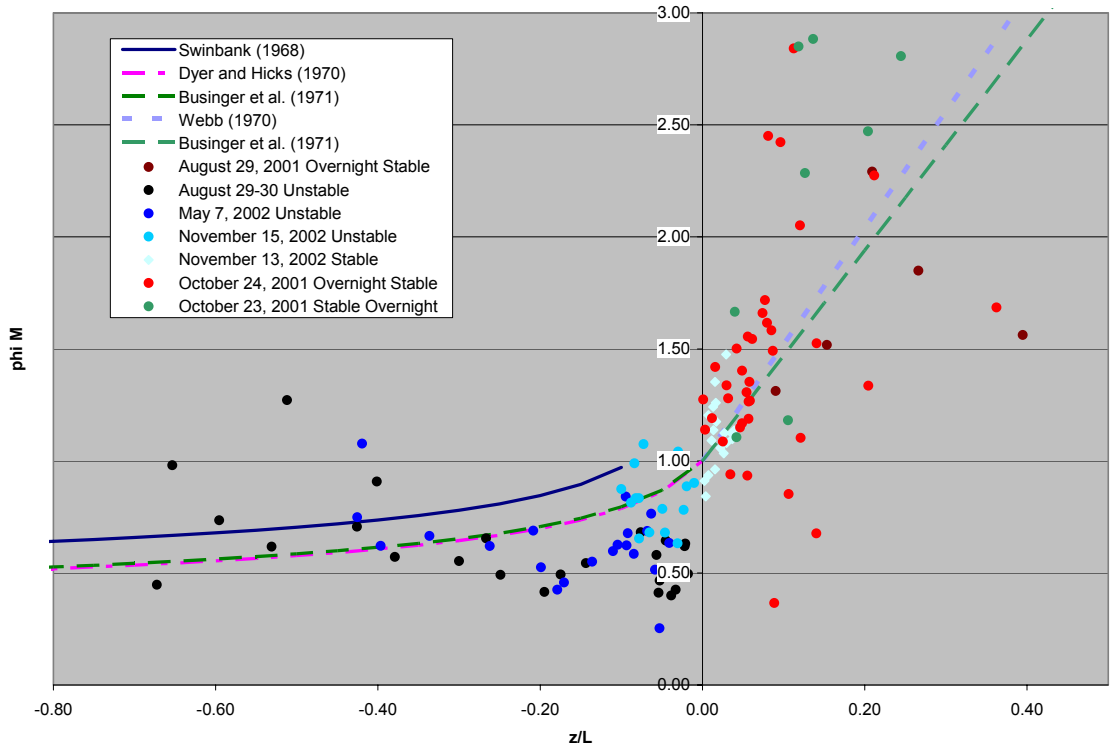

Figure 47. Relationship between calculated stability correction factors for momentum exchange (ϕ_M) and z/L.

The flux of PCB's depends on the properties of the treated dredged material and on the atmospheric conditions. In this study, only some gross aspects of the dependence of the flux on the properties of the dredged material can be inferred. During the May 2002 sampling campaign amended dredged material was placed upwind of the instrumentation site just hours prior to the first sampling interval. The calculated flux for this interval of the order of 15,000 ng m^{-2} s^{-1} was the highest found during this study, exceeding the next highest value by a factor of three. The pattern of fluxes calculated for the first four sampling intervals in May 2002 would indicate that there is a marked decrease in flux with age of the placed materials over the first few hours, which becomes more gradual as the age increases to a day or more.

The effect of atmospheric conditions on the flux of PCB's is a direct dependence on the friction velocity and a less obvious dependence on atmospheric stability. The directly measured values of the friction velocity, u_*, in the individual sampling intervals, varied from 0.10 to 0.59 m s^{-1}. Thus, by itself, this range in the value of u_* would produce a factor of 6 variation in PCB flux. The stability factor, estimated from either Φ_W or Φ_H exhibited a range of values from 0.3 to 1.8 which again provides for a factor of 6 variation in PCB flux.

A difficulty arose for several sampling intervals in the determination of the stability correction factor for evaporation. The resolution of the measurement of the average vapor pressure at the two fixed elevations was 0.01 mb. On several occasions the vertical gradient was less than this instrumental resolution. In contrast, the temperature gradient was always measurable and the stability correction

factor for sensible heat flux could be reliably measured. In cases where the factor for evaporative flux could not be found, the factor for sensible heat flux was used as a surrogate for the stability correction factor for the flux of PCB's. It has been argued in the literature; see, for example, Dyer and Hicks (1970) that the factors for heat and vapor behave similarly with identical numerical values with variation in atmospheric stability.

An estimate of the magnitude of horizontal gradients expected at the landfill can be made using the following assumptions:

Typically the lagoon of freshly placed dredged material had a horizontal dimension of the order of 100 m. The expected height of the concentration boundary layer for PCB's at the downwind edge of this lagoon for wind speeds of about 2 m s^{-1} would be of the order of 10 m or less. If the vertical flux is of the order of 1000 ng m^{-2} h^{-1}, then the increase in concentration, ΔC, between an upwind and downwind perimeter station can be found for a simple box model; the excess flux per unit width of PCB's through a vertical section with height, h = 10 m, and average velocity u = 2 m s^{-1} must equal the vertical flux of 0.3 ng m^{-2} s^{-1} over a patch length of 100 m.

The result is an expected difference in PCB concentration of the order of 1.5 ng m^{-3}. This is in reasonable agreement with observations on those occasions when there were perimeter measurements upwind and downwind of the recently placed dredge material. On October 24 for example, the wind was blowing from the office trailer toward the pug mill and directly over the site where the vertical flux measurements were being made. The measured concentration at the office trailer was 1.9 ng m^{-3} and at the pug mill it was 3.7 ng m^{-3}. Hence in this instance ΔC= 1.8 mg m^{-3}.

The ΣPCB flux rates measured in this study may be compared to previously determined PCB flux rates over large bodies of water including New York Harbor and Raritan Bay, NJ (Totten et al., 2001) Chesapeake Bay, MD (Nelson et al., 1998), and Green Bay, WI (Achman et al., 1993). The flux rates, determined using thin film theory, were significantly lower than the values calculated in this study. In New York Harbor and Raritan Bay the average flux rates were 1900 and 840 ng m^{-2} d^{-1} respectively with a range of 310 to 2700 ng m^{-2} d^{-1} over a three day period in July 1998. In Chesapeake Bay, the annual mean flux rate was 96 ng m^{-2} d^{-1} with a range of -63 to 800 ng m^{-2} d^{-1}. The annual flux rate found in the Green Bay study was 81 ng m^{-2} d^{-1} with a range of 13 to 1300 ng m^{-2} d^{-1}. Assuming that active volatilization of PCBs occurred only during the daytime (Table 4), the ΣPCB fluxes estimated at the SDM landfill ranged from 870 – 1.8 x 10^5 ng m^{-2} d^{-1}. As found in the air-water exchange studies, the lesser chlorinated PCBs corresponding to lower molecular weight congeners tended to have higher sediment-air fluxes.

The flux rates of PCBs have exhibited a large dependence on the atmospheric and site conditions. Since latent and sensible heat fluxes stop or greatly decline at night, lower PCB flux rates were measured at night. Very low PCB fluxes also occurred during daytime intervals, when it was cloudy and cool, such as on the morning of 23 October 2001 when there were lower heat flux rates. The moisture content of the dredged material may also have an effect on PCB volatilization. The 29-30 August 2001 sampling campaign exhibited vastly different behavior from that found for recently laid SDM. During this campaign, the SDM was dry and a white crust had formed on it. During this time the sensible heat flux was greater than the latent heat flux, suggesting that the transport of water vapor out of the SDM had been restricted. The estimated PCB fluxes during 29-30 August 2001 were

directed into the ground. In a study conducted using a laboratory flux chamber it was concluded that "dry" sediments have a greater affinity for contaminants than wet sediments because of the competition for adsorption or absorption space with water (Valsaraj et al., 1997). As the sediment particles in upper layers of the sediment dry they not only hold the contaminant absorbed to them tighter, they will also absorb free contaminants that would otherwise diffuse to the surface, thus further increasing the sediment-side resistance to contaminant flux to the atmosphere. In another laboratory study conducted with contaminated St. Lawrence River sediment, Chiarenzelli et al. found a very high correlation between the evaporation rate of water and the amount of PCBs volatilized in the first 24 hours of drying (Chiarenzelli et al., 1996).

6.4 Vertical Hg Fluxes at the SDM Landfill

This study presents the first measurements of the emissions of Hg from stabilized or unstabilized freshwater or marine sediments. However, the emissions of Hg from stabilized sediments measured here can be compared with the fluxes of Hg from soils. Modeling studies of the mercury cycle indicate that the average terrestrial emission rate is approximately 1 Mt y^{-1} or 0.8 ng m^{-2} h^{-1} (Lindqvist et al., 1991) and that this rate has changed little since pre-industrial times (Mason et al, 1994). Since this value is the average for all land surface types, it greatly underestimates the emission from more reactive pools in the terrestrial environment including soils. Estimates of soil-air Hg fluxes for uncontaminated natural soils range from –2.2 to 45 ng m^{-2} h^{-1} (Kim and Lindberg, 1995; Carpi and Lindberg, 1998; Poissant and Casmir, 1998; Engle et al., 2001). An assessment of the emissions of Hg from geologically enriched soils such as those in Nevada suggests that the Hg flux in these areas ranges from 3.5 to 13 ng m^{-2} h^{-1}, depending on hydrothermal alteration (Zehner and Gustin, 2002). Contaminated soils such as those near Hg mining activities can have much higher Hg emission rates that range from 10 to 1500 ng m^{-2} h^{-1}(Lindberg et al., 1995; Carpi and Lindberg, 1997; Ferrara et al., 1998). The range of vertical Hg fluxes estimated in this study of SDM (17 to 1043 ng m^{-2} h^{-1}) is certainly within the upper range of soil-air fluxes.

Many estimates of soil-air Hg fluxes were made using flux chambers (Engle et al., 2001; Carpi and Lindberg, 1998; Ferrara et al., 1998). The benefit of using flux chambers is that environmental parameters are well controlled and their effect on Hg volatilization can be assessed. Micrometeorological methods, such as those used in this study, however, are thought to provide more accurate measures of *in situ* vertical fluxes (Gustin et al., 1999). Comparisons show that micrometeorological methods consistently yield fluxes that are nearly three times higher than those determined with flux chambers (Gustin et al., 1999).

The age, temperature and water content of the stabilized sediment are expected to affect sediment-air fluxes of TGM. As the sediment proceeds through the cementation reaction, it is expected that the contaminants will become secure within a matrix, thereby producing a declining flux over the curing time, thus older stabilized sediments should have lowering fluxes. The intensity of incident radiation is also expected to play a significant role in the degree to which mercury is volatilized from land applied sediments.

In addition to meteorological and site conditions, the mercury concentration in the sediments being processed, has a large effect on the observed fluxes. The dredged material is heterogeneous as to its mercury content, but is estimated to range between 1.3 ppm (Con Edison analytical evaluation of the

dredge applied during October 2001) and 2.6 ppm (ETL, 2001), well above the pre-industrial concentration of 0.3 to 0.4 ppm of the Hudson drainage basin (Wakeman and Themelis, 2001). TGM fluxes can be compared with the mercury content of the substrate; e.g., Lindberg et al.(1995), evaluated an impacted site in East Fork Poplar Creek in Oak Ridge, Tennessee, where soils were contaminated by weapons manufacturing activities in the 1950's. The concentration of mercury in the soil ranged from 5 to 50 ug per gram soil and the related flux ranged from 10 to 200 ng m^{-2} h^{-1}. In a study done by Carpi and Lindberg, 1997, the flux of mercury was measured from soils amended with sewage sludge. The average sludge mercury concentration averaged 7.3 ug g^{-1} soil, and the flux was approximately 100 ng m^{-2} h^{-1} above the background flux. [Note: EPA monthly average, maximum allowable pollutant concentration for unrestricted land application is 17 ug g^{-1} sludge (EPA, 1993].

In an extensive study of the flux of mercury from naturally enriched substrates in Nevada, Gustin et al., (2000), proposed a scale in which the soil concentration of mercury is related to the flux out of the soil. For example, the scale projects a flux of approximately 80 ng m^{-2} h^{-1} with a soil concentration of 3 ug g^{-1}. Flux estimates for the SDM landfill in Bayonne, for which sediment concentrations are in the range of 1.3 to 2.6 ug g^{-1}, were higher in August 2001, October 2001, and May 2002 than this relationship would predict (Table 5). Higher than expected fluxes of Hg above SDM (in relation to sediment concentration) may be the result of greater reactivity (thermal or photochemical) of sediment-bound Hg than Hg in soils. Since the temperature of SDM is moderated by the large water content, temperature may play less of a role in Hg emissions from SDM than from soils. A modest, but significant correlation was found between Hg concentrations measured at the NJDEP trailer in Bayonne and air temperature (r^2 of 0.57, $p < 0.05$). This correlation likely reflects temperature driven volatilization of Hg from soils and surface waters in the region and is consistent with other studies showing significant correlations between soil temperature and Hg concentrations in the atmosphere (Gillis and Miller, 2000). Incident radiation has also been found to facilitate the volatilization of Hg from soils. Sunlight has been implicated in the reduction of oxidized mercury to its more volatile elemental state, Hg^0 (Carpi and Lindberg, 1997). This reduction occurs in the shallow layer of surface soil (<0.5 cm) where the penetration of light is possible (Carpi and Lindberg, 1997). This mechanism may play a significant role in the amount of volatilized species observed above land-applied sediments. It has been found that light-enhanced emissions of Hg from natural soils are 1.5 to 116 times emissions in the dark (Gustin, et al., 2002). Poissant and Casmir (1998) found that the Hg flux was correlated to incident radiation with an r^2 of 0.92, whereas the correlation with temperature had an r^2 of 0.38. This information may be used in selecting appropriate times of year to apply stabilized dredged sediments in order to reduce the extent of the potential flux. Wind speed can also drive the vertical flux of volatile contaminants, but in this study, no significant correlation between wind speed and the magnitude of the Hg flux at the SDM landfill in Bayonne was observed (r^2=0.24, $p > 0.05$).

The water content of soil can have an effect on the evaporative flux of the soil bound contaminant so it has been theorized that increased flux of volatile contaminants from moist soil is due to the increase in vapor pressure caused by the displacement of the chemical from the soil surface by the water (Spencer et al., 1969). For example, Hg fluxes from soils have been observed to increase following rain events (Wallschlager et al., 2000). At the SDM landfill, sediments are applied to the land saturated with water, so displacement by rain cannot occur. As SDM dries over days to weeks, the loss of moisture may slow down the volatilization of Hg and other contaminants.

6.5 Contribution of the SDM Landfill to Hg in Bayonne Air

The annual average concentration of gaseous Hg in Bayonne, NJ in 2002-03 (2.19 ng m^{-3}) was slightly higher than the reported range of global average background levels (1.5 to 2.0 ng m^{-3}; Slemr, 1992). In addition to upwind sources such as coal burning power plants and other industry to the west of New Jersey, current and historic industry in the NY/NJ metropolitan area contribute Hg to the air in Bayonne, NJ. As such the potential contribution of Hg from the land application of SDM needs to be assessed in the context of the total steady-state pool of TGM in Bayonne. In order to predict the relative potential contribution of TGM from the SDM landfill to the Bayonne area, a simple box model integrating our measured background TGM concentrations and estimated Hg flux parameters and has been formulated.

The Bayonne landfill covers an area of approximately 5 x 10^5 m^2. In our model, approximately 20% of the total area of the landfill was assumed to be receiving SDM at any given time. A vertical flux of 600 ng m^{-2} h^{-1} was assumed to be representative of the summer (rounded average of daytime fluxes estimated for August 2001 and May 2002) and a flux of 30 ng m^{-2} h^{-1} was used for the winter months (rounded average of positive fluxes estimated for November 2002). Since it has been shown here and elsewhere that soil-air fluxes of mercury are significantly reduced at night, fluxes were estimated over a 12 h day.

During the summer months, the contribution of mercury to the atmosphere from the application of the stabilized dredge sediments is estimated to be 720 mg d^{-1}. Assuming a vertical mixing height of 500 m, which is characteristic of coastal regions (Garrat, 1992), and an average summertime concentration of Hg of 3 ng m^{-3}, the air over the city of Bayonne (10 km^2) contains 15 g of gaseous Hg. Therefore, Hg emissions from the SDM landfill would contribute approximately 5% d^{-1} of the ambient concentration of the total gas phase Hg during the summer. In the winter, the SDM landfill is estimated to emit 36 mg Hg d^{-1}. Assuming an average Hg concentration of 2 ng m^{-3} in the winter, the atmosphere above Bayonne contains a total of 10 g of gas phase Hg. The SDM landfill would then add approximately 0.4% d^{-1} of the ambient concentration of gas phase Hg in the winter.

7.0 CONCLUSIONS

The results of this project show that PCB concentrations measured at the Bayonne trailer site are of similar magnitude to average concentrations measured in other large urban and industrial areas (Chicago, Illinois; Baltimore, Maryland; Jersey City, New Jersey). The highest ΣPCB concentrations at the NJDEP trailer site occurred under NE winds and not W winds, as would be the case if Newark Bay was the dominant source of PCBs to western Bayonne. Potential sources located to the NE of the trailer site include the city of Bayonne, the Hudson River, and New York City. In addition to wind direction, there is a seasonality to the dataset: gas phase PCB concentrations followed the order of July 2001 > October 2001 > November 2002, May 2002, likely due to enhanced air-surface exchange processes under warmer temperatures.

Average ΣPCB concentrations at the sediment application site were approximately 2X higher than those at the background trailer site and as much as 50X higher than the global continental background (~300 pg/m^3). However, there were sampling periods (6 of 29) when the concentrations at the trailer were greater than each of the three concentrations at the sediment application site. Upwind /downwind

concentration gradients of PCBs were rare (5 of 29 cases) at the SDM landfill site. This suggests that SDM is not the only or dominant source of PCBs to the air above the landfill and that other offsite sources may be important.

Gas phase PCB and Hg concentrations were elevated in the air above the SDM landfill in Bayonne, NJ relative to background concentrations in Bayonne, but are orders of magnitude below exposure limits. Thus PCB air concentrations measured directly above SDM (3 – 14 ng m^{-3}) as it cures were relatively high compared to background values measured in the region (1 – 3 ng m^{-3}), but they were two orders of magnitude below the NIOSH recommended exposure limit of 1μg m^{-3} and five orders of magnitude lower than the OSHA permissible exposure limits of 0.5 to 1.0 mg m^{-3}. The average gaseous Hg concentration measured at the SDM landfill (3.2 ng m^{-3}) was significantly higher ($p < 0.05$) than the average background concentration measured at the NJDEP trailer or in New Brunswick, NJ on days that bracketed the SDM landfill sampling campaigns (1.8 ng m^{-3}), all TGM concentrations measured during this project were well below chronic effects limits for total gaseous mercury (200 ng m^{-3}, Agency for Toxic Substances and Disease Registry-CDC; 300 ng m^{-3}, EPA).

It has been shown through this study that it is possible to quantify vertical gradients in PCB and Hg air concentrations in the surface microlayer of the atmosphere. Using these concentration gradients and a combination of the Aerodynamic Gradient and Eddy Correlation methods, net sediment-air fluxes of PCBs and Hg at the sediment application site were estimated. Vertical fluxes of PCBs and Hg were generally positive during the day and low to negative at night, but they were highly variable and dependent on atmospheric conditions as well as the age and condition of the SDM. Estimated vertical fluxes of PCBs from SDM at the Bayonne landfill ranged from 72 to 15,000 ng m^{-2} h^{-1} and averaged 2050 ng m^{-2} h^{-1}. It appears from this study that although the flux of PCBs from recently treated and placed SDM may be high, it decreases quickly as the SDM dries. Although PCB concentrations are much lower than the limits for Industrial Standards, the contribution of SDM sites to regional PCB air concentrations should be investigated further. Sediment-air Hg fluxes for the Bayonne SDM landfill ranged from 17 to 1043 ng m^{-2} h^{-1}, averaged 312 ng m^{-2} h^{-1}, and were similar to those measured from contaminated soils (Lindberg et al., 1995; Ferrara et al, 1998).

One of the concerns regarding the land application of SDM in populated areas is the potential impact of volatile contaminants to the local atmosphere. The present results demonstrate that the city of Bayonne, NJ, as represented by the NJDEP trailer air monitoring station, is impacted to a greater extent by PCB sources from areas other than the SDM site. This suggests that the SDM landfill is not the primary source of PCBs to the city of Bayonne. A simple box model shows that the contribution of Hg emissions from the SDM landfill to total gas phase Hg in the boundary layer of the city of Bayonne is minimal (<5%).

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