New Jersey Water Resources Research Institute
Annual Technical Report
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Introduction

The New Jersey Water Resources Research Institute supports a diverse program of research projects and information transfer activities. With oversight from the Advisory Council which sets the institute's Research Priorities, the available funds are divided between supporting faculty with 'seed' projects or new research initiatives and supporting graduate students with developing their thesis research. The funding is intended to initiate novel and important research efforts by both faculty and students, and thus emphasizes new research ideas that do not have other sources of funding. We hope to support the acquisition of data that will enable further grant submission efforts, and, in the case of students, lead to research careers focused on cutting-edge research topics in water sciences.

Research projects span a wide range of topics in water resources. In the first faculty project, Rodenburg and colleagues utilized a novel technique, the micrometeorological approach, to investigate the air-water exchange fluxes of polychlorinated biphenyls (PCBs) in the Tappan Zee region of the Hudson River. This research is particularly important in determining the fate of PCBs that originate in the upper sections of the river. The other faculty project employs a proven analytical technique to determine the source of fine-grained sediments in New Jersey streams. Galster and colleagues used radiometric signatures to distinguish between watershed and streambank sources in watersheds with different land uses. The results of this research may eventually influence land management practices such as BMPs and sediment load reduction plans.

Graduate students have similarly carried out an impressive range of research. Loudon and her advisor sought to determine the microbial dehalogenators present in a bioreactor landfill that can debrominate brominated organic compounds, such as PBDEs, that, through leaching, will ultimately find their way into wasterwater treatment plants. Palta and her advisor are using the DNDC process-based model to predict hot spots and hot moments of denitrification in an urban wetland. The results suggest spatial patterning in denitrification dynamics. Rauschenbach and her advisor characterized a selenate/selenite- and arsenate-respiring microbe which may aid in the development of processes to remediate contaminated soils and ground water aquifers. Sae-Khow and her advisor developed a microscale solid phase extraction method utilizing carbon nanotubes for monitoring a wide range of compounds, including pesticides and drug metabolites, in water resources. This method will reduce the amount of time, solvents, equipment, and money required for monitoring. Finally, Wen and her advisor investigated factors, such as seed bank composition and hydrologic conditions, affecting secondary succession in abandoned cranberry farms in the New Jersey Pine Barrens. The research also sought to correlate wildlife species distribution with habitat factors which will improve wetland habitat management plans.

The goal of our information transfer program is to bring timely information about critical issues in water resource sciences to the public, and to promote the importance of research in solving water resource problems. The information transfer program continues to focus on producing issues of the newsletter that provide a comprehensive overview of a particular water resource topic, as well as one issue a year that highlights water research occurring in New Jersey. The program continues to develop the NJWRRI website (www.njwrri.rutgers.edu) into a comprehensive portal for water information for the state. We also collaborate with other organizations in sponsoring and producing conferences.

Research Program Introduction

The New Jersey Water Resources Research Institute has had a policy, yearly re−affirmed by the Advisory Council, of using the research dollars to promote new and novel directions of research. To this end, two projects directed by research faculty at institutions of higher learning around the state are selected, and five grants−in−aid are awarded to graduate students who are beginning their research. In both cases, we expect that the research is exploratory and is not supported by other grants. The intent is that these projects will lead to successful proposals to other agencies for further support. The larger goal of the research component of the Institute's program is to promote the development of scientists who are focused on water resource issues of importance to the state.

Volatilization of PCBs from the Tappan Zee region of the Hudson River

Basic Information

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ABSTRACT

In this research, the micrometeorological technique was applied for the first time to investigate the air-water exchange fluxes of polychlorinated biphenyls (PCBs). A field campaign was conducted in July of 2008 in the Tappan Zee region of the Hudson River. This section of the River is known to be heavily contaminated with PCBs, leading to large volatilization fluxes. By measuring the concentrations of PCBs at two heights above the water surface as well as in the dissolved phase, fluxes and air/water exchange mass transfer coefficients (v_{aw}) were determined for individual PCB congeners. The average gas–phase ΣPCB concentration was 0.7 ng m^{-3}, elevated over regional background by about a factor of 2. Dissolved-phase PCB concentrations ranged from 2 to 14 ng L^{-1}, in good agreement with the measurements of others. In 14 of 16 sampling events, PCB concentrations were higher in the lower air sample, indicating positive fluxes (net volatilization) of PCBs from the water column. Vertical ΣPCB fluxes ranged from 0.2 to 12 μg m^{-2} d^{-1} and were highest on July 10th. Values of v_{aw} ranged from 0.05 to 2.27 m d^{-1}. The relationships between v_{aw} for PCB congeners and various meteorological variables such as wind speed and air temperature were investigated. v_{aw} and sensible heat flux were inversely correlated, while v_{aw} was mostly positively correlated with latent heat flux. Both wind speed and friction velocity (u*) displayed positive relationships with v_{aw}. In addition, temperature usually displayed a positive correlation with v_{aw}. Correlations between v_{aw} and Henry's law constants for individual PCB congeners were found to be not significant, in agreement with theoretical predictions.

PROBLEM AND RESEARCH OBJECTIVES

Much effort has been spent trying to predict the fate of PCBs in the Hudson River and the New York/New Jersey Harbor. PCBs were dumped into the Upper Hudson River by two plants owned by General Electric (*1*), resulting in contamination that has caused fish consumption advisories. As a result, the entire stretch of the Hudson River from the GE plants at Hudson Falls south to New York City is a Superfund site. GE has agreed to dredge portions of the Upper Hudson River. This management decision was based on water quality models (*2, 3*) which predict that volatilization is the most important loss process for PCBs in the system. These models use mass transfer coefficients (MTCs) for air/water exchange that are based on studies of air/water exchange of gases, such as SF_6 and CO_2, that have very different physicochemical properties from those of PCBs. This practice results in significant uncertainty associated with the MTCs for PCBs, and therefore in the water quality models themselves. Given the importance of volatilization to PCB fate in the Hudson River, it is vital that accurate parameters for volatilization be determined based on the best available technology. In this study we employ a novel technique, the micrometeorological approach, to directly measure MTCs for PCBs in the Tappan Zee region of the Hudson River.

The purpose of this study was, first, to calculate PCB volatilization fluxes from the Tappan Zee using a novel technique based on micrometeorological measurements in the near surface atmosphere. The second purpose was to use these fluxes and measured water column concentrations to derive air/water mass transfer coefficients (v_{aw}) for PCBs. The third purpose was to investigate the relationship between the measured values of v_{aw} and meteorological variables, especially wind speed and friction velocity, as well as the physical-chemical properties of PCBs. Mean wind speed, temperature, water vapor, and PCB 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 were calculated using the Thornthwaite-Holtzmann equation (*4*) modified to account for non-adiabatic conditions.

Air Water Exchange of Organics

Air/water exchange calculations are based on the following equation, in which the chemical flux (F_C) is a function of the air/water mass transfer coefficient (v_{aw}) and the water-air concentration gradient (*5*):

$$F_C = K = v_{aw}\left(C_d - \frac{C_a}{H'}\right) \tag{1}$$

where C_d is the dissolved concentration, C_a is the gas-phase concentration, and H' is the dimensionless Henry's law constant, which is a function of temperature and salinity. Values of v_{aw} have not been measured directly for organic chemicals. They are predicted based on values of v_{aw} measured for tracer gases, such as CO_2 and SF_6, which have physicochemical properties that are very different from those of PCBs.

A typical method of calculating v_{aw} for an organic chemical is to use the Whitman two-film model (7), which states that the overall mass transfer coefficient, v_{aw}, comprises resistances to mass transfer in both the air (v_a) and water (v_w) (*5*):

$$\frac{1}{v_{aw}} = \frac{1}{v_w} + \frac{1}{v_a \cdot H'} \tag{2}$$

For compounds with very large H' (often linked to low solubility), v_w will dominate v_{aw}. In contrast, compounds with low H' (frequently very soluble gases), v_a will dominate. For organic chemicals such as PCBs with H' between about 10^{-2} and 10^{-4}, both v_a and v_w are important (*6*). The mass transfer coefficients (v_a and v_w) have been empirically defined based upon experimental studies using tracer gases such as CO_2, SF_6, and O_2 (see refs. (*5*) and (*7*) for a review). Typically these mass transfer coefficients are determined as a function of wind speed, since wind is typically the major source of energy for driving mass transfer at the air/water interface. In flowing rivers, the water currents can also provide energy for mass transfer, and can be incorporated into the expression for v_w (*8, 9*). Differences in diffusivity (D) or Schmidt number (Sc) between these gases and PCBs are then used to estimate v_a and v_w for PCB congeners. This approach implicitly assumes that differences in solubility between the various gases are unimportant, an assumption which has been called into question (*10*).

Most studies (*11-16*) have calculated v_{aw} for PCBs via the relationship for v_a for H_2O recommended by Schwarzenbach et al. (where u_{10} is the wind speed in m s^{-1} at 10 meters and v_a is in cm/s) (*5*):

$$v_{\mathrm{a}}(H_2O) = 0.2u_{10} + 0.3 \tag{3}$$

In contrast, different relations for v_w are frequently used. Achman et al. (*11*) invoked the relationship suggested by Liss and Merlivat in 1986 (*17*) for air-water exchange calculations in Green Bay:

$$\begin{aligned} v_{\mathrm{w}} &= 0.17u_{10} \text{ for } \mathrm{u}_{10} < 3.6\,\mathrm{m/s} \\ v_{\mathrm{w}} &= 2.85u_{10} - 9.65 \text{ for } 3.6 < \mathrm{u}_{10} < 13\,\mathrm{m/s} \\ v_{\mathrm{w}} &= 5.9u_{10} - 49.3 \text{ for } \mathrm{u}_{10} > 13\,\mathrm{m/s} \end{aligned} \tag{4}$$

Others (*7, 18*) used the Wanninkhoff equation (*19*):

$$v_{\mathrm{w,CO2}} = 0.45{u_{10}}^{1.64} \tag{5}$$

At wind speeds from 0 to about 7 m s^{-1}, this equation yields higher values of v_w than the Liss and Merlivat prediction with the maximum difference (a factor of 6) occurring at u_{10} = 3.6 m s^{-1}. Meteorological data from Newark Airport indicates that the wind speed in this area is below 4 m s^{-1} about 50% of the time, so this discrepancy has a significant impact on predictions of air/water exchange of PCBs in this region. Wanninkhoff and McGillis (*20*) have established a new relationship for the effect of wind speed on v_w. This cubic relationship is an update of the most commonly applied semi-quadratic relationship established by Liss and Merlivat (*17*) and the quadratic relationship of Wanninkhoff (*19*). The cubic relationship is a better predictor of field data from (*10*), particularly for higher wind speed conditions (> 6 m s^{-1}). However, the cubic relationship tends to underpredict field measurements of $v_{w,CO2}$ (the mass transfer coefficient for CO_2) at low wind speeds. There is a great deal of variation observed in v_w values for various tracers, especially at low wind speeds.

The sources of error in the calculation of v_{aw} for PCBs are now apparent. They are chiefly associated with the algorithm chosen to calculate v_w for the tracer compound and the assumption that the resulting v_w can be scaled up to a suitable v_w value for PCBs by use of the Schmidt number. The approach typically used for PCBs assumes that mass transfer is solely a function of wind speed, even though many studies have suggested that other factors are important, such as wave fetch, boundary layer instability and surface films ((*21*) and references therein). Previous investigations of air/water exchange of PCBs (*12, 14*) that have estimated v_{aw} as described above have estimated that the inherent uncertainty in the resulting fluxes ranges from 40% to 900% (*12*). This high level of uncertainty prompted the present study.

Theory of the Micrometeorological Technique

The present work has determined v_{aw} values for PCBs, using flux estimates derived from measurements of the vertical concentration gradients of PCBs, micrometeorological parameters and water vapor fluxes in the lower boundary layer above the Tappan Zee. The method used captures the effects of boundary layer turbulence and surface roughness better than the kind of empirical relationships between v_{aw} and wind speed described above. This work represents the first time this approach has been applied to the Hudson River/Harbor area, although the PIs have successfully used this technique to measure PCB fluxes emanating from stabilized NY/NJ Harbor sediments deposited in a landfill in Bayonne, NJ (*22, 23*).

Measurement of turbulent fluxes in the near surface atmosphere can be accomplished via several methods. The approach that has been used in the present work is the use of an Aerodynamic Gradient (AG) method to determine the profile of wind speed, temperature and water vapor in the near surface atmosphere (*24, 25*). These gradients, along with concurrent measurements of PCB air concentrations at two heights, were used to determine the vertical fluxes of PCBs out of the water column. In addition to the AG measurements, an Eddy Correlation (EC) system was used to directly measure fluxes of momentum, sensible heat and latent heat. These measurements will allow for corrections to the PCB concentration profile for non-adiabatic conditions.

The theoretical basis for the AG method can be described using the expressions that have been developed for fluid flow over a flat plate. The full derivation may be found in Korfiatis et al. (*22*) and will only be summarized here. Primary among these is the equation that describes the gradient of wind speed orthogonal to the flow of the fluid:

$$\frac{\partial u}{\partial z} = \frac{u_*}{\kappa z} \tag{6}$$

where u is the fluid velocity in the x-direction, z is the distance from the plate, κ is von Karmen's constant, and u_* is the friction velocity. The friction velocity represents the flux of momentum orthogonal to the mean direction of the wind. This equation can be integrated between heights z_1 and z_2 to derive an equation that describes the profile of wind speed:

$$u_2 - u_1 = \frac{u_*}{\kappa} \ln\left({z_2}\big/{z_1} \right) \tag{7}$$

Similar equations can be derived for the profiles of temperature and water vapor concentration:

$$\frac{\partial \theta}{\partial z} = \frac{H}{\rho C_p \kappa u_* z} \tag{8}$$

$$\frac{\partial \rho_e}{\partial z} = \frac{Le}{\lambda \kappa u_* z} \tag{9}$$

where 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. Similar to the wind speed gradient equation, these can be integrated between two heights to describe the profile of temperature and water vapor density in the near surface atmosphere.

The above equations were developed for conditions in which there are no stability effects. In real-world applications, stability will exert a large influence on turbulent fluxes. A commonly used measure of atmospheric stability is z/L. The term z is the measurement height and L is the Monin Obukov length scale (*26*), which is calculated as:

$$L = \frac{\rho C_p {u_*}^3 \theta}{\kappa g H} \tag{10}$$

This can be modified to account for the effects of water vapor by replacing H with (H+0.07Le). Three cases are given for this classification scheme; (1) if z/L<0 stratification is unstable and the energy of turbulence is increased, (2) if z/L>0 stratification is stable thus hindering the development of turbulence, and (3) z/L=0 stratification is neutral and does not affect the formation of turbulence. Monin and Obukov (*26*) used similarity theory to derive expressions for the profiles of wind speed, temperature and moisture content of the air that take into account the possibility of non-adiabatic conditions. These equations are as follows:

$$\frac{\partial u}{\partial z} = \frac{u_*}{\kappa z}\phi_M \tag{11}$$

$$\frac{\partial \theta}{\partial z} = \frac{H}{\rho C_p \kappa u_* z}\phi_H \tag{12}$$

$$\frac{\partial \rho_e}{\partial z} = \frac{Le}{\lambda \kappa u_* z}\phi_W \tag{13}$$

The values ϕ_M, ϕ_H, and ϕ_W represent atmospheric stability correction factors for momentum, heat and water vapor, respectively. 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 a function of z/L. In order to calculate the values of the atmospheric stability factors from the above equations, it is necessary to have measurements of u_*, H and Le. These measurements can be collected using high-resolution sensors that can directly measure turbulent fluctuations in wind speed, temperature and water vapor concentration. Thus it is possible to calculate:

$$u_* = \overline{u'_x u'_z} \tag{14}$$

$$H = C_p \overline{\theta' u'_z} \tag{15}$$

$$Le = \lambda \overline{\rho_v' u'_z} \tag{16}$$

Although the value for z/L is obviously a function of height (z), it has been hypothesized that holding its value constant over a relatively small extent such as the two meters that will be used for the proposed study will result in very little error. Comparisons made between a constant correction factor and integration over the measurement interval have revealed that for values of z/L < -0.1 there is approximately a ten percent error and for z/L < -0.5 there is less than a three percent error (*22*). As a result the atmospheric stability factors can be calculated using the following set of equations.

$$\phi_M = \frac{\kappa(u_2 - u_1)}{u_* \ln(z_2/z_1)} \tag{17}$$

$$\phi_H = \frac{\rho C_p \kappa u_* (\theta_2 - \theta_1)}{H \ln(z_2/z_1)} \tag{18}$$

$$\phi_W = \frac{\lambda \kappa u_* (\rho_{e2} - \rho_{e1})}{Le \ln(z_2/z_1)} \tag{19}$$

Using the profiles of wind speed, temperature and water vapor, it is possible to create a similar profile for PCB concentration. Using this profile, the flux of PCBs can then be calculated. The following expression can be derived for the flux of PCBs:

$$F_{PCB} = \frac{C_1 - C_2}{\kappa u_* \ln\left({}^{z_2}\!/_{z_1} \right) \phi_C} \tag{20}$$

Every term in this equation is directly measured except ϕ_C, the atmospheric stability factor for the chemical of interest. One of the other stability factors (ϕ_M, ϕ_H, and ϕ_W) is substituted for ϕ_C, allowing the calculation of the PCB flux. After deriving the fluxes from the use of the meteorological technique v_{aw} can be determined from equation 1 above. Because the water column of the Tappan Zee is greatly oversaturated with PCBs relative to the gas phase, the C_a/H' term in equation 1 is negligible and can be ignored.

METHODOLOGY

Field work commenced on 8 July 2008 at the Piermont fishing pier in the Tappan Zee region of the Hudson River (Figure 1). This section of the river is tidal, so the height of the air sampler intakes above the water surface was constantly changing. The sampling campaign was designed so that each discrete sampling event would last about four hours, the minimum amount of time necessary to collect sufficient mass of PCBs in the air samples for analysis. Each sampling event consisted of:

- An upper and lower air sample (gas and aerosol phases)
- Duplicate water samples for PCB analysis (dissolved and particle phases)
- Duplicate water samples for dissolved organic carbon (DOC) and particulate organic carbon (POC) analysis
- Continuous monitoring of wind speed, temperature, and water vapor pressure at two heights (Aerodynamic Gradient system)
- Continuous monitoring of friction velocity and latent and sensible heat fluxes (Eddy Correlation system)
- Frequent measurement of the water level at the pier

Figure 1. Map of the Piermont fishing pier in the Tappan Zee region of the Hudson River. The tip of the pier is at 41°02’35”, 73°53’46”. Map courtesy of Google Earth.

DOC and POC samples were collected so that the truly dissolved PCB water phase concentrations could be calculated. A total of 16 sampling events were collected from 8th July to 15th July. The air sampling apparatus was set up at the upwind edge of the pier and the air sampling ports were oriented to allow the prevailing wind to blow directly into the surface of the QFF holder. In some conditions the wind direction changed, but in these cases the sampling setup was correspondingly relocated. With the exception of 8th July, on which no water sample was collected, and 9th and 11th July on which only one water sample was collected, two water samples were collected for each sampling day for a total of 12 water samples. There were duplicate DOC and POC samples for each sampling day for a total of 26 samples. The morning sampling event began between 9 and 11 am and ended between 1 and 3 pm, while the afternoon sampling started between 1:30 and 3:30 pm and ended between 5:30 and 7:30 pm. On 14th July no sample was taken due to adverse weather conditions while on 15th and 17th July afternoon thunderstorms abruptly ended the sampling process.

Gas Phase PCB Sampling

Air sampling was performed by procedures similar to those used in a Bayonne study (*22, 23*) and the New Jersey Atmospheric Deposition Network (*27*). Gas-phase PCB samples were collected over a 4-h period using high-volume air samplers (Tisch Environmental, Village of Cleves, OH) operated at a calibrated airflow rate of ~0.5 m^3 min^{-1}. Air was passed through precombusted 0.7 um pore size quartz fiber filters (QFF) to capture the particle phase. Subsequently the gas phase PCBs were captured on a cartridge containing XAD-2 resin sandwiched between two layers of polyurethane foam (PUF) whose surface area was 300 cm^2. The XAD-2 resin was used to prevent breakthrough of mono and di-chloro PCB congeners that are usually lost when PUF alone is used in gas sampling (*28*). The capturing of these lower molecular weight congeners was essential, since they exhibit some of the highest fluxes. Prior to field sampling, PUF and XAD-2 resin were cleaned by Soxhlet extraction using acetone and petroleum ether. The two high-volume samplers were modified to sample air at the two heights of the micrometeorological sensors by attaching flexible aluminum duct to their sampling ports (figure 2). The high-volume samplers consist of a vacuum pump and an oil manometer that can be connected to the vacuum pump to allow the measurement of the output pressure of the pump. The output pressure of the pump is then used to determine the air flow rate through the sampler. The samplers' oil manometers were calibrated prior to the sampling event to ensure that flow measurements were accurate. The oil 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. The Tisch adjustable orifice was connected to a water manometer that records input air flow while at the same time the oil manometer was connected to the vacuum pump. A known input flow was used that prevented the breakthrough of PCBs during sampling.

Water Phase PCB Sampling

Water phase PCB sampling followed protocols published previously (*16*). Water samples for PCB analysis were obtained by pumping water via Teflon tubing first through a filter head containing a 0.7 μm glass fiber filter (GFF) to capture particle phase PCBs, and subsequently through a Teflon column containing XAD-2 resin that captured the apparent dissolved phase PCBs.

Chemical Analysis

All PCB samples after sampling were taken within 24 hours to Rutgers University laboratories and stored in refrigerators until they were analyzed. Prior to extraction, samples were spiked with PCB surrogate standards (PCB IUPAC congener 14, 23, 65, and 166) to determine analytical recovery efficiencies. The vertical gradient PUF-XAD sandwich samples were Soxhlet extracted for 24 hours using a 4:1 (v/v) mixture of petroleum ether (PE) and dichloromethane (DCM). GFF and XAD-2 used in water sampling were Soxhlet extracted using 1:1 (v/v) hexane:acetone. In order to remove polar interferences, the XAD and GFF water sample extracts also underwent liquid-liquid extraction with 60 mL of Milli-Q® water in separatory funnels with 1 g sodium chloride. The aqueous fractions were then back-extracted with 3×50 mL hexane. QFFs were not extracted since the air particulate phase PCB do not undergo air-water exchange and are not needed in the determination of MTCs. Extracts were then concentrated by rotary evaporation and/or blowing down under a gentle stream of nitrogen. The concentrated extract requires a clean-up step prior to analysis. This was done using 3%

water deactivated alumina (Brockman neutral activity 1- mesh size: 60-325). The PCB fraction is eluted with hexane, concentrated under a gentle stream of nitrogen gas, and injected with internal standards (PCBs 30 and 204) prior to analysis.

Congener-specific quantification of PCBs was performed by an Agilent 6890 Gas Chromatograph (GC) equipped with a ^{63}Ni electron capture detector (ECD). This system uses a 60m, 5% diphenyl-dimethylpolysiloxane column (DB-5: 60m, 0.32mm ID, 0.25mm film thickness). Helium was used as the carrier gas and a P5 mixture (5%-CH_4, 95% Ar) was used as the make-up gas. Fifty-six chromatographic peaks, representing 89 PCB congeners were quantified. The ECD method has several drawbacks. First, the ECD is a non-selective detector and gives a response for any chemical that captures electrons. Because of this, organochlorine and organobromine compounds can cause interferences within the chromatogram. This is particularly a problem in the early portion of the chromatogram where mono- and di-chlorobiphenyls elute, so these congeners were not quantified. Second, when PCB congeners co-elute, they are quantified as the sum, even if the congeners have different numbers of chlorines. These problems can be overcome by using a mass spectrometry detector (MSD), but the most common MSD configuration, which features a single quadrupole, is not sensitive enough to detect PCBs in most environmental samples. Thus we have developed a method for PCB quantification on our tandem quadrupole instrument (Waters Quattro Micro GC/MS/MS) (*29*) and plan to re-analyze all of the Tappan Zee samples on this instrument.

Quality assurance and quality control was determined using laboratory 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 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 not employed.

Water column characteristics

DOC and POC sampling were conducted by filtering a known volume of river water through 0.25 μm GFF. The filtrates were analyzed for DOC while the particles that were collected on the filter were analyzed for POC and total suspended matter (TSM). These samples were sent to Chesapeake Biological Laboratories (CBL) for analysis.

Micrometeorology

Micrometeorological data was collected in order to determine the vertical fluxes of PCBs. This was carried out using two micrometeorological systems from Campbell Scientific of Logan, Utah, USA (www.campbellsci.com). The first, the Aerodynamic Gradient system, simultaneously measured temperature, water 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 74μm. These thermocouples have a resolution of 0.006°C with 0.1 μV rms noise. The water 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 to clear the air from the previous interval, while the second is when the readings are collected. The air is drawn at a flow rate of 0.4 liters/minute with 2 liter mixing chambers to give a 5 minute time constant. The Dew-10 has a resolution of approximately ±0.01 kPa. The wind speeds were measured using R. M. Young 03001-5 Wind Sentries. These include a cup anemometer and a directional wind vane. The anemometer has a range of 0 to 50 meters/second with a threshold value of 0.5 meters/second. All measurements taken with the Aerodynamic Gradient system were averaged over ten minute intervals. Figure 2 is a picture of the Aerodynamic Gradient system and Eddy correlation system in operation as well as the Hi-Vol samplers.

Figure 2. The air sampling and micrometeorology equipment set up on the south end of the Piermont pier.

The second system, the Eddy Correlation system, 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-minute averages of friction velocity and latent and sensible heat fluxes. The Eddy Correlation system consists of three sensors. First, the CSAT3 is a 3-D Sonic Anemometer that can sample at 60 Hertz, with noise in the horizontal directions of 1 mm/s, 0.5 mm/s in the vertical, and 0.002 ^{o}C for the sonic temperature measurement. The range of wind speed measurement is ±65.535 m s^{-1}. Second, 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. Third, the system also includes a

FW05 fine wire thermocouple. This is a 0.0005 inch thermocouple that measures very accurately at high sampling rates and is not affected by solar radiation.

PRINCIPAL FINDINGS AND SIGNIFICANCE

Micrometeorology

The values for the meteorological variables and the latent (Le) and sensible (H) heat fluxes given in Table 1 are averages over each sampling interval. There were two sampling events when the sensors failed (07/08 am and 07/15 pm). Average wind speeds ranged from 0.7 to 6 m s^{-1}, while the average temperatures ranged from 298.1 to 307.2 K. Because these parameters varied over a relatively small range, correlations between v_{aw} and these parameters will provide limited information. The latent heat flux was always positive, indicating that water was evaporating from the river during all samples events, as would be expected on hot summer days. The sensible heat flux was occasionally negative, indicating that the water was generally cooler than the air, again as expected for a hot summer day.

Date	**Local Time**	**Wind speed ($m\ s^{-1}$)**	**Temp (^0K)**	**u* ($m\ s^{-1}$)**	**H ($W\ m^{-2}$)**	**Le ($W\ m^{-2}$)**
07/08	11:18 – 15:20	4.77	NA	NA	NA	NA
07/08	15:40 – 18:40	4.10	304.0	0.24	-1.55	74.70
07/09	10:20 – 14:20	6.02	302.0	0.32	-1.47	180.4
07/09	15:45 – 17:10	4.53	303.5	0.29	-1.70	152.7
07/10	9:45 – 13:45	4.50	298.7	0.50	29.71	388.4
07/10	13:55 – 18:00	3.56	301.5	0.53	29.75	496.0
07/11	9:45 – 13:45	1.42	298.1	0.93	24.06	85.0
07/11	13:50 – 18:50	1.51	301.4	0.11	30.40	122.2
07/15	10:05 – 15:30	2.23	300.4	0.16	31.45	148.0
07/15	15:40 – 19:40	1.22	NA	NA	NA	NA
07/16	10:40 – 14:30	0.71	300.5	0.08	9.14	96.2
07/16	14:55 – 18:55	0.72	303.4	0.09	0.09	85.1
07/17	9:30 – 13:30	1.76	301.2	0.09	12.39	112.0
07/17	14:05 – 17:05	1.93	304.3	0.18	40.54	126.9
07/18	10:15 – 14:15	1.97	304.0	0.20	12.82	115.0
07/18	14:20 – 18:20	2.53	307.2	0.31	14.00	270.7

Table 1. Meteorological conditions at the sampling site. NA = Not available

Water column characteristics

DOC concentrations (Table 2) ranged from 3.94 to 44.09 mg C L^{-1} while POC concentrations ranged from 0.77 to 3.36 mg C L^{-1}. The DOC concentrations seem unusually high and duplicate samples are not in good agreement. In August of 2007, our research group measured DOC and POC concentrations at the pier ranging from 2.22 to 3.37 mg C L^{-1} and 0.72 to 1.45, respectively. The relative standard deviation in DOC concentrations was less than 15%. In their model of the New York/New Jersey Harbor, Farley et al (*2*) used a DOC concentration of 3.07 mg C L^{-1} and a POC concentration of 0.75 mg C L^{-1} for the Tappan Zee. This comparison supports our conclusion that the high DOC concentrations we measured in 2008 were the result of a sampling or analytical error, possible related to taking the DOC samples too close to the shore, where carbon from the nearby marsh or from goose droppings may have resulted in elevated DOC measurements.

	DOC (mg C L^{-1})		**POC (mg C L^{-1})**	
Event	**Sample A**	**Sample B**	**Sample A**	**Sample B**
07/08/08 2.30pm	3.94	23.60	1.18	1.67
07/08/08 6.20pm	25.35	14.94	1.52	1.63
07/09/08 2.30pm	18.76	16.08	1.78	2.97
07/10/08 12 noon	9.92	15.12	1.88	1.41
07/10/08 2.30pm	14.72	34.62	1.52	0.77
07/11/08 9.00am	4.62	11.95	1.22	1.29
07/11/08 1.45pm	5.42	15.19	3.36	3.62
07/15/08 8.50am	13.83	10.35	1.11	1.32
07/15/08 3.50pm	4.24	44.09	1.21	0.79
07/16/08 1.30pm	13.33	NA	3.34	NA
07/16/09 5.30pm	35.62	NA	2.00	NA
07/17/08 9.30am	9.41	20.28	1.35	1.99
07/18/08 9.00am	23.59	16.69	1.71	2.15
07/08/8 4.30am	32.52	26.57	1.77	1.65

Table 2. Dissolved organic carbon (DOC) and particulate organic carbon (POC) concentrations in duplicate samples.

Gas and water phase PCB concentrations

Table 3 summarizes the ΣPCB concentrations measured in the gas and apparent dissolved phases during the August intensive sampling campaign. The upper samples are thought to be more representative of the atmosphere as a whole. The average gas phase ΣPCB concentration in these upper samples was 0.7 ng m^{-3}, somewhat elevated over ΣPCB concentrations measured as a regional background in this area by the New Jersey Atmospheric Deposition Network (NJADN) (*27*). NJADN results suggest that the year-round background ΣPCB level is about 0.2 ng m^{-3}, with summertime concentrations perhaps a factor of two higher. Gas-phase ΣPCB air concentrations in this study were lower than the annual averages reported for Raritan Bay (1.0 ng m^{-3}) (*30*) and Jersey City (1.2 ng m^{-3}) (*27*). The PCB levels measured over the Tappan Zee are probably elevated due to volatilization out of the water column, so direct comparison with

NJADN samples may be misleading. It is possible that PCBs measured nearby, for example in the town of Piermont, would be at regional background levels.

ΣPCBs in the dissolved phase ranged from 2 to14 ng L^{-1}. This is in good agreement with data from the Contamination Assessment and Reduction Project (CARP), which measured 8 to 15 ng L^{-1} ΣPCBs in the Haverstraw Bay (Tappan Zee) region (*31*). Compared to other aquatic systems, the dissolved ΣPCB concentrations in this study were significantly higher than recently reported for southern Lake Michigan (range 0.08 – 0.48 ng L^{-1}; (*18*)), Chesapeake Bay (0.92 ng L^{-1}; (*14*)), Raritan Bay (1.4 – 1.8 ng L^{-1}; (*30*)), and New York Harbor (3.5 – 4.2 ng L^{-1}; (*30*)). These high PCB concentrations drive large volatilization fluxes and are the main reason why the Tappan Zee is an excellent location for this study.

EVENT DATE	Gas phase (ng m^{-3})		Dissolved Phase (ng L^{-1})
	Upper	Lower	
07/08/2009 am	0.78	1.43	NA
07/08/2009 pm	1.17	32.03	NA
07/09/2009 am	1.05	1.53	NA
07/09/2009 pm	1.13	1.75	8.2
07/10/2009 am	1.0	NA	NA
07/10/2009 pm	0.41	0.95	13.7
07/11/2009 am	0.43	0.66	4.4
07/11/2009 pm	0.69	2.32	7.8
07/15/2009 am	0.59	0.65	4.0
07/15/2009 pm	0.53	5.84	2.4
07/16/2009 am	0.28	0.66	2.0
07/16/2009 pm	0.67	0.56	3.3
07/17/2009 am	0.78	0.73	4.5
07/17/2009 pm	0.57	0.82	10.8
07/18/2009 am	0.52	0.88	2.0
07/18/2009 pm	0.55	0.62	2.5

Table 3. ΣPCB concentrations measured in the gas and apparent dissolved phases.

Fluxes

The difference in PCB concentration between the upper and lower air sample indicates the net flux. Here, a significant difference is defined as greater than 20%. This definition was chosen based on our long experience with side-by-side air sampling for PCBs, which typically has a reproducibility of ±20%. Of the 16 sampling events listed in Table 3, one did not yield a viable lower air sample. In 11 of the remaining 15, the ΣPCB concentration was significantly higher in the lower air sample, suggesting that the net air/water exchange flux was positive (i.e. indicating net volatilization of PCBs from the water column to the air). In the remaining four sampling events, the difference between the upper and lower gas-phase ΣPCB concentration was not significant, indicating a negligible net flux. Thus on an aggregate (ΣPCBs) basis, the net flux of PCBs is positive, as expected. Vertical ΣPCB fluxes ranged from +210 to +12,000 ng m^{-2} d^{-1} and were highest on 10th July. On this day, dissolved phase ΣPCB concentrations and latent heat fluxes were relatively high. These are the first fluxes of PCBs over water ever to be measured using the micrometeorological technique. All other studies reporting air/water exchange fluxes of PCBs used the Whitman two-film model to predict v_{aw}, as described above. For example, Totten et al. (*15*) reported ΣPCB fluxes in Raritan Bay of +400 ng m^{-2} d^{-1} and in New York Harbor of +2100 ng m^{-2} d^{-1} (the positive sign indicates the net flux results in volatilization). Nelson et al. (*14*) reported a ΣPCB flux of +2120 ng m^{-2} d^{-1} in Baltimore Harbor and Chesapeake Bay. Thus our measured fluxes are reasonable in comparison with values reported in the literature.

	PCB congener										
EVENT DATE	**17+15**	**18**	**22**	**28**	**31**	**44**	**47+48**	**52+43**	**99**	**146**	**183**
07/08 pm	942	-980	1701	1503	219	3338	1101	26	-174	626	1456
07/09 am	640	706	32	947	614	NS	NS	535	189	114	92
07/09 pm	316	464	1237	421	316	391	248	415	-24	107	30
07/10 pm	468	657	-46	-532	3337	491	315	859	NS	80	-60
07/11 am	NS	8	-17	8	NS	5	8	13	1	NS	NS
07/11 pm	37	44	NS	-22	NS	33	20	36	12	7	-1
07/15 am	NS	NS	147	-43	NS	NS	NS	NS	13	NS	-3
07/16 am	16	22	53	33	9	7	15	20	2	NS	NS
07/16 pm	NS	NS	16	-38	-12	NS	-4	-12	-2	NS	NS
07/17 am	NS	NS	12	66	-121	8	11	14	-9	NS	-21
07/17 pm	NS	68	-59	85	39	28	100	44	14	12	NS
07/18 am	111	134	76	143	103	105	23	NS	41	34	-19
07/18 pm	NS	NS	NS	588	-649	NS	105	NS	149	28	60

Table 4. Calculated air water exchange fluxes (ng m^{-2} d^{-1}) for individual PCB congeners. NS = not significant, i.e. the difference in gas phase PCB concentration between the upper and lower sampler was less than 20%.

Calculation of mass transfer coefficients must be done on a congener specific basis. Thus fluxes for selected individual congeners are presented in Table 4. The calculated fluxes for individual congeners are sometimes negative. This does not necessarily mean net absorption into the water column was occurring. Instead, these negative fluxes may have resulted from variable atmospheric conditions during those sampling periods that resulted in inverted concentration gradients. It is also possible that the occasional negative flux arises from the analytical difficulties associated with the ECD method, as described above.

	PCB congener										
EVENT DATE	**17+15**	**18**	**22**	**28**	**31**	**44**	**47+48**	**52+43**	**99**	**146**	**183**
07/09 am	5.92	5.48	NS	1.56	1.37	NC	NC	2.38	2.80	5.63	7.0
07/09 pm	2.93	3.60	9.80	0.69	0.71	2.43	0.84	1.84	NS	5.32	2.28
07/10 pm	1.53	2.0	NS	ND	3.07	1.40	0.59	1.81	NS	1.24	ND
07/11 am	NS	0.08	ND	0.03	NS	0.05	0.08	0.10	0.04	NS	NS
07/11 pm	0.35	0.34	NS	ND	NS	0.27	0.24	0.42	0.14	0.32	NS
07/15 am	NS	NS	1.60	ND	NS	NS	NS	NS	ND	NS	NS
07/16 am	0.33	0.29	NS	0.58	0.15	0.12	0.23	0.27	0.08	NS	NS
07/16 pm	NS	NS	0.29	ND	ND	NS	ND	ND	ND	NS	NS
07/17 am	NS	NS	0.03	0.29	ND	0.09	0.09	0.11	ND	NS	ND
07/17 pm	NS	0.36	ND	0.10	0.06	0.14	0.28	0.14	0.14	0.39	NS
07/18 am	1.87	1.57	2.77	1.71	1.48	1.21	0.37	NS	2.39	NS	NS
07/18 pm	NS	NS	NS	2.72	ND	NS	0.88	NS	5.46	NS	NS

Table 5. Calculated air/water exchange mass transfer coefficients (v_{aw} in m d^{-1}) for individual PCB congeners. NS = not significant, ND = not determined due to negative flux.

Mass transfer coefficients

Mass transfer coefficients (v_{aw}) were calculated from the positive fluxes by dividing by the dissolved phase PCB concentration (equation 1). Due to the very high dissolved phase concentrations compared to the gas phase concentrations, back diffusion of PCBs into the water column (i.e. the absorption flux) was negligible, so the C_a/H' term in the equation was ignored. The values of v_{aw} range from 0.03 to 9.8 m d^{-1} with a mean of 1.5 m d^{-1} and a median of 0.6 m d^{-1}. As the difference between the mean and median values suggests, the values are log normally distributed and are therefore best characterized by the geometric mean, which is 0.6 m d^{-1}. This value is in excellent agreement with values calculated from the Whitman two-film model for Baltimore Harbor and Chesapeake Bay (*14*). Similarly, Farley et al. (*2*) used a value of 0.5 m d^{-1} in their model of the fate of PCBs with three or more chlorines in the Hudson River Estuary (which includes the Tappan Zee). This geometric mean is an aggregate number, however, and v_{aw} is expected to vary with meteorological conditions and as a function of the physicochemical properties of the PCB congener.

Correlations with Meteorological Conditions and Physicochemical Properties

The proposed work hypothesized that v_{aw} for organic compounds can be accurately predicted by parameters such as wind speed and friction velocity. These relationships are shown for select PCB congeners in Figures 3-7. Sensible heat fluxes (H) displayed a negative correlation with v_{aw}, while latent heat fluxes (Le) mostly produced positive relationships (Table 6). Both wind speed (WS) and friction velocity (u*) displayed positive relationships with v_{aw}. Additionally, temperature was usually positively correlated with v_{aw}.

PCB	**H**		**Le**		**WS**		**u***		**T**	
Congener	Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2
17+15	-0.10	0.46	0.0	< 0.01	0.95	0.85	5.01	0.16	0.613	0.16
18	-0.89	0.52	0.004	0.07	1.03	0.94	7.46	0.34	0.314	0.11
22	-0.23	0.51	0.097	0.46	2.71	0.89	45.6	0.9	1.08	0.18
28	-0.03	0.15	0.013	0.68	0.18	0.11	6.65	0.52	0.241	0.5
31	0.0	< 0.01	0.006	0.78	0.218	0.15	6.41	0.8	-0.16	0.05
44	-0.03	0.25	0.003	0.16	0.782	0.83	3.93	0.46	0.219	0.26
47+48	-0.01	0.17	0.001	0.29	0.22	0.62	1.58	0.54	0.086	0.51
52+43	-0.036	0.34	0.004	0.32	0.51	0.87	5.18	0.67	0.2	0.15
99	-0.075	0.26	0.03	0.84	0.581	0.24	18.4	0.77	0.53	0.57
82+151	-0.096	0.84	-0.003	0.14	0.615	0.46	-0.03	0.33	0.75	0.19

Table 6. Correlations between v_{aw} and meteorological variables.

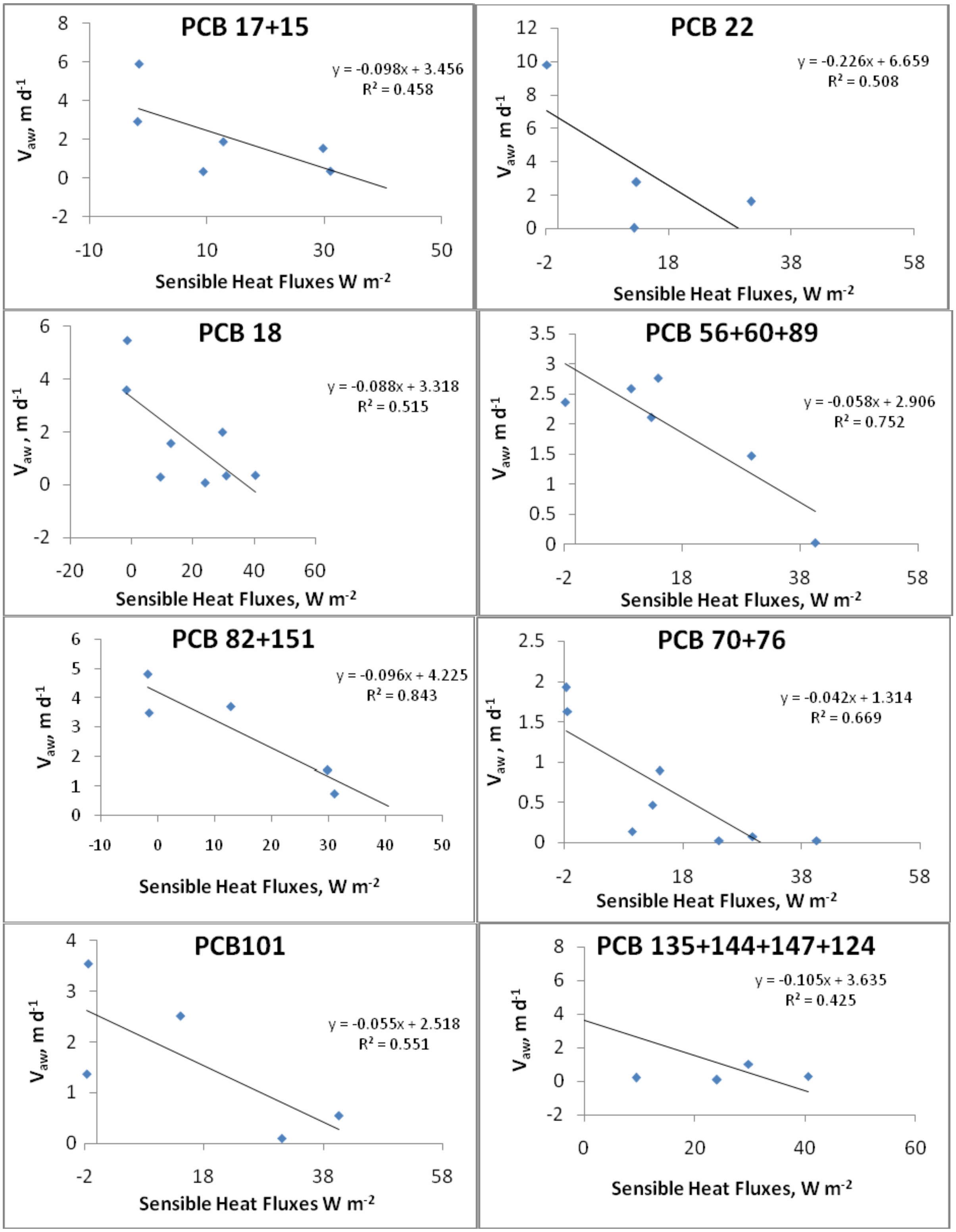


Figure 3. Correlations between v_{aw} and Sensible Heat Fluxes for select PCB congeners.

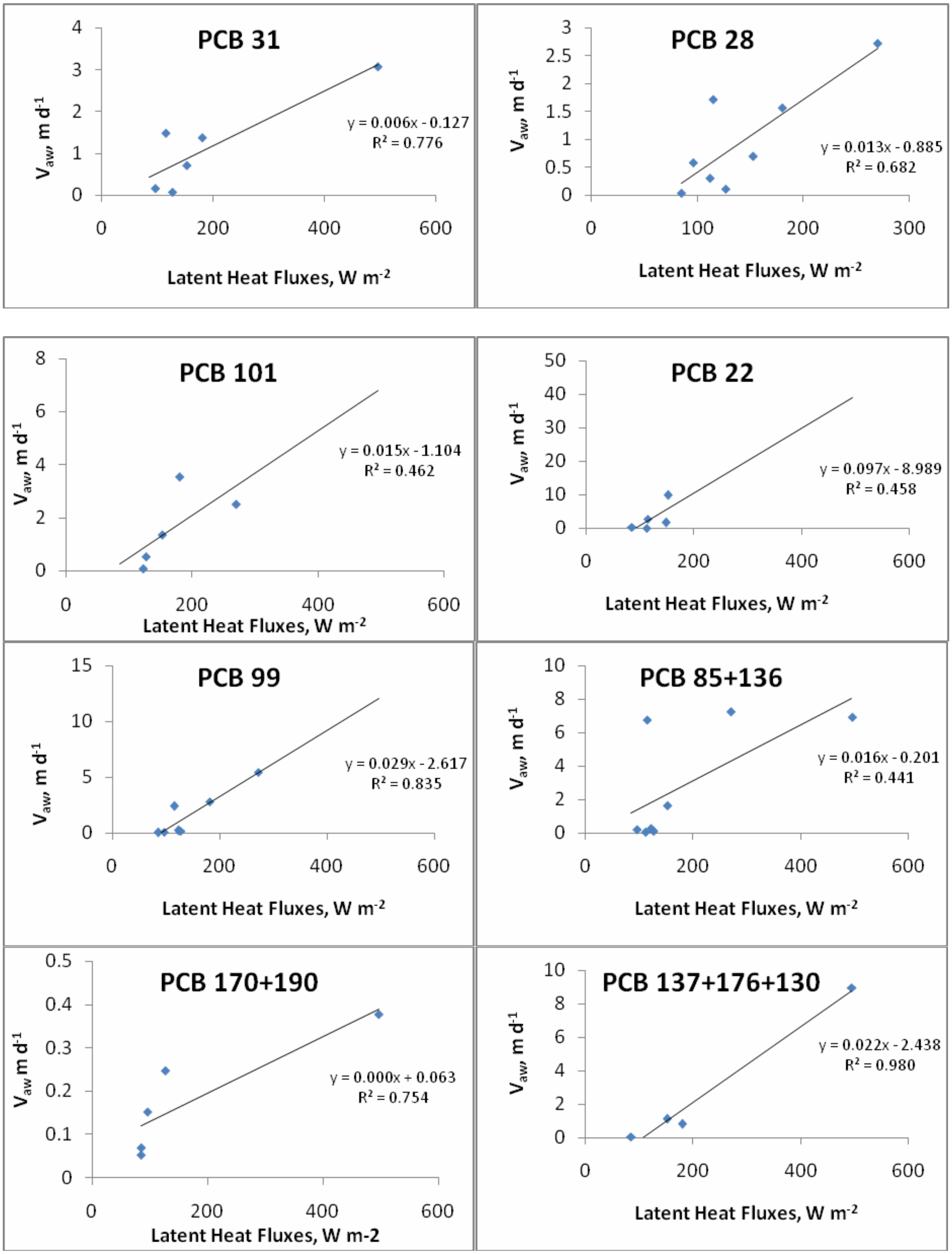
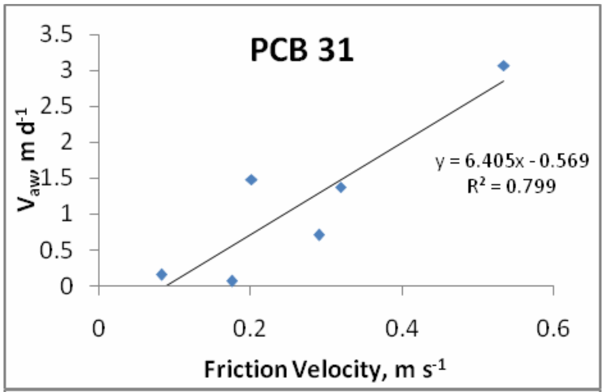
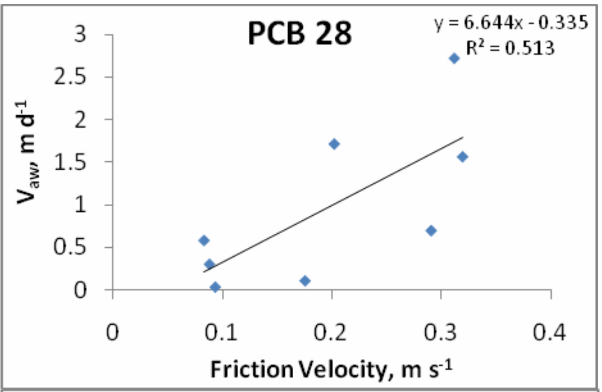
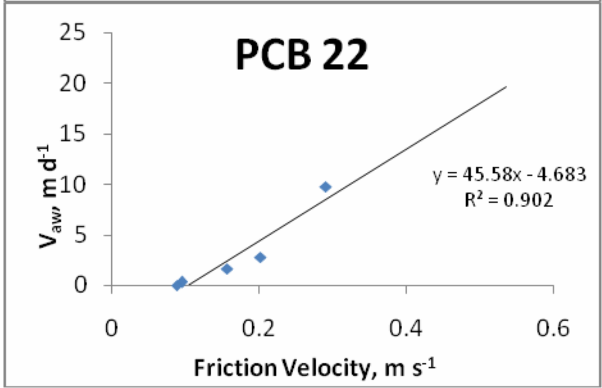
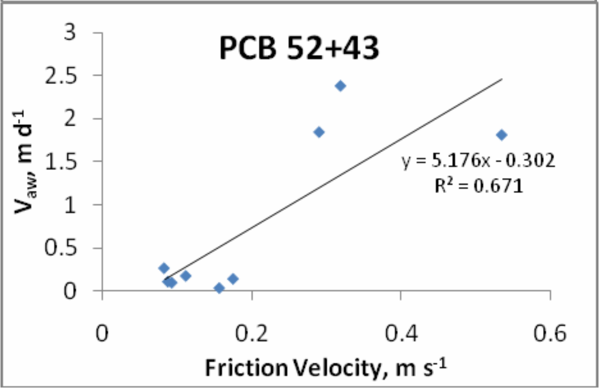


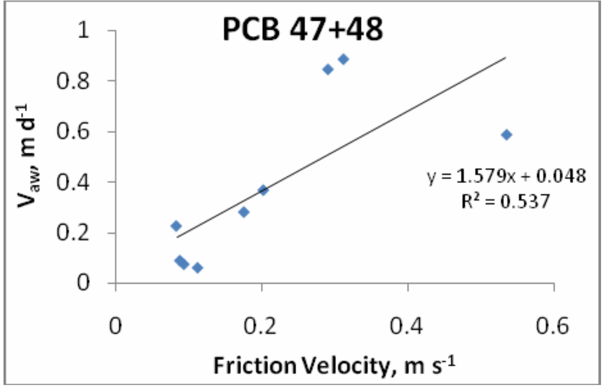
Figure 4. Correlations between v_{aw} and Latent Heat Fluxes for select PCB congeners.

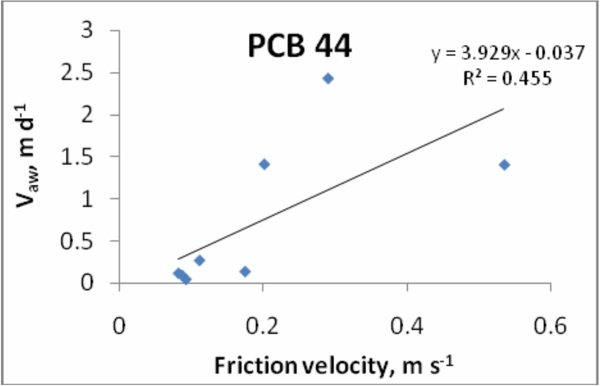

PCB 31
3.5
3
2.5
2
1.5
1
0.5
0
V_aw, m d-1
y = 6.405x - 0.569
R² = 0.799
0
0.2
0.4
0.6
Friction Velocity, m s-1

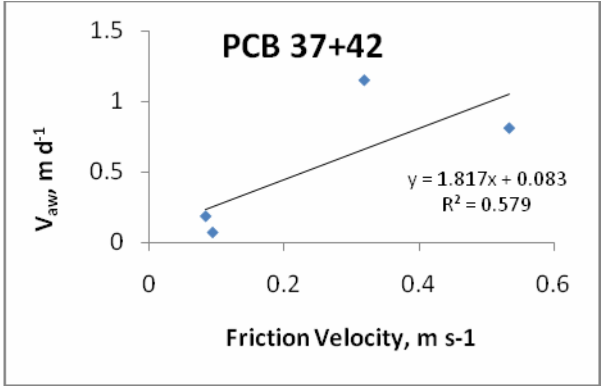

PCB 28
y = 6.644x - 0.335
R² = 0.513
3
2.5
2
1.5
1
0.5
0
V_aw, m d-1
0
0.1
0.2
0.3
0.4
Friction Velocity, m s-1

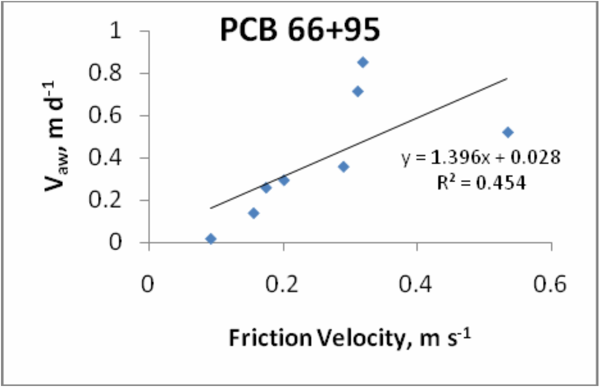

PCB 22
25
20
15
10
5
0
V_aw, m d-1
y = 45.58x - 4.683
R² = 0.902
0
0.2
0.4
0.6
Friction Velocity, m s-1


PCB 52+43
3
2.5
2
1.5
1
0.5
0
V_aw, m d-1
y = 5.176x - 0.302
R² = 0.671
0
0.2
0.4
0.6
Friction Velocity, m s-1


PCB 47+48
1
0.8
0.6
0.4
0.2
0
V_aw, m d-1
y = 1.579x + 0.048
R² = 0.537
0
0.2
0.4
0.6
Friction Velocity, m s-1


PCB 44
y = 3.929x - 0.037
R² = 0.455
3
2.5
2
1.5
1
0.5
0
V_aw, m d-1
0
0.2
0.4
0.6
Friction velocity, m s-1


PCB 37+42
1.5
1
0.5
0
V_aw, m d-1
y = 1.817x + 0.083
R² = 0.579
0
0.2
0.4
0.6
Friction Velocity, m s-1


PCB 66+95
1
0.8
0.6
0.4
0.2
0
V_aw, m d-1
y = 1.396x + 0.028
R² = 0.454
0
0.2
0.4
0.6
Friction Velocity, m s-1

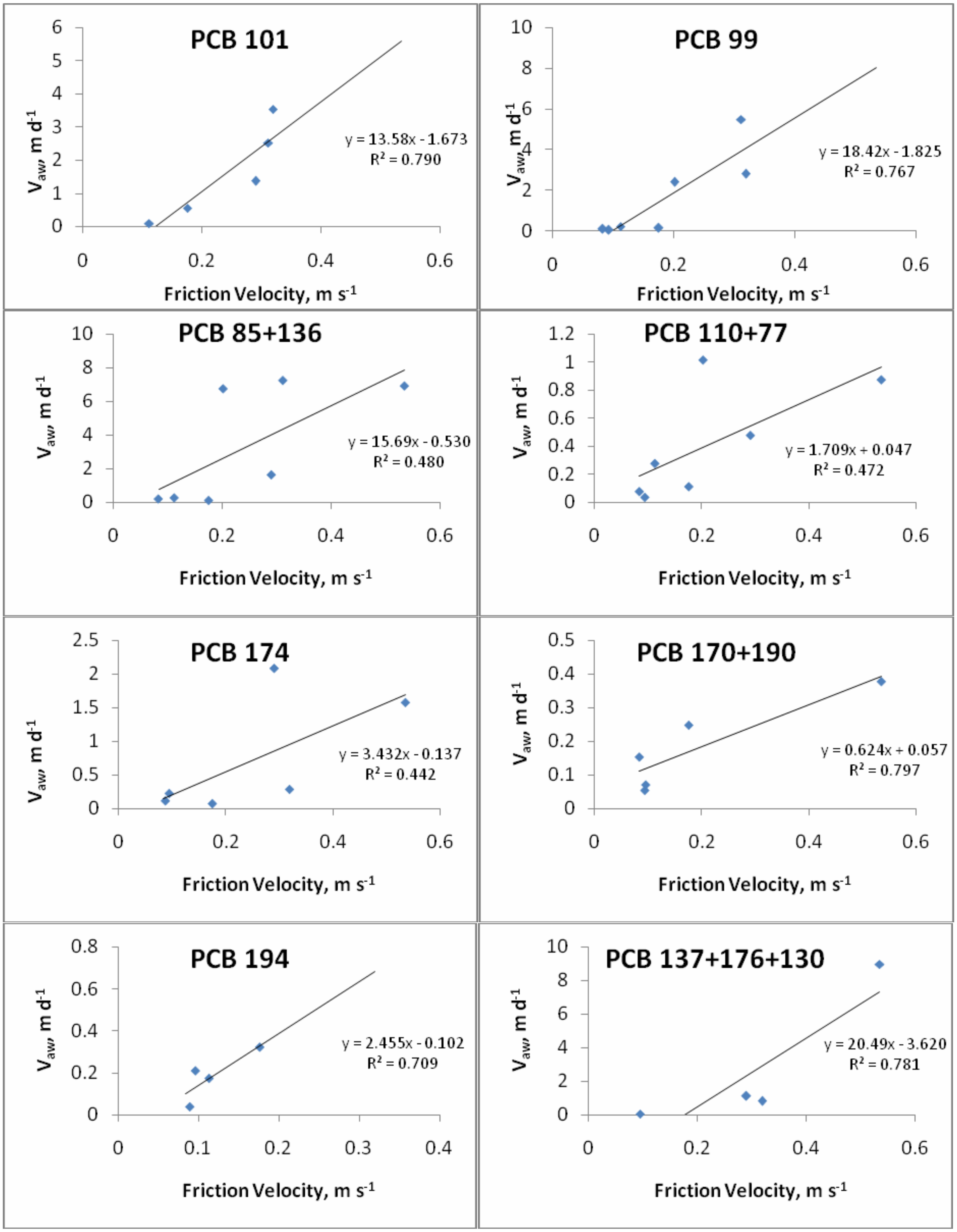


Figure 5. Correlations between v_{aw} and Friction Velocity for select PCB congeners.

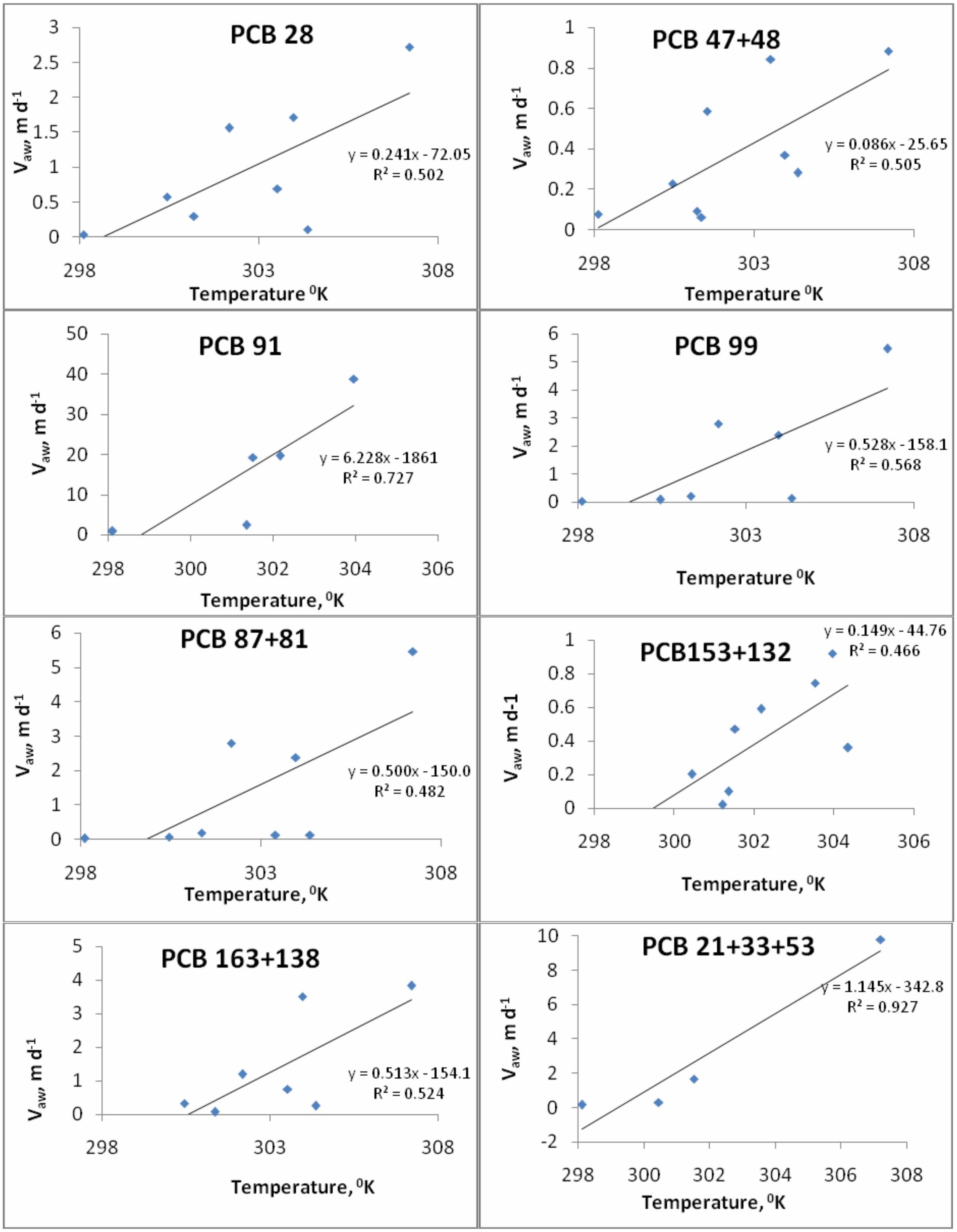
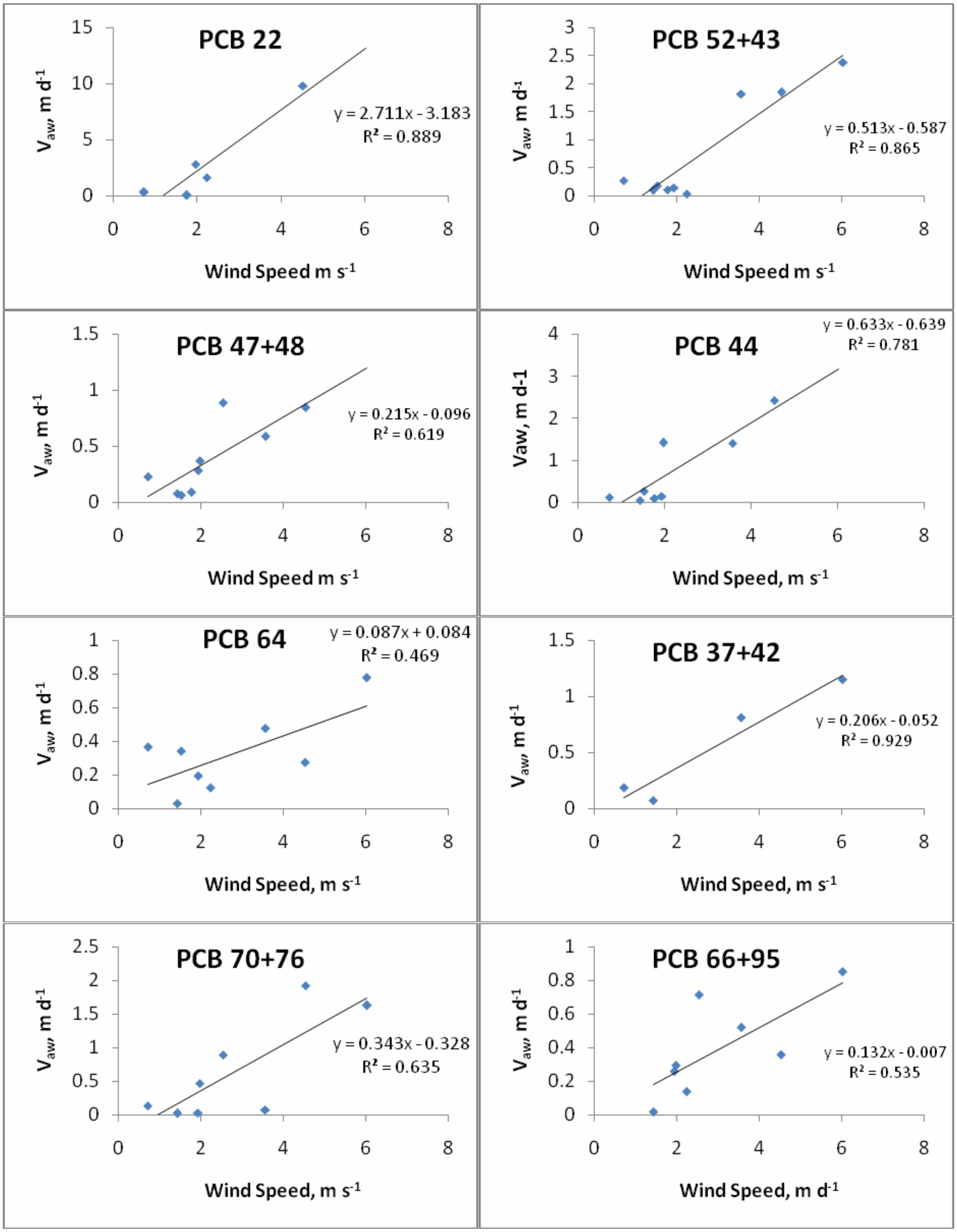


Figure 6. Correlations between v_{aw} and temperature for select PCB congeners.


PCB 22
V_aw, m d-1
15
10
5
0
0
2
4
6
8
Wind Speed m s-1
y = 2.711x - 3.183
R² = 0.889
PCB 52+43
V_aw, m d-1
3
2.5
2
1.5
1
0.5
0
Wind Speed m s-1
y = 0.513x - 0.587
R² = 0.865
PCB 47+48
V_aw, m d-1
1.5
1
0.5
0
Wind Speed m s-1
y = 0.215x - 0.096
R² = 0.619
PCB 44
Vaw, m d-1
4
3
2
1
0
Wind Speed, m s-1
y = 0.633x - 0.639
R² = 0.781
PCB 64
V_aw, m d-1
1
0.8
0.6
0.4
0.2
0
Wind Speed, m s-1
y = 0.087x + 0.084
R² = 0.469
PCB 37+42
V_aw, m d-1
1.5
1
0.5
0
Wind Speed, m s-1
y = 0.206x - 0.052
R² = 0.929
PCB 70+76
V_aw, m d-1
2.5
2
1.5
1
0.5
0
Wind Speed, m s-1
y = 0.343x - 0.328
R² = 0.635
PCB 66+95
V_aw, m d-1
1
0.8
0.6
0.4
0.2
0
Wind Speed, m d-1
y = 0.132x - 0.007
R² = 0.535

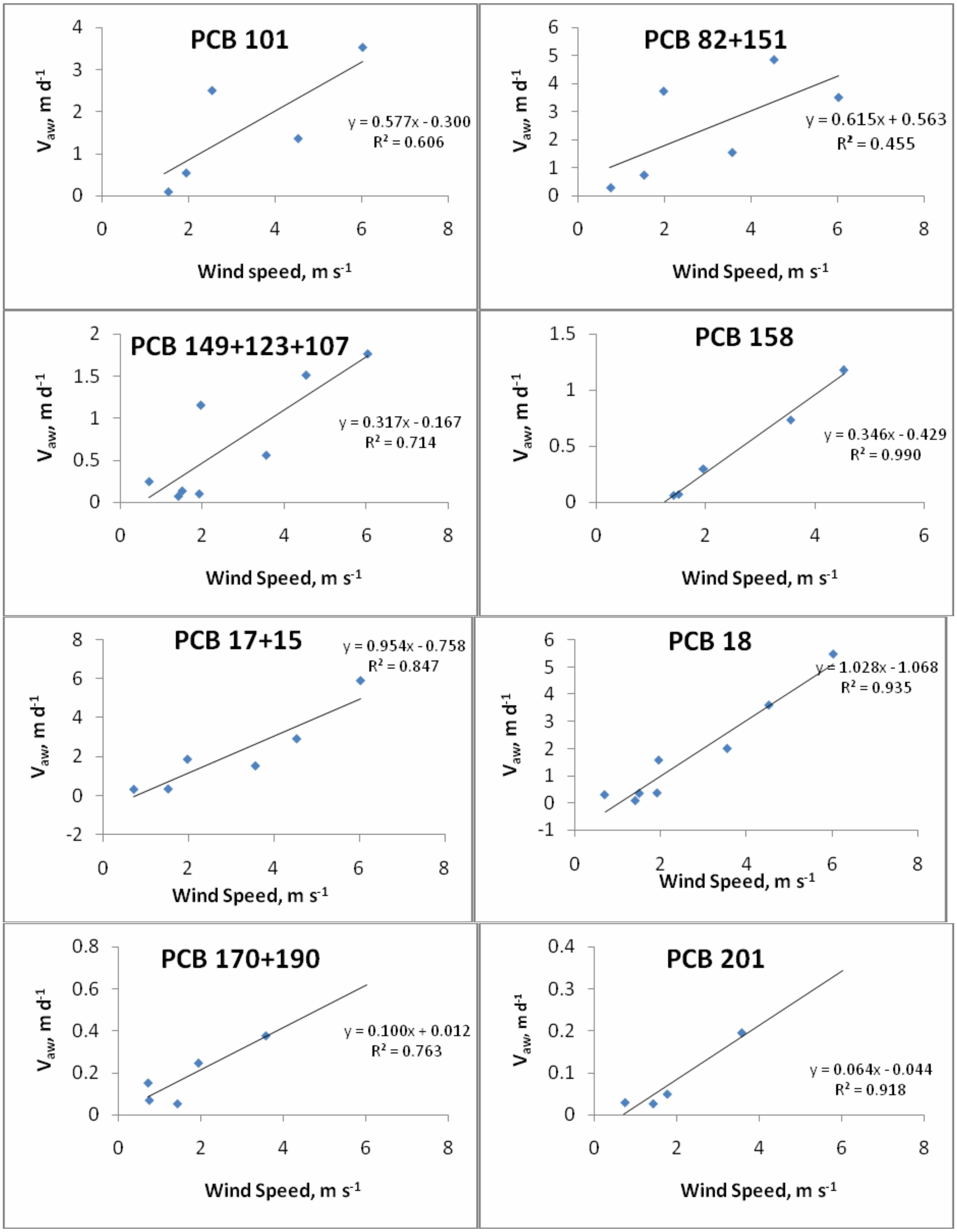


Figure 7. Correlations between v_{aw} and wind speed for select PCB congeners.

The relationship between v_{aw} and Henry's law constant was also investigated. Chemicals with H' greater than about 10^{-2} are predicted to be under water phase control (i.e. v_w dominates v_{aw}; see equation 2), and therefore v_{aw} is not a function of H'. Thus, slopes were expected to be zero. Although mostly positive slopes ranging from 0.06 to 0.8 were obtained, the p-values were not significant. Only one sampling event displayed a significant correlation between H' and v_{aw}.

EVENT	SLOPE	r^2	P value
07/09/08 am	0.69	0.01	0.04
07/09/08 pm	0.13	0.001	0.5
07/10/08 pm	0.21	0.009	0.5
07/11/08 am	0.06	0.001	0.8
07/11/08 pm	-1.15	0.11	0.1
07/15/08 am	0.59	0.06	0.4
07/16/08 am	-0.09	0.003	0.9
07/17/08 pm	0.07	0.001	0.9
07/18/08 am	0.60	0.02	0.5
07/18/08 pm	0.82	0.03	0.6

Table 7. Correlation of log v_{aw} with log Henry's Law Constant.

Significance

This study has produced the first direct measurement of the volatilization of PCBs out of the water column. As expected, the net direction of the air/water exchange flux in the highly contaminated Hudson River Estuary is positive, resulting in volatilization of PCBs out of the water column. This observation supports the conclusion that volatilization is the most important loss process for PCBs in the Hudson River Estuary. This study has also produced the first direct measurements of the air/water exchange mass transfer coefficients (v_{aw}) for PCBs. The values obtained are in good agreement with estimates calculated via the Whitman two-film model, but further study is required to determine the effects of wind speed, friction velocity and physicochemical properties on v_{aw}.

The field work performed as part of this project has yielded an excellent data set for the determination of fluxes and mass transfer coefficients for large hydrophobic organic chemicals. In future work, we will re-analyze the samples generated using a variety of methods. For better quantitation of PCBs, we will use GC/MS/MS analysis. In addition, we will analyze the samples for a variety of other organics, including organochlorine pesticides, polycyclic aromatic hydrocarbons and brominated diphenyl ethers via GC/MS methods (*32*-*34*). The results will provide v_{aw} values for organic compounds with a wider range of physicochemical properties, allowing a better analysis of the effects of these properties on the mass transfer of these chemicals across the air/water interface.

Despite its strengths, the data set collected in this study has a crucial weakness. All of the field work was performed in one month, when the temperature varied little (less than 10°C) and the water column characteristics (i.e. POC) were relatively stable. The range of wind speeds sampled was also relatively small from 0.7 to 6.0 m s^{-1}. A more thorough understanding of the effects of meteorology and water column dynamics on the air/water exchange of organic chemicals will require additional field campaigns. Ideally three to four additional campaigns in all four seasons would be performed.

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Process-based modeling of nitrogen removal dynamics in brownfield and intact remnant wetland systems

Basic Information

Title:	Process-based modeling of nitrogen removal dynamics in brownfield and intact remnant wetland systems
Project Number:	2008NJ156B
Start Date:	3/1/2008
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Research Category:	Climate and Hydrologic Processes
Focus Category:	Nitrate Contamination, Wetlands, Hydrology
Descriptors:	None
Principal Investigators:	Monica Marie Palta, Joan G. Ehrenfeld

Publication

1. Palta, Monica M. 2008. Composition and distribution of vegetation, soils, and hydrologic conditions as predictors of denitrification hotspots and hot moments in urban riparian ecosystems. Preliminary proposal for PhD research (defended and accepted by Department of Ecology & Evolution, Rutgers University, New Brunswick, NJ, 10/24/08). 25 pp.
2. Lafond, Jonathan. 2008. Carbon fractionation of an urban wetland soil. Research project written to fulfill requirements for Independent Research in Biology, Rutgers University, New Brunswick, NJ. 15 pp.

Project summary:

Problem and Research Objectives

Nitrogen (N) removal is commonly cited as a rationale behind wetland restoration projects, since wetlands have demonstrated the ability to prevent movement of excess N from upland areas into streams through the microbial process of denitrification. As important as N removal is to ecosystem health, however, there are few locations with measurements adequate to quantify denitrification rates and how they vary at a range of spatial and temporal scales. Further, despite a broad understanding of the multiple environmental factors that control rates of denitrification, we have limited ability to integrate this knowledge to construct and validate robust and predictive numerical models of denitrification. Wetlands in urban settings pose a particular challenge in linking ecosystem services (like denitrification) with their environmental drivers, mainly because urban wetlands have been little studied, and each urban system has its own unique set of altered conditions. These issues are especially true of wetlands that develop on brownfield sites, on highly modified soil materials.

Though “hot spots” and “hot moments” have been identified by a number of comparative studies (where certain areas or time periods exhibit higher denitrification than others), none have undertaken the identification of periods or areas of high denitrification through quantitative modeling or spatial analysis of the process. I proposed to undertake process-based modeling to identify and predict the occurrence of “hot spots” and “hot moments” of denitrification in the urban wetland environment. My study objective was to collect the data needed to utilize a process-based model (DeNitrification-DeComposition, or DNDC (Li et al. 1992)) for an urban wetland site; this model was to be used to identify and predict hot spots and hot moments of denitrification within the site.

Methodology

For this study, I identified a highly modified wetland in Hudson County, NJ (Liberty State Park). Soils at this site are a mix of trash, construction fill and partially decomposed organic matter, and the wetland is dominated by *Phragmites australis,* an invasive grass. Water sources come from stormwater, precipitation and shallow groundwater.

NO_3^- removal via denitrification is a process mediated by three controlling factors: (1) the availability of organic carbon substrate (C); (2) the availability of nitrate (NO_3^-); and (3) the presence of suboxic (<0.2 mg O_2/L) conditions. The study wetland has two potentially important gradients across which denitrification dynamics could vary: first, a gradient of moisture (i.e. elevation), with the wettest area being where standing water is found and the driest area being at the edges of the *Phragmites* stand; second, a gradient of exogenous NO_3^- inputs, with the highest input being near the inflows feeding the wetland. I have therefore divided the wetland into discrete areas based on elevation and surface water inputs using a topographic map and a dye test during a storm event, to determine where and at what rate surface water is reaching various points across the wetland. Within each area, measurements relevant to parameterizing and validating the process-based model of denitrification (i.e. measurements creating a water, C, and N budget for each area) were taken. I am in the process of compiling my collected data and plan on simulating denitrification dynamics at the site on a daily time step for one year (2008-2009).

To create a water budget for each discrete area, I measured the following parameters: total daily precipitation (using NOAA climate stations near the study sites), runoff inputs and outputs, groundwater inputs and outputs (using autowells and piezometers), and evapotranspiration. Temperature of the soil was determined using NOAA climate station data. Key soil properties influence water movement and temperature fluxes through the soil. I therefore measured the following key soil properties to develop my model: bulk density, wilting point and field capacity, and porosity.

The study wetland exhibits high variability in the amount of C available to denitrifying bacteria, since the depth of the organic layer, density of vegetation (presence/absence of vegetation and root:shoot biomass of individual plants), and dissolved organic C (DOC) available from surface inflows all exhibit high spatial variation. These variables, as well as the percent total organic matter and light and heavy fractions of C available in the soil, were quantified for the discrete wetland areas. Plant C:N ratio of the roots, shoots and seeds of five clumps of plants distributed across the length of the wetland were measured as a determinant of plant uptake of inorganic N, and as a determinant of N inputs from *Phragmites* litter.

To create an N budget for the wetland relevant to wetting and drying cycles, NO_3^- concentrations in rainfall and stormwater were measured. Endogenous NO_3^- production will be simulated when the model is run based on the "anaerobic balloon" approach used in the DNDC model. The model will be simulated for a one-year period, based on climate data from 2008-2009, once it is obtained from NOAA. Model output will be examined for areas across space and over time that demonstrate significantly higher denitrification levels than adjacent areas and time periods. A sensitivity analysis will be used to judge which model parameters are most important in driving high levels of denitrifier activity.

To test how accurately the model predicts denitrification rates in the soil, field measurements of denitrification have been collected and will continue to be collected using pore water collectors (peepers); pore water will be analyzed for dissolved gas content using the membrane inlet mass spectrometer (MIMS).

Principal Findings and Significance

The DNDC model has not been run yet, so I still have to determine where and when the hot spots and moments of denitrification occur in the study wetland. However, I do have some interesting initial findings that are suggestive of spatial patterning in denitrification dynamics across the wetland. The soil profile in the study wetland appears to be composed of two layers in the upper surface: an O horizon of highly organic (42 ± 2% organic matter) muck composed of partially decomposed plant material, underlain by rocky gravel with occasional pieces of trash. Soil profiles were highly heterogeneous in their structural and chemical properties, both horizontally and vertically: depth of the organic layer, soil C fractions within the organic layer, and hydraulic properties through the vertical profile varied greatly. Organic layer depth differed in some cases by 20 cm or more between points less than 8 meters apart in horizontal space. Variation in soil C fractions over horizontal space was high (Figure 1). Surprisingly, however, variation between sample points in relative amounts of light and heavy C fractions within the organic layer appeared to be independent of whether or not the soil at a particular sampling point had vegetation growing on it (Figure 1). This trend suggests that mixing and exchange of sediments is likely high throughout the wetland (Figure 1). It is expected that when the model is run, the presence or absence of plants will not factor heavily into the C budget of a given area. The presence of plants may, however, influence the N budget of a particular area, by competing with denitrifiers for NO_3^-.

The latter will be revealed by examining the C:N ratios of the plants. The spatial heterogeneity in availability of C will likely play a large role in creating denitrification hotspots, where areas with high C availability (i.e. high relative free light fractions, and a deep organic layer) will also have high rates of denitrification.

NO_3^- concentrations in the soil were below detection limit; this is either indicative of low levels of endogenous NO_3^- production (nitrification), or it is indicative of tightly coupled denitrification and nitrification in time and space. This distinction will be confirmed by running the model, which simulates endogenous NO_3^- production. Stormwater samples, once run for NO_3^-, will indicate whether storm events (which supply exogenous NO_3^-) or wetland drydown events (when endogenous production of NO_3^- is high) are more important in driving hot moments of denitrification.

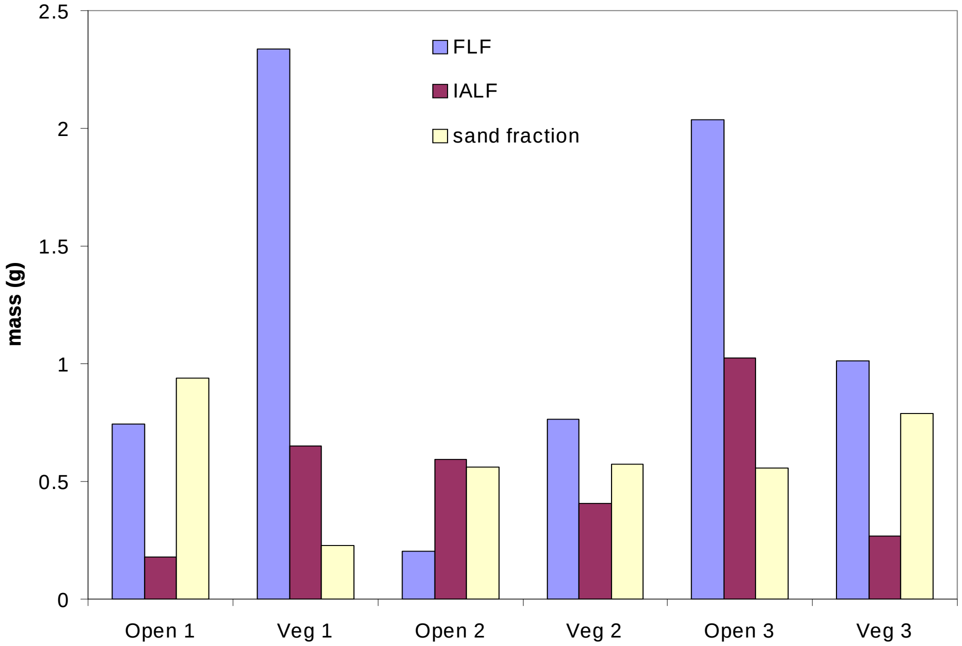

Figure 1. Soil C fractions by mass in grams in open (“open”) and vegetated (“veg”) sites (numbers refer to site location). FLF = free light fraction, IALF = intra-aggregate light fraction.

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PBDEs and Other Brominated Compounds in a Bioreactor Landfill

Basic Information

Title:	PBDEs and Other Brominated Compounds in a Bioreactor Landfill
Project Number:	2008NJ157B
Start Date:	3/1/2008
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Focus Category:	Wastewater, Groundwater, Water Quality
Descriptors:	None
Principal Investigators:	Jennifer Loudon, Donna E. Fennell

Publication

1. Loudon, Jennifer; Keith R. Cooper, Uta Krogmann, Beth Ravit, and Donna Fennell. 2008. Fate of chlorinated ethenes in landfill microcosms. New Jersey Water Environment Association 93rd Annual Conference, Atlantic City, NJ. (poster presentation)
2. Loudon, Jennifer; Keith R. Cooper, Lori A. White, Uta Krogmann, Beth Ravit, and Donna Fennell. 2008. Chlorinated ethenes in landfill microcosms. Society of Environmental Toxicology and Chemistry- North America 29th Annual Meeting, Tampa, FL (poster presentation)
3. Loudon, Jennifer; Keith R. Cooper, Lori A. White, Uta Krogmann, Beth Ravit, and Donna Fennell. 2009. Reductive Dechlorination of Tetrachloroethene and Trichloroethene in Landfill Microcosms. Battelle: The Tenth International In Situ and On- Site Bioremediation Symposium. Baltimore, MD (poster presentation)
4. Loudon, Jennifer; Keith R. Cooper, Lori A. White, Uta Krogmann, Beth Ravit, and Donna Fennell. 2009. Reductive Dechlorination of Chloroethenes in Landfill Microcosms. Battelle: The Tenth International In Situ and On- Site Bioremediation Symposium. Baltimore, MD (invited guest speaker)
5. Loudon, Jennifer; Keith R. Cooper, Lori A. White, Uta Krogmann, Beth Ravit, and Donna Fennell. 2009. Anaerobic Dehalogenation of Chloroethenes in Landfill Microcosms. New Jersey Water Environment Association 94th Annual Conference, Atlantic City, NJ (poster presentation)
6. Loudon, Jennifer; Keith R. Cooper, Lori A. White, Uta Krogmann, Beth Ravit, and Donna Fennell. 2009. Dechlorination of Chloroethenes in Landfill Microcosms. American Society for Microbiology 109th General Meeting, Philadelphia, PA (poster presentation)

Project Summary

Problem - Polybrominated diphenyl ethers (PBDEs) have been considered the next PCBs by many in the environmental field (La Guardia et al., 2007). These compounds have been used over the past 30 years as added flame retardants in furniture and carpeting, electronic equipment, vehicles, and building materials/polyurethane foam (Hale et al., 2006). When the treated material is thrown away in the garbage, it is brought to a landfill where it is "never heard from again". The average person does not stop to think about the fate of that additive over time. Once the PBDE treated material is in a landfill system, the solid material will start to break down into smaller particles. The problem is that PBDEs are very lipophilic so they will stay sorbed to these particles as they percolate down through the landfill mound into the leachate. The leachate then gets sent to a wastewater treatment facility and released into the environment as treated effluent. PBDEs have two possible fates within the wastewater treatment plant. If the particles are small enough to pass through the settling tanks and remain in the final effluent, they may eventually be deposited in the sediment of the receiving water. PBDEs sorbed to larger particles will accumulate in the sludge from the wastewater treatment facility. If this sludge is then used for land application, the accumulated PBDEs enter the soil. Currently there is a growing amount of research looking at these compounds in wastewater treatment systems, but if we could identify and possibly enhance the natural debromination of these compounds to desirable end products while they are still in the landfill system, then that would take much of the burden off of the wastewater treatment plants. This could potentially decrease the concentrations of PBDEs and other brominated organic compounds finding their way into the rest of the ecosystem.

Research Objectives - Qualitatively determine the diversity of microbes in the BCRRC landfill leachate and solids. Identify dehalogenators present. Through microcosms using landfill waste, stimulate dehalogenation of halogenated organic compounds that may be found in a landfill. Obtain toxicological information about the landfill using *Danio rerio* (zebrafish) as a model organism.

Methodology - All landfill materials were collected from Burlington County Resource Recovery Center (BCRRC), Bordentown, New Jersey. An embryo larval assay (ELA) was conducted on *Danio rerio* (zebrafish) using exposure concentrations of 0.5%, 1%, 2%, 4%, 8%, 16%, and 32% (volume per volume) whole leachate in embryo rearing solution. The experiment was terminated after 72 hours of exposure. This protocol follows the procedure used by Kaur et al. (1996). Anaerobic microcosms were created using fine solids (170 mg/L total solids) elutriated from cheesecloth-enclosed landfill waste suspended in anaerobic mineral medium (personal communication, Professor Francis de los Reyes of North Carolina State University, December 2007). Killed and live experimental microcosms were created in triplicate and initially amended with 10 μmol tetrachloroethene (PCE) and 10 μmol trichloroethene (TCE) as model halogenated compounds. Similar microcosms were developed using landfill leachate solids that were concentrated 10 times via centrifugation. Killed and live experimental microcosms were created in triplicate and initially amended with 10 μmol PCE as a model halogenated compound. 250 μL of headspace from the microcosms was used for gas chromatography coupled to flame ionization detection to quantify methane and chlorinated ethenes. Samples from the elutriated landfill fine solids, whole leachate and experimental microcosms were centrifuged and the pellet collected for DNA extraction. DNA from the landfill materials was extracted using the Ultra Clean Power Soil DNA Kit (MoBio Laboratories). Amplification of 16S rRNA genes was performed using polymerase chain reaction (PCR) with primers universal to eubacteria (Muyzer et al., 1993). Denaturing gradient gel electrophoresis (DGGE) was performed on the PCR products using the D-Code universal mutation detection system (BioRad Laboratories). The products were applied to a 8% polyacrylamide gel containing a urea-formamide denaturant gradient from 35% to 70%. Electrophoresis was carried out for 4.5 hours at 150 V (Muyzer et al., 1993).

Principal Findings and Significance - The ELA indicated that landfill leachate is highly toxic to zebrafish. We observed 100% mortality within 24 hours in solutions containing 32% and 16% leachate by volume. The 8% solution exhibited 100% mortality within 72 hours. Figure 1 shows some of the common lesions displayed by the surviving larvae after 72 hours of exposure.

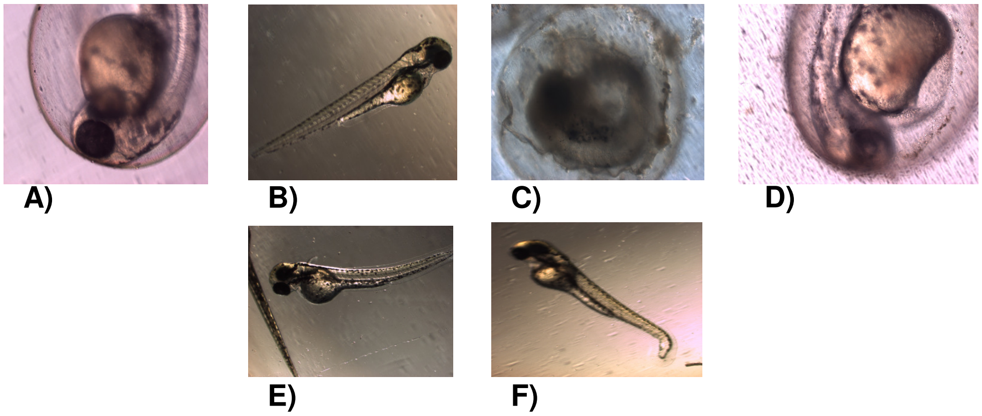

Figure 1- Embryo Larval Assay (ELA). A) 48 hours: control (0%). B) 72 hours: control 0% C) 72 hours: 8%. D) 48 hours: 4%. E) 72 hours: 1%. F) 72 hours: 4%

Swelling and hemorrhage (D), spinal and tail curvature (E and F, respectively), slowed motility, and reduced heart rate were observed in many of the treatments. These results correspond with previous studies exposing Japanese Medaka to landfill leachate (Kaur et al., 1996). In the future, we will use embryo-larval analysis as an analytical tool to assess how the biotransformation activities, such as dehalogenation, affect leachate toxicity.

Using PCE and TCE as model halogenated compounds we were able to illustrate that dehalogenation may occur in a landfill system. We observed dechlorination of PCE to ethene via TCE, *cis*-1,2-dichloroethene (cDCE), and vinyl chloride (VC) in PCE-amended live microcosms developed with solids concentrated from landfill leachate. Dechlorination products were not detected in PCE-amended killed (autoclaved) microcosms (Figure 2). We observed dechlorination of PCE to cDCE as a final product in PCE-amended live microcosms developed with elutriated landfill solids. Despite multiple PCE respiking events over 400 days, no further dechlorination of cDCE was observed. Dechlorination products were not detected in PCE-amended killed microcosms (Figure 3). Both sets of live microcosms continued to produce methane (Figure 4). In the future, we will be creating new microcosms using other halogenated organic compounds (i.e. brominated) as amendments.

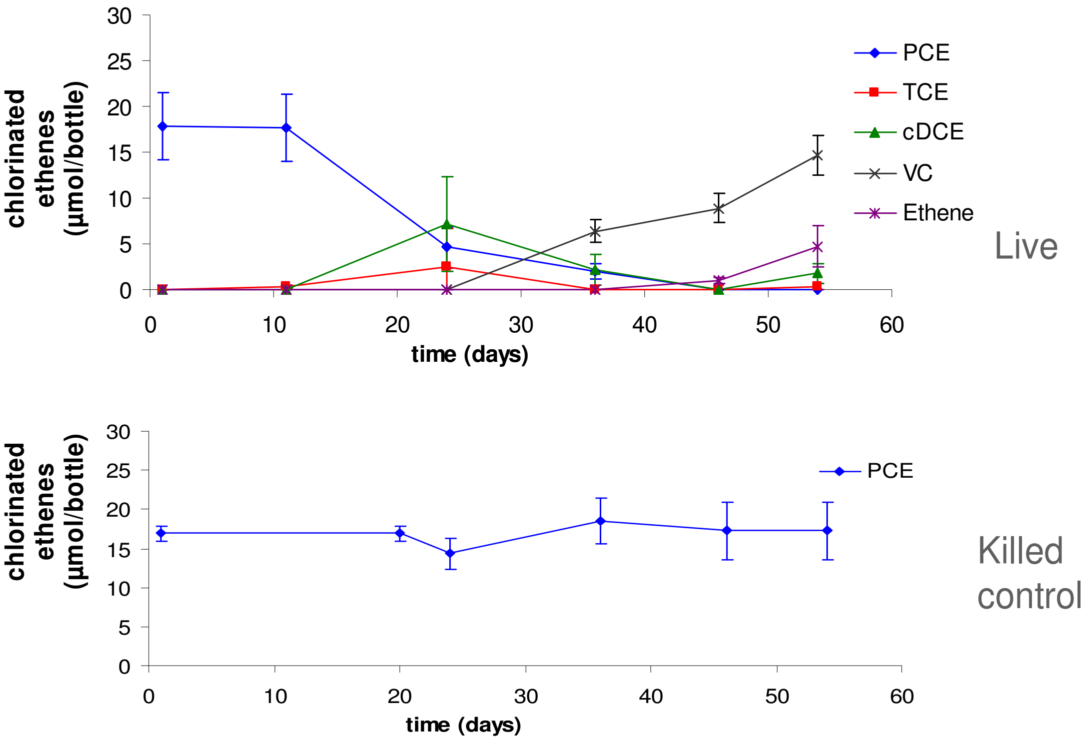

Figure 2 – Concentrated leachate solids- live and killed control. Symbols are averages of triplicate bottles and error bars represent one standard deviation.

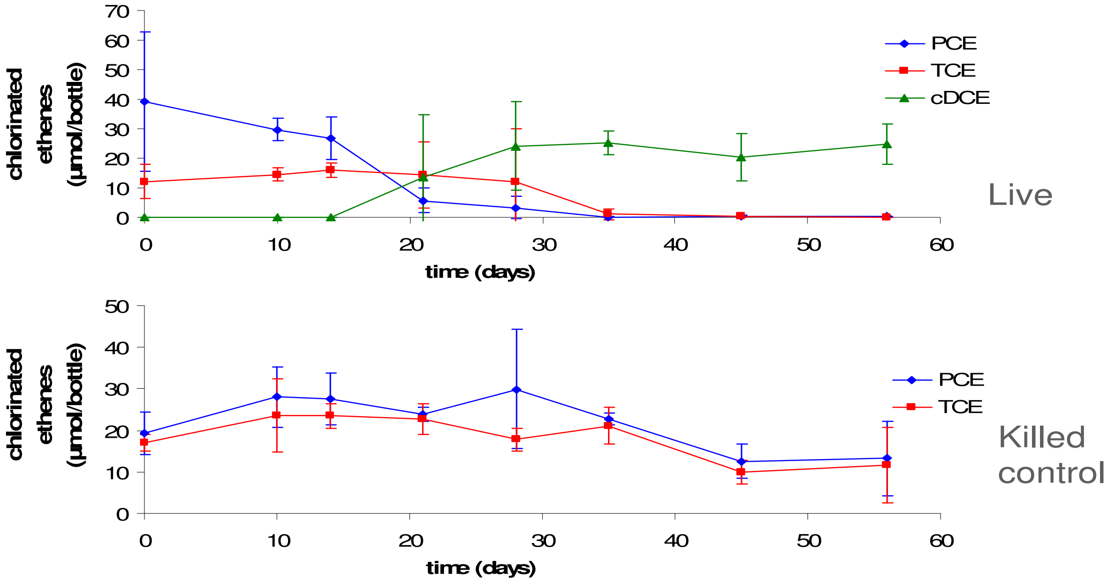

Figure 3 – Elutriated solids microcosms- live and killed control. Symbols are averages of triplicate bottles and error bars represent one standard deviation.

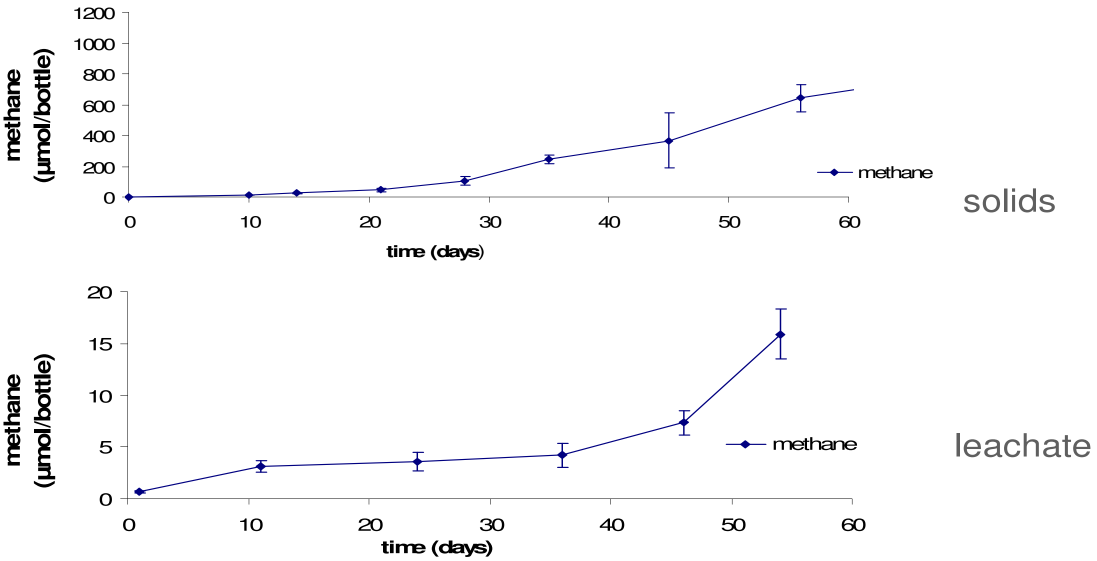

Figure 4 – Methane production in live microcosms. Symbols are averages of triplicate bottles and error bars represent one standard deviation.

PCR-DGGE analysis of bacterial 16S rRNA genes from landfill materials and microcosms suggest significant differences between original material and the communities enriched under varying conditions (Figure 5). Preliminary sequencing results suggest the presence of *Clostridium, Actinobacterium, Dehalococcoides, Bacteroidetes,* and *Pseudomonas* within the landfill; these results correspond with previous studies (Huang et. al., 2004). Further work is needed to determine all of the identities of bacterial community members visualized on the DGGE gel.

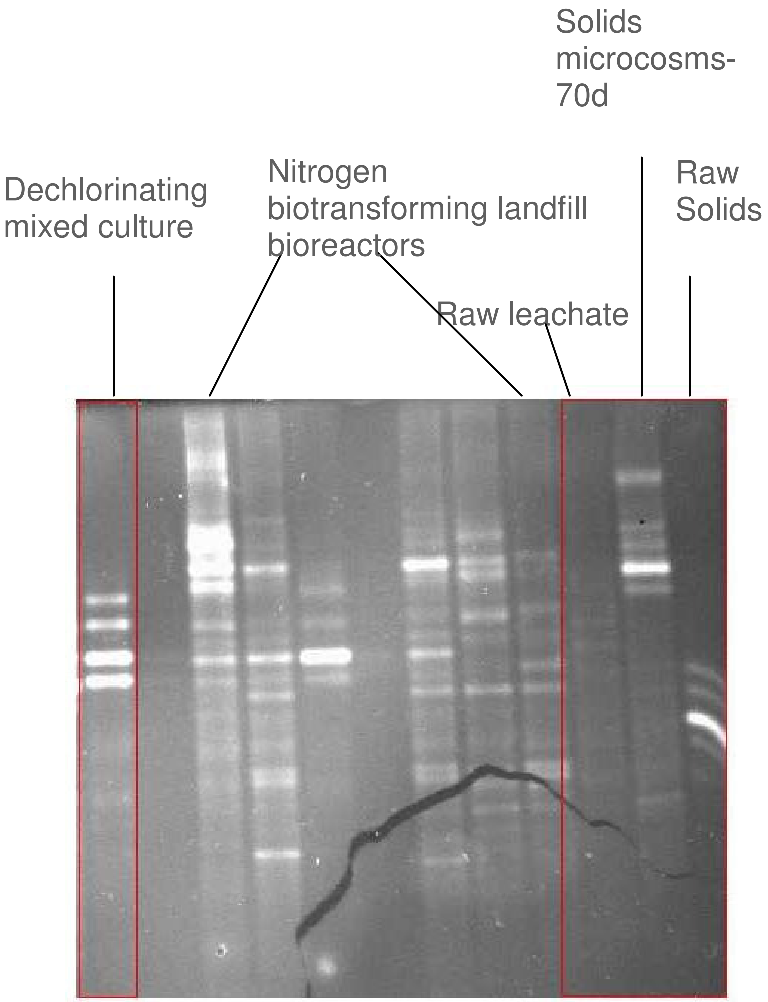

Figure 5 – Denaturing Gradient Gel Electrophoresis (DGGE) results.

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Microbial Mobilization of Arsenic and Selenium Oxyanions in Subsurface Aquifers

Basic Information

Title:	Microbial Mobilization of Arsenic and Selenium Oxyanions in Subsurface Aquifers
Project Number:	2008NJ161B
Start Date:	3/1/2008
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Focus Category:	Groundwater, Toxic Substances, Water Quality
Descriptors:	None
Principal Investigators:	Ines Rauschenbach, Max M Haggblom

Publication

1. Rauschenbach, I. and Max M. Häggblom. 2008. Ubiquitous Microbial Respiration of Selenium Oxyanions in Soils and Subsurface Aquifers. American Society for Microbiology General Meeting, Boston, MA. (poster presentation)
2. Rauschenbach, I., Narasingarao, P. and Max M. Häggblom. 2009. Selenium Oxyanion Reduction – A Ubiquitous Process in the Environment. American Society for Microbiology General Meeting, Philadelphia, PA. (poster presentation)

Project Summary:

Problem and Research Objectives

Arsenic (As) and selenium (Se) toxicity, and their ever-increasing contamination of groundwater and soil, has become a global concern threatening the lives of tens of millions of people. High concentrations of selenium in tissues can cause birth-defects and other malformations in fish and waterfowl (Muscatello et al. 2006; Narasingarao 2006). Long-term exposure to arsenic may cause skin lesions, circulatory disorders, diabetes, arsenicosis, arseniasis, and death (Bhattacharyya et al. 2003; Stolz et al. 2006). In order to prevent high concentrations of arsenic and selenium in groundwater, national and state-wide standards have been established. The NJ Department of Environmental Protection sets an upper concentration limit in ground water of 5 ppb for arsenic and 50 ppb for selenium (Obropta and Evrard 2005).

As and Se are ubiquitous oxyanions naturally found in aquatic and terrestrial environments. Arsenic is commonly found in sedimentary and volcanic rocks, fossil fuels and ores of metals, such as lead, copper and gold (Stolz & Oremland, 1999; Oremland & Stolz, 2003). Selenium is also found in fossil fuels, as well as in shales and alkaline soils. The natural abundance of both elements is low, less than 0.0002% for arsenic and less than 0.0001% for selenium, but they can easily accumulate to micro molar concentrations under certain environmental conditions (Stolz and Oremland 1999). Anthropogenic sources, such as mine drainage, combustion of fuel and coal (fly ash and flue gas) and run-off from irrigated selineferous soils contribute to accumulation of both elements (Narasingarao and Häggblom 2007a).

Speciation of As and Se, which affects their toxicity and mobility in the environment, is greatly affected by both environmental conditions and activity of the microbial population that mediate the transformations (Oremland and Stolz 2003). Arsenic has four oxidation states, but As(V) and As(III) are the most prevalent in nature. Arsenate (As(V)) is mainly associated with aerobic environments and is readily adsorbed to the surface of several common minerals that reduce its hydrologic ability and thus make it a less toxic compound in the environment. Arsenite (As(III)) is prevalent in anaerobic conditions. It adsorbs less strongly and to fewer minerals and is therefore more mobile and more toxic. The soluble forms selenate (Se(VI)) and selenite (Se(IV)) are the primary forms of selenium in oxic environments and both are toxic. Elemental, water-insoluble selenium (Se(0)) is the dominant species in anoxic sediments and is non-toxic. The oxidation and reduction of the As and Se are mediated predominantly by the microbial populations present in the subsurface environments (Stolz and Oremland 1999; Smedley and Kinniburgh 2002).

Dissimilatory selenate and arsenate reduction is the process which utilizes oxyanions as alternate terminal electron acceptors in the electron transport chain for anaerobic respiration. Selenate is thereby sequentially reduced from selenate to selenite to elemental selenium, and arsenate is reduced to arsenite. Selenate/selenite and arsenic respiration display a broad phylogenetic diversity. They can be found among archaea (selenate reduction only), thermophilic bacteria, Proteobacteria, Deferribacters, Firmicutes, and Actinobacter (Narasingarao and Häggblom 2007a). Over the past several years, concerted efforts have been made to isolate and characterize new microbial species. Identifying the environments where these elements play a role, and subsequent development of selective media, has led to an increasing number of new isolates. Our lab has also isolated several new selenate-respiring bacteria that are phylogenetically and physiologically diverse (Narasingarao and Häggblom 2006; Narasingarao and Häggblom 2007b). Their ability to use terminal electron acceptors such as selenate, selenite, arsenate, nitrate, sulfate, and/or iron plays a major role in the oxidation of organic carbon in sediments and contributes to the biochemical cycling of these elements in nature.

Despite identification of many new isolates and ongoing research on the reduction and oxidation of the As and Se oxyanions that has taken place, we still do not know much about the physiology and ecology of the diverse group of bacteria that mediate these processes. To date, only the respiratory arsenate reductases (Arr) from *Chrysiogenes arsenatis* and *Bacillus selenitireduces* and one selenate reductase from *Thauera selenatis* have been purified (Schroeder et al. 1997; Krafft et al. 1998; Affkar et al. 2003). Further knowledge about selenate/selenite/arsenate-respiring organisms will provide a better understanding of the role microbes play in the cycling of these oxyanions. Advanced characterizations of such microorganisms may lead to the development of processes that aid in the remediation of contaminated soils and ground water aquifers.

Our laboratory has recently isolated the anaerobic, selenate/selenite- and arsenate-respiring bacterium "*Desulfurispirillum indicus"* strain S5. "*D. indicus"* uses pyruvate and lactate as electron donors and is capable of respiring a variety of electron acceptors, such as arsenate, selenate, selenite, and nitrate, to gain energy for its cellular metabolism. It is not capable of fermentative growth on pyruvate. The strain can respire selenite alone and is capable of completely reducing selenate to elemental selenium. Only five other strains, *Bacillus selenitireducens, Azospira oryzae,* and three strains of *Aquificales*, can use selenite as a terminal electron acceptor (Blum et al. 1998; Takai 2002; Hunter 2007). Electron micrographs have shown that elemental selenium granules of 0.1 to 0.3μm closely associate with the cells (Narasingarao and Häggblom, 2007). Strain S5 has been selected by the Department of Energy for whole genome sequencing (Bini and Häggblom 2007).

16S rRNA gene analysis has revealed that strain S5 shares a 98% 16S rRNA gene homology with *Desulfurispirillum alkaliphilum* and a 93% 16S rRNA gene homology with *Chrysiogens arsenatis* (Macy et al. 1996; Narasingarao and Häggblom 2007a; Sorokin et al. 2007). Since both *C. arsenatis and D. alkaliphilum* are not capable of respiring selenate, *S. indicus* will be the first selenate respiring organism to be fully sequenced. Therefore, this organism can be used as a model organism to fully understand the respiration of selenium and arsenic and the key genes encoding reductases that are involved in this process.

Methodology

Strain S5 was previously isolated from soil enrichments established from the Buckingham Canal in Chepauk, India. Multiple additional dilutions to extinctions were necessary to obtain a pure culture of the strain. Cultures of strain S5 were grown at 28°C in anaerobic tubes amended with each 10mM of Arsenate, Selenate, or Nitrate as electron acceptor and 20mM of Pyruvate as carbon source. Biological activity of the samples was monitored via ion chromatography (oxyanions) and high performance liquid chromatography (carbon source). Growth analyses were performed with a spectrophotometer. In addition, DNA for Degenerate Gel Gradient Electrophoresis (DGGE) and whole genome sequencing was extracted as previously described (Knight et al. 1999).

Principal Findings and Significance

Strain S5 cells are slender spirals, about 4 to 6 μm long and about 0.5 μm wide. They are highly motile, gram negative and strictly anaerobic with respiratory metabolism. The strain uses arsenate, selenate, selenite, and nitrate as final electron acceptors and utilizes the short chain fatty acids lactate and pyruvate as electron donors and carbon source. It is not capable of fermentative growth. S5 is neutrophilic with an optimum pH of 7 and mesophilic with a maximum temperature at 37ºC and an optimum at 28ºC. The predominant fatty acids in the membrane lipids include 12:0, 16:0, 16:1w7c, 18:0, 18:1w7c. The G + C content of the genomic DNA is 56 %mol (Fatty acid and G + C content were previously done by Narasingarao and Häggblom, 2007a). Strain S5 shares a 98% 16S rRNA gene homology with *Desulfurispirillum alkaliphilum* and a 93%16S rRNA gene homology with *Chrysiogens arsenatis*, its closest known relatives. Thus, the proposed new name for this organism will be *"Desulfurispirillum indicus."*

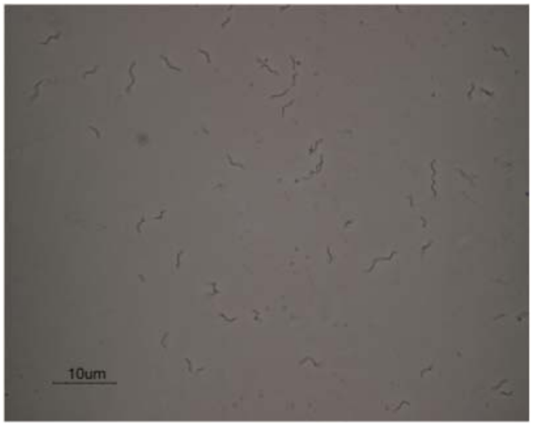
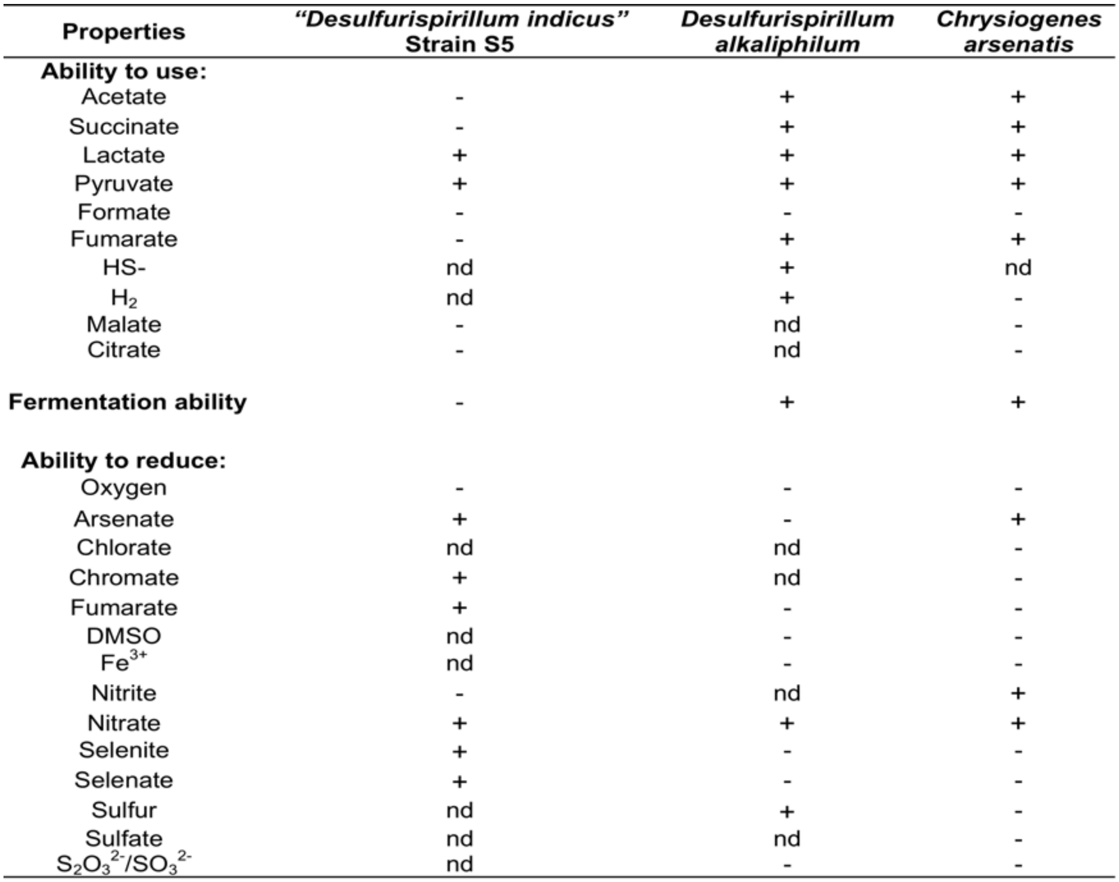


Figure 1. Photomicrograph of strain S5

Table 1. Growth properties of strain S5

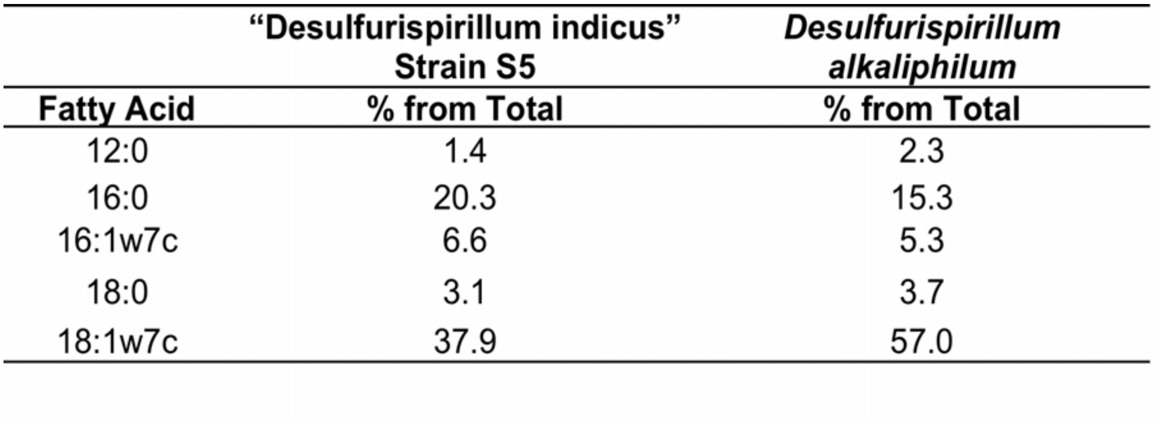
Properties	***"Desulfurispirillum indicus"* strain S5**	***Desulfurispirillum alkaliphilum***	***Chrysiogenes arsenatis***
Growth Temperature	21 - 37°C	35°C (max. 45°C)	25-30°C
pH Range (Optimum)	Neutrophilic	8.0 – 10.2 (9.0)	Neutrophilic
Salt Range	0 – 0.5M	0.1 – 2.5M	Na-Independent
%G+C Content	56 mol%	44.8 mol%	49 mol%
Habitat	Estuarine Canal in India	Bioreactor	Gold Mine

Table 2. Phenotypic comparison of strain S5 and related bacteria.



Properties	*"Desulfurispirillum indicus"* Strain S5	*Desulfurispirillum alkaliphilum*	*Chrysiogenes arsenatis*
Ability to use:			
Acetate	-	+	+
Succinate	-	+	+
Lactate	+	+	+
Pyruvate	+	+	+
Formate	-	-	-
Fumarate	-	+	+
HS-	nd	+	nd
H_2	nd	+	-
Malate	-	nd	-
Citrate	-	nd	-
Fermentation ability	-	+	+
Ability to reduce:			
Oxygen	-	-	-
Arsenate	+	-	+
Chlorate	nd	nd	-
Chromate	+	nd	-
Fumarate	+	-	-
DMSO	nd	-	-
Fe^{3+}	nd	-	-
Nitrite	-	nd	+
Nitrate	+	+	+
Selenite	+	-	-
Selenate	+	-	-
Sulfur	nd	+	-
Sulfate	nd	nd	-
$S_2O_3^{2-}/SO_3^{2-}$	nd	-	-

Table 3. Fatty acid composition of polar lipids in strain S5 and related strain *D. alkaliphilum*.



	"Desulfurispirillum indicus" Strain S5	*Desulfurispirillum alkaliphilum*
Fatty Acid	**% from Total**	**% from Total**
12:0	1.4	2.3
16:0	20.3	15.3
16:1w7c	6.6	5.3
18:0	3.1	3.7
18:1w7c	37.9	57.0

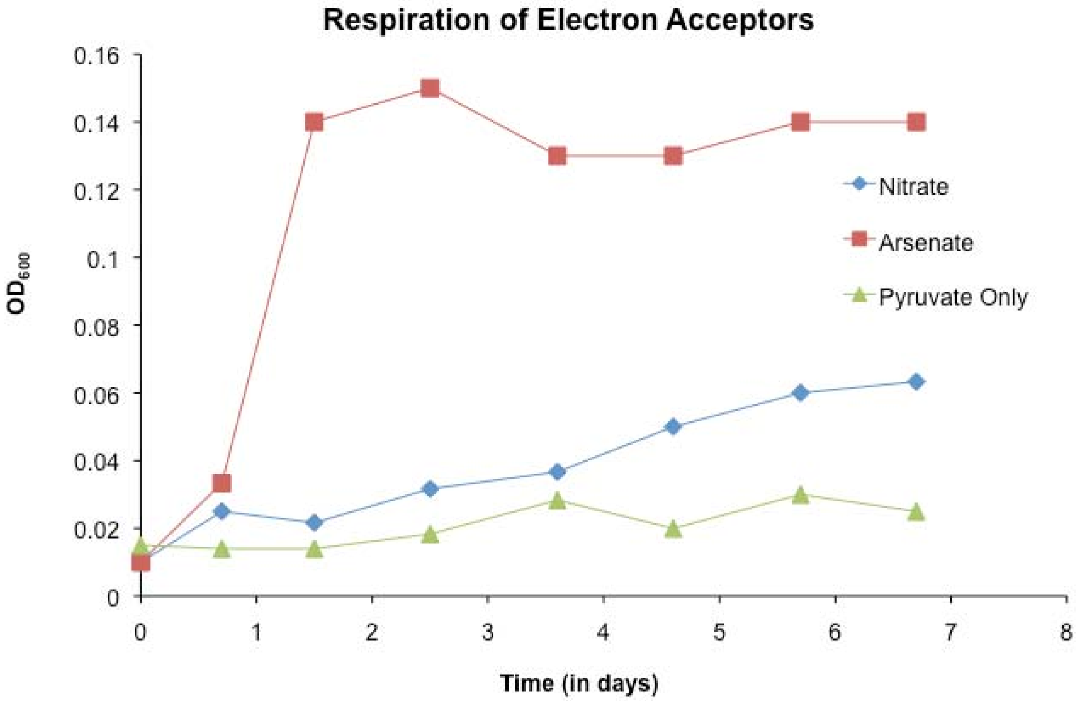


Figure 2. Anaerobic growth of strain S5 with 20mM pyruvate only, 10mM nitrate and 20mM pyruvate, and 10mM arsenate and 20mM pyruvate. The cultures were incubated at 28ºC.

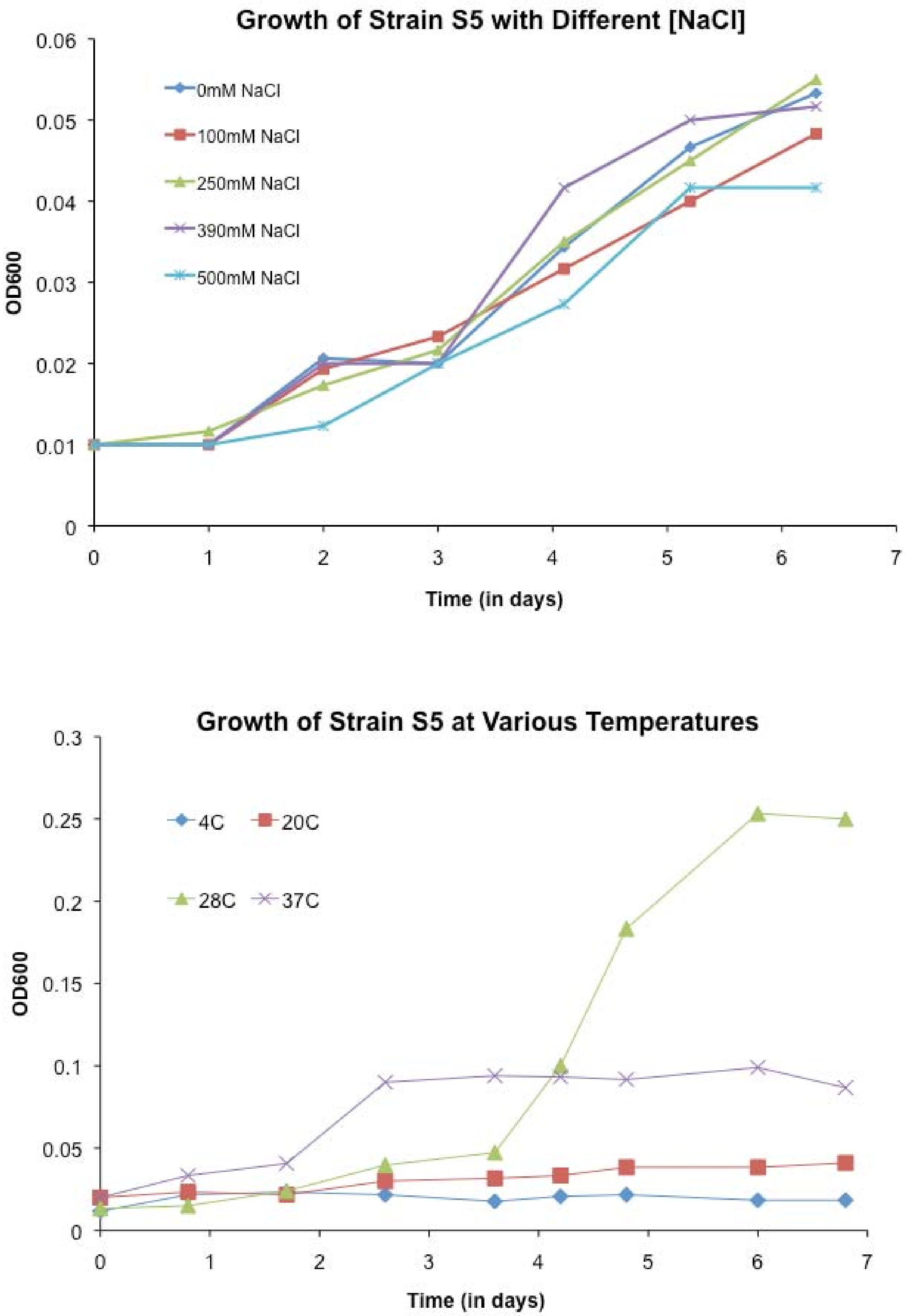


Figure 3. Influence of [NaCl] and temperature on the anaerobic respiration of nitrate. Strain S5 cultures were amended with 10mM nitrate and 20mM pyruvate. The cells were grown at 28ºC.

Although only a few selenate respiring bacteria have been characterized to date, those that have been identified are found among a large variety of bacterial phyla. Strain S5 shares a 98% 16S rRNA gene homology with *Desulfurispirillum alkaliphilum* and a 93%16S rRNA gene homology with *Chrysiogens arsenatis*, its closest known relatives. Thus, the proposed new name for this organism will be *Desulfurispirillum indicus.* Strain S5 displays great metabolic versatility. It utilizes pyruvate and lactate to respire a variety of substrates, such as selenate, selenite, arsenate (As), and nitrate. Further growth characterizations of S5 will elucidate whether the isolate is capable of respiring additional electron acceptors.

The sequencing of the genome of *"Desulfurispirillum indicus"* strain S5 will provide us with the opportunity to use it as a model organism to characterize metabolic pathways for energy production and to determine how these pathways are regulated depending on the availability of As and Se oxyanions or the presence of alternate electron acceptors. We will then establish microcosms from environmental samples collected in New Jersey and test for the presence of homologous genes within the bacterial community and determine regulating factors.

Specific Future Objectives:

1) Annotate the genome of *"Desulfurispirillum indicus"*
2) Identify genes encoding respiratory reductases for arsenic and selenium by mutagenesis and/or disruption
3) Characterize gene regulation in presence/absence of arsenic and selenium and other respiratory electron acceptors (e.g. nitrate)
    a. Which oxyanion is preferred? Which genes and to what extent are functional genes up- or down-regulated?
4) Examine arsenic and selenium respiration from contaminated sites in New Jersey
    a. Use *Selenospirillum indicus* as a model organism and compare its genes to functional genes present in the cultures.

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Micro Scale Solid Phase Extraction using Carbon Nanotubes for Rapid Detection of Organic Pollutants in Water Resources

Basic Information

Title:	Micro Scale Solid Phase Extraction using Carbon Nanotubes for Rapid Detection of Organic Pollutants in Water Resources
Project Number:	2008NJ162B
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End Date:	2/28/2009
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Congressional District:	10
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Focus Category:	Water Quality, Toxic Substances, Methods
Descriptors:	None
Principal Investigators:	Ornthida Sae-Khow, Somenath Mitra

Publication

1. Sae-Khow, O. and S. Mitra, 2009, Carbon nanotubes as the Sorbent for Integrating μ-SPE within the Needle of a Syringe, J. Chromatogr. A, 1216, 2270-2274.
2. Sae-Khow, Ornthida and Somenath Mitra, 2008, “Carbon Nanotubes as the Sorbent for Microscale Enrichment,” Eastern Analytical Symposium, Somerset, NJ. November 17, 2008. (poster presentation)
3. Sae-Khow, Ornthida and Somenath Mitra, 2008, Fabrication and Characterization of Carbon Nanotubes Immobilized in Porous Polymeric Membranes, Eastern Analytical Symposium, Somerset, NJ. November 17, 2008 (oral presentation)
4. Sae-Khow, Ornthida and Somenath Mitra, 2009, Fabrication and Characterization of Carbon Nanotubes Immobilized in Porous Polymeric Membranes, J. Mater. Chem., DOI: 10.1039/b822879e
5. Sae-Khow, Ornthida and Somenath Mitra, 2009, Micro Scale Solid Phase Extraction Using Carbon Nanotubes as Adsorbents, North Jersey Chromatography Group 2009 Student Research Poster Competition, Somerset, NJ. April 2009 (poster presentation)

1. Problem and Research Objectives

Recent evidence has shown that the number of trace contaminants including pesticides and pharmaceuticals is increasing in surface and other natural waters all across the nation. In a 2003 Environmental Science and Technology article[1,2] a USGS study revealed the presence of a large number of "emerging contaminants," such as antibiotics and households chemicals, in the drinking water of many homes in the New York metropolitan area including New Jersey. The synergism between these chemicals could also increase their impact on human health. The major challenge in monitoring these contaminants is that their concentrations are quite low, often in the low ppb or ppt levels.

While they can be detected by conventional methods such as HPLC, LC/MS and others, their low concentrations require extensive sample pretreatment that makes the overall process time-consuming and expensive. The conventional monitoring approach involves field sampling followed by laboratory based methods such as liquid-liquid extraction (LLE)[3] and solid-phase extraction (SPE)[4-6]. For example, SPE, which is more or less state of the art, involves the extraction of analytes on sorbent such as C18. This is followed by clean up and solvent desorption. However, it is a multi-step process that uses a relatively large amount of solvent, and an additional sample concentration step may be necessary. Therefore, the overall analysis involves significant amounts of time, solvents and money. The development of relatively simple, fast sampling techniques that require microliters of solvents would be of great importance because it will allow widespread monitoring of these pollutants. An example of such a functionally simple, yet effective, sampling/sample preparation device is solid-phase microextraction (SPME). It is an excellent alternative to the above mentioned classical methods that incorporates sample extraction, concentration and sample introduction into a single procedure[7]. Here, a fiber incorporated in the needle of a syringe is used for sample preconcentration. However, SPME is a microextraction technique that relies on the equilibration between the pollutant and the sorbent phase. Typical extraction efficiencies are quite low, leading to high detection limits. It would be greatly beneficial to implement SPE in the needle of a syringe and carry out the extraction in a small amount of sorbent followed by elution using a few microliters of a solvent. Extraction efficiencies and enrichment are expected to be significantly higher than SPME.

The objective of this research is to explore the development of microscale solid phase extraction (μ-SPE) for the extraction of a wide range of compounds including pesticides and drug metabolites in our water resources. The specific goals of this project are as follows:

- Implement μ-SPE in the needle of a syringe for easy sampling, enrichment and injection.
- Explore the possibility of using carbon nanotubes (CNTs) as novel, high performance sorbents for μ-SPE.
- Implement the CNTs in a packed as well as in an open tubular, self assembled format.
- Optimize μ-SPE to combine sampling and desorption.

2. Methodology

The proposed μ-SPE device consists of a syringe attached to a removable capillary probe (0.53mm in ID) containing CNTs. This is shown in Figure 1. The CNTs were used in self-assembled (open tubular) as well as in packed formats. The self-assembly of CNTs was carried out in a tube furnace by a chemical vapor deposition (CVD)[8]. For the packed format, 0.3 mg of CNTs was introduced into the 100 mm long capillary plugged with glass wool at both ends. Mechanical shaking with a vibrator was used to obtain a uniform packing. Acetonitrile and distilled water were used to activate the sorbent phase prior to μ-SPE. The CNTs and their functionalized analogs were obtained from CheapTubes, Inc. The results were compared with conventional C-18 phase (Alltech, Deerfield, IL, USA).

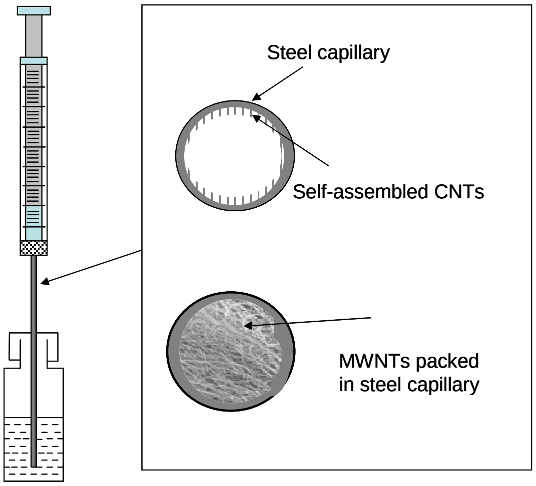

Figure 1. Schematic diagram of the μ-SPE system.

A water sample (3–5 mL) was drawn into the syringe through the probe, where the CNTs retained and enriched the analytes. The water was ejected out. In the elution step, 50–200 μL of acetonitrile was drawn through the probe to desorb the analytes from the CNTs. The solutes were now concentrated in the solvent, and could be directly injected into HPLC. This device allowed small sample volumes to be detected, lowering solvent consumption, eliminating a separate concentration step and reducing analysis times. The analysis was carried out using high performance liquid chromatography (Hewlett-Packard 1050) equipped with a Waters 486 tunable absorbance UV detector, and a 4.6mm×150mm, 5 μm Zorbax column. Peak Simple ver. 3.29 (SRI Instruments, Torrance, CA, USA) was used for chromatographic data acquisition and analysis. The nanotubes were characterized using Leo 1530 VP (Carl Zeiss SMT AG Company, Oberkochen, Germany) field emission scanning electron microscope (SEM).

3. Principal Findings and Significance

The morphology of the self-assembled CNTs inside the μ-SPE probe was characterized by SEM, which are presented in Figure 2(a). It shows the presence of vertically aligned CNTs attached to the inner surface of the tubing. The CNTs were purified to remove the nontubular carbons (NTC) on their surface before using them as µ -SPE. The NTC coverage reduces the availability of CNT surface for adsorption because the analytes have to diffuse through these porous structures to reach the CNT. The diffusion introduces mass transfer limitations, slowing both adsorption and desorption. The purified CNTs provide sorption sites on the wall and interstitial spaces between tubes. These sites are easily accessed for both adsorption and rapid solvent desorption. Figure 2(b) and (c) shows the SEM images of SWNTs and MWNTs used in µ-SPE. The SEM images revealed densely packed clusters of CNTs that filled the inside of the tube. They also show that the CNTs were relatively pure.

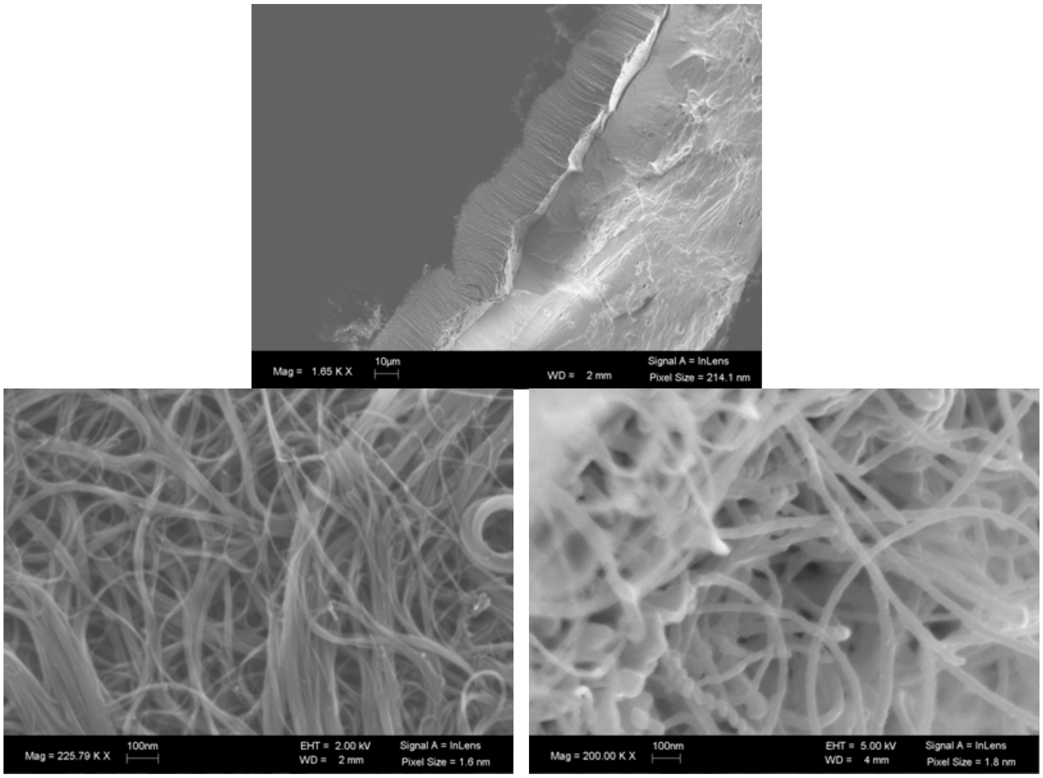

Figure 2. (Counterclockwise from top) SEM images of (a) CNTs in self-assembled in the capillary probe, (b) SWNTs, and (c) MWNTs used for packing the µ-SPE probe.

3.1 Extraction Efficiency and Enrichment Factor Enrichment factor (EF) is defined as the ratio of analyte concentration in the final extract to that in the original water sample:

$$EF = \frac{C_s}{C_w} \tag{1}$$

where, C_s is the analyte concentration in the final extract and C_w is the analyte concentration in the original water sample. A higher EF leads to a higher sensitivity and a lower detection limit. Extraction is usually quantified as extraction efficiency (EE), which is the fraction of analyte removed by the acceptor from the original water sample[9] and was computed as:

$$EE = \frac{n_s}{n_w} = \frac{C_s V_s}{C_w V_w} = EF\,\frac{V_s}{V_w} \qquad (2)$$

where, n_s and n_w are the analyte mass in the final extract and in the original water sample, and V_s and V_w are the volume of the concentrated extract and the original water sample, respectively.

The EF and EE for self-assembled CNTs, SWNT and MWNTs were compared to C-18. Table 1 lists these values for 2-nitrophenol, 2,6-dichloroaniline and naphthalene. The results show that 300 μg of C-18 was not sufficient to accomplish an EF higher than one. However, CNTs were quite effective as μ-SPE sorbent with higher EE and EF. This is in agreement with previous publications which showed significantly larger amounts of C-18 were needed to accomplish the same level of enrichment as the CNTs[10,11]. The CNTs had strong interaction with these analytes, especially the aromatic compounds. The hexagonal arrays of carbon atoms in graphene sheets exhibit strong π-π interaction with the benzene rings. Additionally, open ended CNTs have adsorption sites on both internal and external surfaces[12]. The internal surfaces of open-ended CNTs are known to exhibit stronger binding energy and adsorption affinity for these compounds as well.

Table 1. The enrichment factor (EF) and extraction efficiency (EE) of 2-nitrophenol, 2,6-dichloroaniline, and naphthalene after preconcentration on four different sorbents.

Sorbents	**2-Nitrophenol**		**2,6-Dichloroaniline**		**Naphthalene**		**Breakthrough**
	EF	**EE (%)**	**EF**	**EE (%)**	**EF**	**EE (%)**	**volume (mL)**
C-18	0.3	1.3	0.6	2.5	0.6	2.5	5
Self Assembled	0.6	2.3	0.7	2.8	1.9	7.5	7.5
SWNTs	2.8	11.1	4.1	16.2	6.2	24.7	17.5
MWNTs	3.4	13.7	3.7	14.8	6.8	27.1	17.5

The performance of SWNTs and MWNTs were comparable. For 2,6-dichloroaniline, SWNTs showed higher enrichment compared to MWNTs, and it was opposite for 2-nitrophenol and naphthalene. In general, the EF of naphthalene was higher than the other two compounds, which had higher polarity.

As seen from the SEM images, the self-assembled CNTs formed a layer on the inner surface of the μ-SPE in an open tubular format that was a few microns thick. Therefore, the mass of the sorbent was relatively low and the void volume was large. A relatively large fraction of the sample passed through the probe without sorption on the active CNT site. The dense packing in the packed tubes provided a more intimate contact with the sorbent. Therefore, the EF in this format was significantly higher.

3.2 Quantitative Aspects of μ-SPE Calibration curves were obtained for C-18, self-assembled CNTs, SWNTs, and MWNTs. The results presented in Table 2 indicated good linearity and high correlation coefficients in the concentration region studied (100-2000 ng/mL for C-18, 60-1000 ng/mL for self-assembled CNTs, 10-1000 ng/mL for SWNTs and MWNTs). The reproducibility was determined by five repeated extractions. The relative standard deviations (RSD) were between 0.8 and 3.4% for C-18, 1.9-3.9% for self-assembled CNTs, 3.2-4.4% for SWNTs, and 1.7-3.9% for MWNTs. The sensitivities for determination of these compounds (slope of calibration curve) in the packed formats (0.16-1.8) were higher than those in the self-assembled (0.03-0.29) and considerable higher than C-18 packed format (0.02-0.08).

The chromatograms in Figure 3 show that μ-SPE with MWNTs resulted in analytical signals that were significantly higher than the direct injection of a standard solution. Method detection limits (MDLs) were obtained based on signal to noise of three (S/N = 3). MWNTs provided the lowest MDL for naphthalene which was 0.1 ng/mL compared with 10 ng/mL from C-18. These results clearly indicate that CNTs have outstanding enrichment capabilities, and can be successfully used for trace analysis.

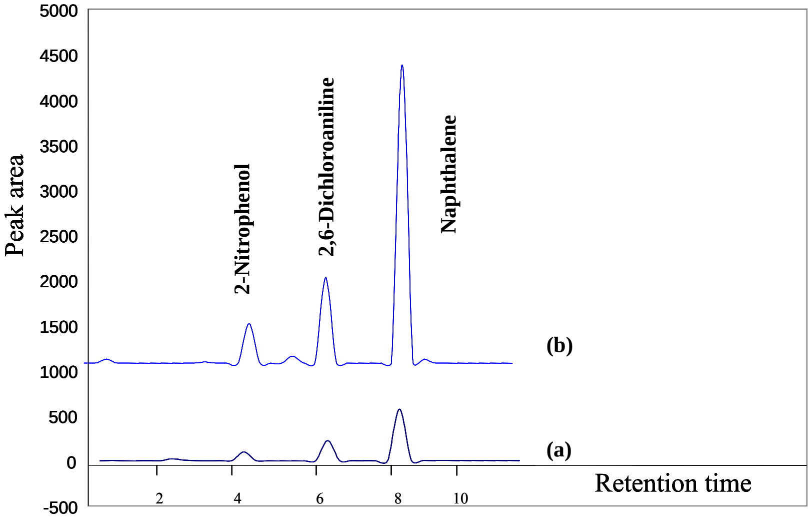

Figure 3. HPLC chromatograms of (a) the original sample and (b) sample enriched by μ-SPE with MWNT.

Table 2. Quantitation using μ-SPE.

Sorbents	**2-nitrophenol**				**2,6-dichloroaniline**				**naphthalene**			
	corr coeff (r)	**RSDs (%)**	**slope**	**MDL (ppb)**	**corr coeff (r)**	**RSDs (%)**	**slope**	**MDL (ppb)**	**corr coeff (r)**	**RSDs (%)**	**slope**	**MDL (ppb)**
C-18[a]	0.9997	2.5	0.02	70	0.9987	3.4	0.03	16	0.9935	0.8	0.08	10
Self-Assembled[b]	0.9966	2.4	0.03	25	0.9996	3.9	0.05	12	0.9992	1.9	0.29	2
SWNTs[c]	0.9945	4.1	0.21	3.2	0.9951	4.4	0.52	0.8	0.9915	3.4	1.82	0.2
MWNTs[c]	0.9704	2.8	0.16	3	0.9894	3.9	0.32	1	0.9952	1.7	1.76	0.1

Concentration ranges studied: [a]100-2000, [b]60-1000, and [c]10-1000 ppb. Precision were calculated using a 125 ppb standard.
RSD: Relative Standard Deviation
MDL: Method Detection Limit

3.3 Sorbent breakthrough To obtain the reliable analytical results and high enrichment factor, it is important to obtain satisfactory enrichment factors for all analytes from as large a volume as possible. Breakthrough volume was computed as follows. The effects of sample volumes on the EF of naphthalene using the different sorbents are shown in Figure 4. It was found that the EFs increased linearly before reaching a maximum, after which it more or less stayed constant. In addition, it was evident that carbon nanotubes were the most effective sorbents demonstrating the highest breakthrough volumes.

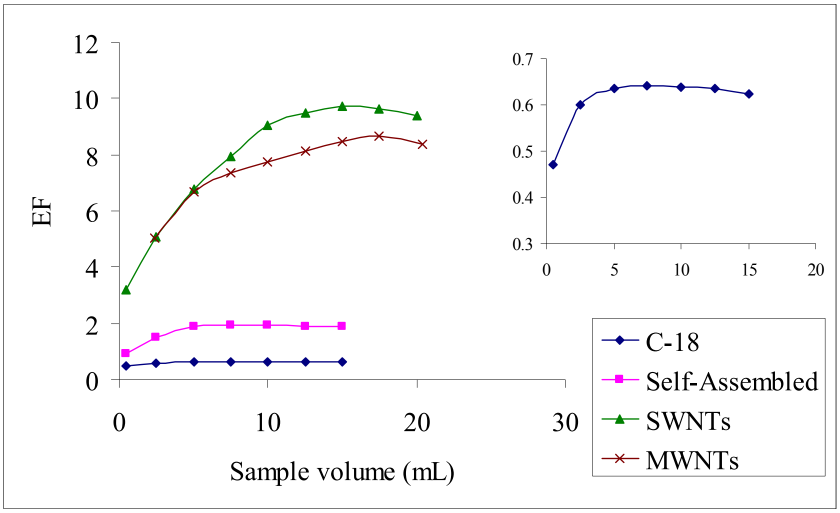

Figure 4. EF as a function of sample volume for 1 μg/mL naphthalene on different sorbents.

3.4 Functionalized CNTs as Sorbents for μ-SPE The chemistry on the CNTs and the subsequent sorption capacity can be effectively altered by changing the functionalities on the CNTs surface. The adsorption capacities of functionalized SWNTs and MWNTs containing hydroxyl and carboxylic groups were compared to the pure SWNTs and MWNTs respectively. The results in Table 3 show that SWNTs and MWNTs functionalized with hydroxyl and carboxyl groups had higher capacity to retain 2-nitrophenol and 2,6-dichloroaniline than pure SWNTs and MWNTs. 2-nitrophenol was adsorbed more strongly on SWNTs with hydroxyl than on the carboxylated CNTs. On the other hand, EF of 2,6-dicholoaniline improved dramatically on functionalized MWNTs compared to the SWNTs. While aromatic groups could interact with the CNTs through π-π interaction, the hydroxyl group of 2-nitrophenol and the amine group of 2,6-dichloroaniline could form hydrogen bonds with the carboxyl and hydroxyl groups on the CNTs surface. The underivatized CNTs showed higher adsorption capacity to retain naphthalene than the functionalized analogs.

Table 3. The effect of functionalization.

Types of sorbent	Enhancement over SWNT or MWNT (%)		
	2-Nitrophenol	**2,6-Dichloroaniline**	**Naphthalene**
SWNTs-OH	12	15	-7
SWNTs-COOH	5	17	-7
MWNTs-OH	11	54	-12
MWNTs-COOH	6	56	-12

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Cranberry Farms' Habitat Function in the Wetland System of the New Jersey Pine Barrens

Basic Information

Title:	Cranberry Farms' Habitat Function in the Wetland System of the New Jersey Pine Barrens
Project Number:	2008NJ163B
Start Date:	3/1/2008
End Date:	2/28/2009
Funding Source:	104B
Congressional District:	6
Research Category:	Water Quality
Focus Category:	Wetlands, Ecology, Water Use
Descriptors:	None
Principal Investigators:	Ai Wen, David Ehrenfeld

Publication

1. Wen, Ai. 2008. Species composition in the seed bank of abandoned cranberry farms: from a restoration perspective. PS 67-151. 93rd ESA Annual Meeting, Milwaukee, Wisconsin. (poster presentation)
2. Wen, Ai. 2008. "Seed bank composition and its function in farmland succession in abandoned cranberry farms." Firman E. Bear Chapter of the Soil and Water Conservation Society Annual Meeting. Chatsworth, New Jersey. (oral presentation)

1) Project Summary:

a. Problem and Research Objectives:

The study aimed to determine the interaction between cranberry farms and the surrounding Pine Barrens wetland ecosystem from two perspectives.

First, I investigated the factors that can potentially affect the early stage of secondary succession in abandoned wetland farms. I examined whether the seed bank in abandoned cranberry farms exhibits different species density and composition at different soil depth (i.e. soil accumulated before and after the farm was constructed). I also examined whether the seed bank density and composition varies in cranberry bogs with low and high water table levels. Further, in order to use my study to provide farm restoration information, I applied two common restoration treatments, flooding and ground cover removal, to soil acquired from cranberry bogs with different hydrological condition (low vs. high water table), different soil depth (bottom, middle and top soil layer) and different ground cover species (cranberry runner vs. *Carex* cover vs. redroot cover). With this application, I was able to depict whether the common wetland restoration methods can produce homogeneous effects across different post-abandonment habitat conditions. I hypothesized that flooding treatment will significantly change the species composition and density of the plant community germinated from the seed bank. I also hypothesized cranberry bogs with low and high water tables exhibit different seed bank composition, and the legacy effect from agriculture, specifically, the soil stratification during cranberry cultivation, has significantly changed seed bank composition in different strata. I further hypothesized that the removal of remaining cranberry runners as well as the removal of dominant pioneer vegetation would increase the seed bank germination, regardless of the species of the dominant plant.

The second objective of the research was to improve the integrity of the wetland ecosystem by enhancing the wildlife habitat of cranberry farms. I surveyed the wildlife (avian and anuran) in active and abandoned cranberry farms. I am going to correlate their distribution with different habitat factors (i.e. vegetation and landscape) of the active and abandoned cranberry farms. The data analysis of this project will be finished this summer. This project will reveal the important factors correlating to wildlife distribution within active and abandoned farms. This information will be important for habitat management in both abandoned and active cranberry farms.

b. Methodology:

Objective 1:

In June 2007, soil cores were taken from eight abandoned cranberry bogs. Previous survey has shown four of the bogs have a relatively high water table, while the other four have a low water table. In each bog, four soil cores were taken in its central region, except in one bog where six were taken. In the greenhouse, each soil core was divided into three layers: the bottom layer included the preagricultural wetland soil, the middle layer included the agricultural strata, and the top soil included the most recent cultivation medium that has been exposed after bog abandonment. In the greenhouse, subsamples of equal amounts (thickness) were taken from each layer of each core in order to compare the germination quantitatively. Each subsample was evenly spread onto a 25cm x 25cm greenhouse germination tray over 1cm sterile potting soil, which was underlaid by 1cm of sand. There was a total of 102 trays (34cores * 3 layers). The germinated seedlings were harvested and identified throughout the growing season until the end of October 2007. The unidentifiable seedlings were kept until spring 2008 to be identified. The germination density was compared among different treatments and habitat factors using Bayesian zero-inflated poisson model in order to determine the germination probability (i.e. whether there is any germination) and germination density (i.e. how many seedlings were observed), respectively. The species composition was ordinated using NMDS analysis, and the NMDS scores were compared among different factors using Bayesian generalized linear model.

In June 2008, soil blocks (25cm X 25cm) were excavated from abandoned cranberry farms with three types of ground covers: Runner, *Carex* and Redroot. "Runner" areas were unvegetated but covered with dense remaining cranberry runners (labeled as R+, where R represents "runners"). "*Carex*" areas were covered with dense *Carex striata* and cranberry runners (labeled as P+R+, where P represents "plants"), while Redroot areas were covered with dense *Lachnanthes caroliana* and cranberry runners (also labeled as P+R+). Each plant type had four sites as replicates. Within each site, three (Runner) or five (*Carex* and Redroot) soil blocks were taken, on which different removal treatments were applied in the greenhouse (see Table 1). Soil blocks were kept in the greenhouse from June to October, 2008. The germination density under different ground cover types and with different treatments was compared using Bayesian generalized linear model, and the species composition was ordinated using NMDS method. The NMDS scores were further compared using Bayesian generalized linear model.

Table1. Factorial design of ground cover types and removal treatments: P—plant, R—runner

Ground cover types Removal treatments	Runner (4sites)	*Carex* (4sites)	Redroot (4sites)
Original ground cover (control)	R+	P+R+	P+R+
Runner removal	R-	P+R-	P+R-
Plant removal	—	P-R+	P-R+
Both runner and plant removal	—	P-R-	P-R-
Both runner and plant removal; loosen surface soil	Loose	Loose	Loose

Objective 2:

Three abandoned DeMarco farms (532W, 532E, 563S) and three active cranberry farms (70S, 530NS, CranBlue) will be used for this study.

Bird survey: in each farm, four boundary and four dike transects are established. From June 2007, each farm has been surveyed once every two weeks. Surveys begin immediately after sunrise and finish within three hours. Birds observed on the dike, in the ditch and within five meters outside the dike are recorded. The species, number and the location where they were first seen (e.g. ditch, tree, ground, etc.) is also recorded. The survey is conducted both during breeding season (June to September) and winter (December to March).

Anuran survey: Adult anurans are surveyed by their calling intensity, which is classified into four categories (one individual, 2-5 individuals, 5-10 individuals, and >10 individuals). From early March to late August, each site is surveyed at least twice a month. After sunset, I monitor calling intensity at set locations for five minutes per location. In all six sites, the locations are set to include four types of micro-habitats: reservoirs, main ditches, side ditches along cranberry beds, and cranberry beds. At each location the calling intensity of each species within the five minutes is recorded. After each survey, the calling intensity of each species is ranked for different microhabitat (i.e. reservoir, main ditch, side ditch, cranberry bed).

c. Principal Findings and Significance:

Objective 1:

As shown in Figure 1, the germination probability in wet bogs (81%±5%) was higher than in

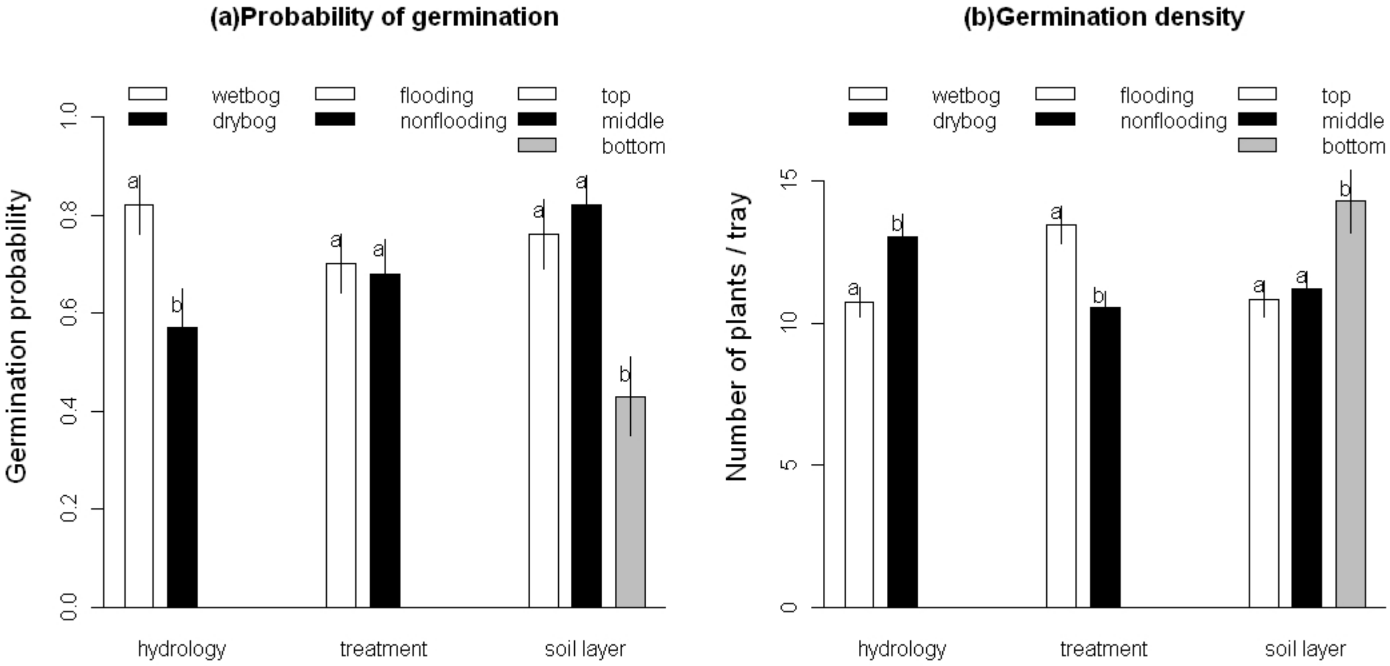

Figure 1. The comparison of (a) germination probability and (b) germination density of wet vs. dry bogs, flooding vs. non-flooding treatment, and top vs. middle vs. bottom layer. Bars represent mean probability or density±SD. Letters indicate significant differences among values. Different letters indicate the difference's 95% credible interval (CI) does not overlap 0.

dry bogs (57%±8%). However, in trays where germination did occur, the plant density was higher in dry bogs (13.1±0.8 seedlings/tray) than in wet bogs (10.8±0.5 seedlings/tray) . Similarly, only 43% of trays from the bottom layer exhibited germination, which was significantly lower than the top (75.9%±7%) and middle layer (81.9%±6%). But the germination density (14.3±1.1 seedlings/tray) from bottom layers was significantly higher than the top (10.9±0.6 seedlings/tray) and the middle layer (11.2±0.7 seedlings/tray). The flooding treatment did not significantly change the germination probability (flooding 70%±6%; non-flooding 68%±6%), but the density of germination increased about 2.9 seedlings/tray compared with non-flooding treatment.

Twenty-three species were observed in the experiment. Four NMDS axes were used (stress=0.15) which is within the range of “fair ordination” (0.10 to 0.20) of typical ecological studies (McCune & Grace, 2002). Overall, 85.2% of the variance was explained by the four axes. NMDS1 itself accounted for 47.5% of the variance, while NMDS4 only explained 9.9% of the total variance.

As shown in Figure 2, bog hydrology and soil layers exhibited a strong effect on species composition. Along NMDS1 the germination from wet bogs and dry bogs had been clearly separated (Figure 2; the mean difference between wet and dry bogs is △NMDS1 = 0.61±0.07). The top layers were also separated from the middle and bottom layers along NMDS1, but the difference was not as

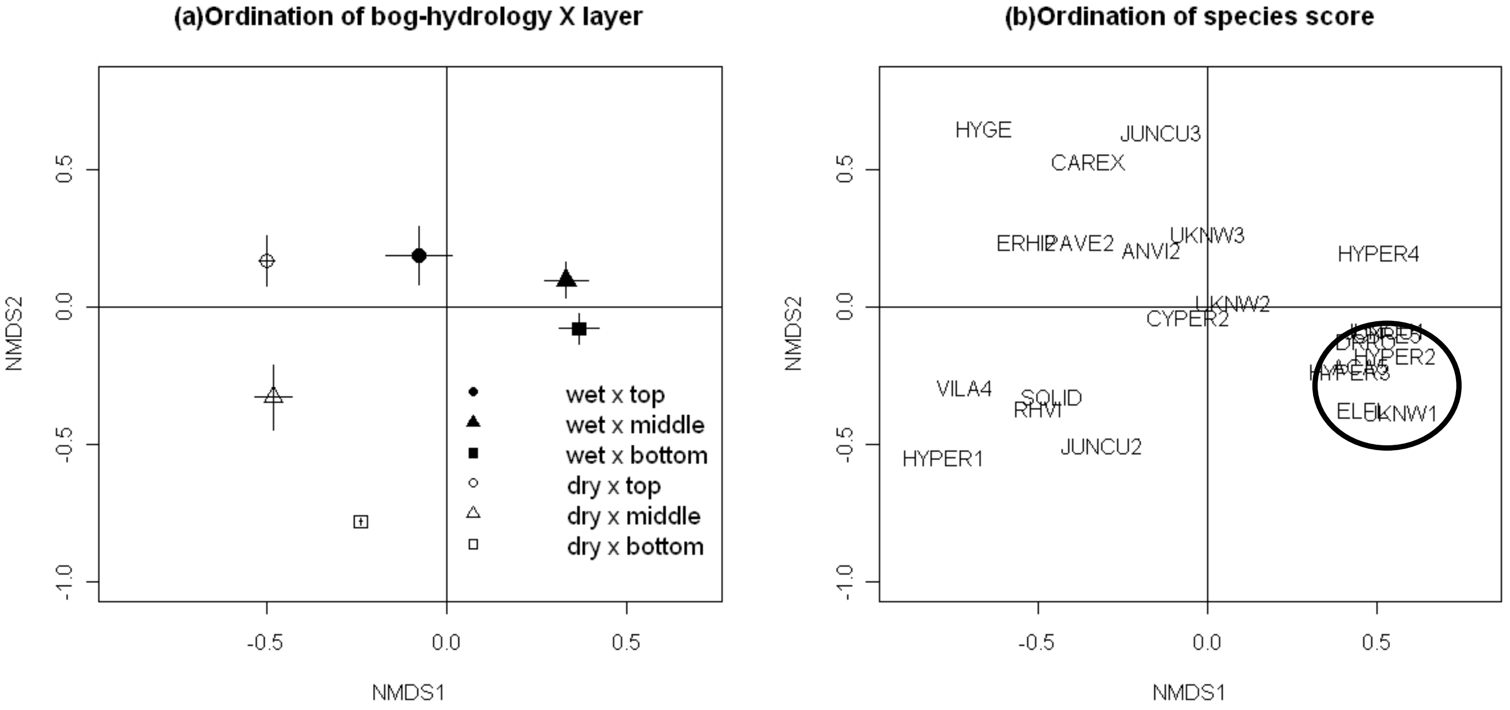

Figure 2: Ordination of species composition from each bog hydrology **x** layer. (a) Ordination of top, middle and bottom layer in wet and dry bogs. For simplicity, rather than the germination result of all 69 trays, each bog hydrology **x** layer combination is plotted with its mean value along axis 1 and 2. The error bars indicate ±SE. (b) Ordination of plant species along NMDS 1 and 2. The species cluster within the oval shape corresponds to the wet x bottom ordination in graph (a).

strong (top-middle △NMDS1=-0.21±0.06; top-bottom △NMDS1=-0.35±0.10). Rather, the three layers' species composition is separated strongly along NMDS2 (top-middle △NMDS2=0.29±0.08; top-bottom △NMDS2=0.61±0.13; middle-bottom △NMDS2=0.31±0.13). The species composition of flooded and non-flooded trays had no significant difference along NMDS1 or NMDS2. Their difference along NMDS3 was significant (△NMDS3=0.19±0.07), but since NMDS3 only accounted for 11.6% of the variance, this result suggested that flooding treatment did not have as strong of an effect on the species composition compared to the bog hydrology and soil layers.

The ordination plot of the species scores revealed clusters corresponding to the trays from the bottom layer of the wet bogs (Figure 2 (a) and (b)). This cluster is composed of *Cyperus retrorsus*, *Drosera rotundifolia*, *Lachnanthes caroliana*, *Eleocharis flavescens*, one *Juncus* spp. and one *Hypericum* spp (St. John's Wort). The four identifiable species are listed as "obligate wetland" or "facultative" wetland species (U.S Fish & Wildlife Service, 1996), while genus Juncus and St. John's Wort species are also usually considered as wetland species.

In summary, I found although flooding is believed to be an effective restoration practice in natural wetlands, in an agricultural wetland, human alteration of the soil profiles and water tables are the major factors that determine the density and composition of germinating seedlings. Flooding treatments did little to overcome these effects. The result suggests different restoration practices need to be applied according to the habitat heterogeneity as a result of human disturbance. On the other hand, ground cover removal was shown to be an effective method to increase germination density, regardless of the species of dominant vegetation. I concluded that in restoring post-agricultural wetland habitat, it is necessary to enact flexible restoration strategies corresponding to heterogeneous post-abandonment conditions. Usual wetland restoration strategies can be less productive due to the long-term impact of human disturbance.

Objective 2:

The animal survey was finished in September 2008. At the end of the two years of field survey, 125 bird species and 8 anuran species were recorded. I will start data analysis in May 2009 and is expected to be done by July 2009. The result will be defended in my Ph.D. defense in fall 2009.

Literature Citation:

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Identifying the source of excess fine-grained sediments in New Jersey rivers using radionuclides

Basic Information

Title:	Identifying the source of excess fine-grained sediments in New Jersey rivers using radionuclides
Project Number:	2008NJ164B
Start Date:	3/1/2008
End Date:	2/28/2009
Funding Source:	104B
Congressional District:	8
Research Category:	Water Quality
Focus Category:	Sediments, Methods, Hydrogeochemistry
Descriptors:	None
Principal Investigators:	Joshua C. Galster, Kirk Barrett

Publication

1. Galster, Josh, Kirk Barrett, Huan Feng, Nicole Bujalski, Jared Lopes, 2008, Characterizing the source of fine-grained sediments in New Jersey rivers using radionuclides, in Geological Society of America Abstracts with Programs, Denver, Colorado, v. 40, p. 194.
2. Galster, Josh, Kirk Barrett, Huan Feng, Jared Lopes, Nicole Bujalski, 2008, Identifying the source of excess fine-grained sediments in New Jersey rivers using radionuclides, in NEGSA Abstracts with Programs, Denver, Colorado, v. 40.

Problem and Research Objectives

This proposal directly addresses a NJWWRI stated research Priority IV, Methods of analysis of contaminants. We will be testing a proven analytical method to determine the source (watershed vs. streambank) and the residence time of sediments in stream channels.

Sediment is well known to be an important aquatic pollutant in New Jersey and elsewhere. Sediment carried into streams, lakes and estuaries adversely affects aquatic biota by, for example, smothering benthic habitats and carrying attached pollutants such as heavy metals, organic pollutants and nutrients through sediment runoff. Excess sediments decrease light penetration, water clarity and can interfere with respiration. Sedimentation also affects humans by filling in lakes and diminishing their recreational value and water storage capacity. Sedimentation was listed as the number one cause of river and stream impairment in the USEPA's most recent "National Water Quality Inventory" (USEPA, 2007). In New Jersey, the NJ Department of Environmental Protection (NJDEP) has identified nearly 50 "assessment units" (mostly equivalent to HUC14s) that are impaired by excessive suspended sediment concentrations, encompassing 370 square miles and over 700 stream miles (NJDEP, 2006). Over 100 additional assessment units were biologically impaired, with the cause of the impairment unknown; sedimentation is a likely cause in many of these cases.

Our objective is to assess how successful these established methods are at identifying the source of the fine-grained sediment within streams in New Jersey. Using radionuclides to "fingerprint" sediment coming from different sub-watersheds and from channel bank vs. surficial soil erosion within a drainage basin is an established technique, and has been used in a variety of geologic settings and in watersheds of various size (Bonniwell et al., 1999; Walling et al., 1999; Whiting et al., 2001; Polyakov and Nearing, 2004; Collins and Walling, 2004; Walling, 2005; Matisoff et al., 2005; Whiting et al., 2005). We propose to use the technique to distinguish between landscape and channel bank erosion in two New Jersey watersheds with different land uses, and to eventually influence land management practices (e.g., BMPs). Our hypothesis is that the fine-grained sediment in urban/suburban fluvial systems originates mostly from stream bank material produced from channel-widening erosion and will show relatively lower radionuclide activities, whereas, in areas with significant row-crop agriculture, substantial sediment originates from the landscape and will show relatively higher activities.

Methodology

Two watersheds with contrasting land uses were chosen for this project. The East Branch of the Rahway River, Essex County, New Jersey is predominantly (>80%) urban land use, while the Cold Brook watershed, Hunterdon County, New Jersey is predominantly agricultural land use. Within each watershed two sampling locations were selected, for a total of four field sites. Field samples were collected during the summer and fall of 2008.

At each of the four sample sites, samples were collected from the bank of the stream, the channel of the stream and from three soil pits, each approximately 5 m from the stream. Two bank samples were taken at each site. A tape measure was placed vertically down the bank face to measure depth, and a trowel was used take 5 cm grab samples. Five samples were taken from each bank at equally spaced intervals. The average bank height of the four sites is 95 cm. The samples were placed into a pre-labeled, plastic bag.

Each soil pit was dug with a shovel until rocks were hit, or it was deeper than 22 cm. The samples were taken in one centimeter intervals from the surface to 10 cm of depth. The deeper samples were taken at two centimeter intervals, from 10 cm depth to the bottom of the soil pit. A trowel was used to remove the sample and place it into a pre-labeled, plastic bag.

Samples from the stream channels were taken in triplicate, approximately 5 m apart. A corer was constructed for this project using two pieces of PVC piping, one inside the other. The corer was pounded into the stream sediment, and samples were taken at 1 cm intervals, until a depth of 10 cm when 2 cm intervals were used. The average depth of the cores was 9 cm. The extruder expelled the sample from the corer and the sediment was removed with a trowel and placed into a plastic bag.

Sediment samples were prepared at Montclair State University. ^{137}Cs and ^{210}Pb were measured by non-destructive gamma spectrometry (Canberra Model BE2020 Gamma detector housed at Montclair State) (Olsen et. al., 1986; Cochran et. al., 1993; Feng, 1997; Whiting et. al., 2005). In brief, samples were counted directly on an intrinsic germanium detector for ~24 hours to ensure sufficient accuracy and precision. ^{137}Cs and ^{210}Pb were determined from the gamma emission at 662 and 46.5 kev, respectively. ^{226}Ra activity was measured via the 352.0 kev ^{214}Pb gamma emission to obtain the supported ^{210}Pb value. The observed count rates of all measured nuclides were corrected for self-adsorption by measuring the attenuation of a known gamma source by the sample (Cutshall et. al., 1983; Cochran et. al., 1993; Feng, 1997). Sample analysis is on-going.

Principal Findings and Significance

Sediment has been analyzed and distinct radiometric signatures have been found in the sediment from each stream (Figure 1). Each watershed's stream banks and soil pits produced similar radiometric profiles. Soil pits had higher activity levels than stream banks, which reinforces our hypothesis of stream banks having older and less active sediment.

The difference between the two streams is in the sediment from each channel. The rural, agricultural watershed (Cold Brook) has channel sediment with much less activity than the channel sediment from the urban (East Branch of the Rahway) watershed. While preliminary, this suggests that more surficial material than previously thought is the source of the excess sediment within the urban stream.

To date this research has verified using this approach to distinguish between different sediment sources. Knowing the source will aid the NJDEP in their regulatory and restoration activities. For most sediment-impaired areas, the NJDEP must develop a “Total Maximum Daily Loads” (TMDL), along with a sediment load reduction plan. To develop this plan it is important to know what proportion of the sediments impacting a stream is coming from streambanks vs. the watershed. Depending on the primary source, the load reduction measures (e.g., streambank stabilization vs. riparian buffer restoration or conservation agriculture) would be quite different.

Sediment analysis at Montclair State is continuing, and will be completed by the end of calendar year 2009. We will analyze the results from the other sites within the agricultural and urban watersheds in order to assess the intrabasin variability in the radiometric signal.

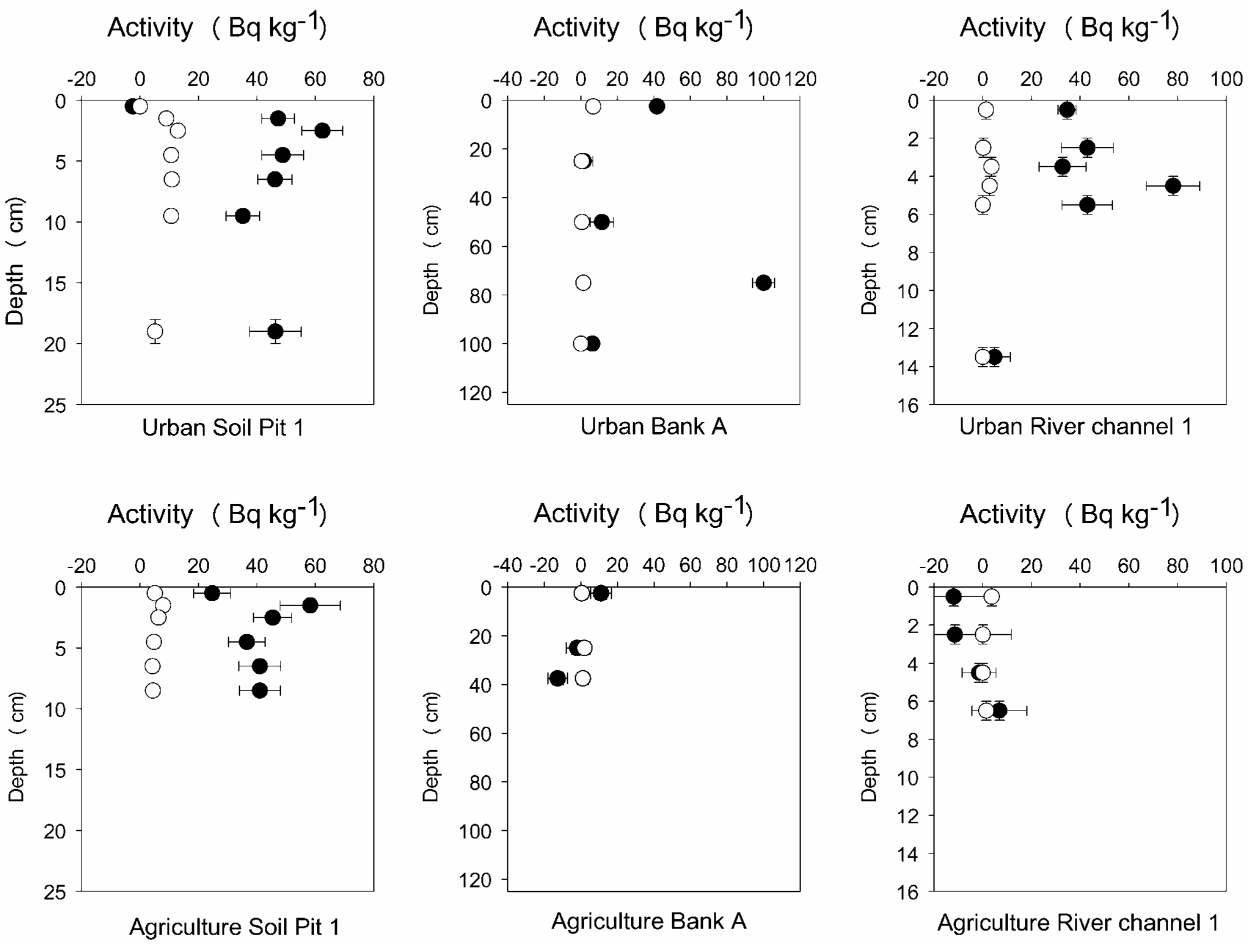

Figure 1. Sediment activity (^{210}Pb in black circles, ^{137}Cs in white) from the urban watershed on top, and the agricultural watershed below. The results are similar between the two except for the higher levels of ^{210}Pb in the urban river channel sediment.

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Information Transfer Program Introduction

The information transfer program serves an important purpose to the state's water resource community. The goal is to bring timely information about critical issues in water resource sciences to the public, and to promote the importance of research in solving water resource problems. The program accomplishes this goal through a variety of means. One focus is on producing a newsletter that provide a comprehensive overview of current water resource issues. The program continues to develop the NJWRRI website (www.njwrri.rutgers.edu) into a comprehensive portal for water information for the state. We also collaborate with other organizations in sponsoring and producing conferences.

Information Transfer Program

Basic Information

Title:	Information Transfer Program
Project Number:	2008NJ159B
Start Date:	3/1/2008
End Date:	2/28/2009
Funding Source:	104B
Congressional District:	6th
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	None
Principal Investigators:	Joan G. Ehrenfeld, Diana Morgan

Publication

Information Transfer Program

The information transfer program has emphasized development of the website and e-based communications with stakeholder groups. It has also focused on the production of substantive newsletters addressing specific water resource issues as an effective way to communicate information to the public.

Two issues of the newsletter were produced, and a third issue is in progress. The Winter 2008 issue allowed WRRI-funded and agency researchers to describe their research on water resource issues; topics covered included the development of new technology for monitoring arsenic contamination, the economic analysis of BMPs, the development of a high school-based climate monitoring network, and a summary of on-going NJ Department of Environmental Protection (NJDEP) research projects. Our annual research update issue is intended to illustrate the importance of research in solving water-related problems. The Fall 2008 issue highlighted the Rain Garden/Bioretention Research and Extension Symposium, held May 29-30, 2008. Several presenters authored articles describing the status of current research, case studies of implementation and education projects, and local government implementation programs. This was an appropriate transition issue for the institute because Dr. Christopher Obropta, whose research includes bioretention and stormwater management, assumed the role of Director on January 1, 2009. We are currently developing an issue on research and extension programs occurring in the Raritan River basin.

Each issue was eight pages, and was primarily distributed via our e-mail lists to approximately 2,000 people throughout the state, and as paper copies to all members of our state legislature and Congressional delegation.

Our website (www.njwrri.rutgers.edu/) has been continually updated with information on water resource events and information in New Jersey, the U.S. and around the world. The home page and ‘events’ pages are regularly updated to highlight upcoming events, publications and other water –related news. The website is our primary means of information transfer to the water community and the public, and we will continue to update and improve its functionality with new pages and greater content.

We continue to expand and use targeted, group-specific e-mail lists to bring relevant information to specific audiences. Targeted lists include a list of scientists/principal investigators, water resource managers, non-governmental organizations and people affiliated with NGOs, and policy-makers. The lists are continuously updated and expanded, and are used to keep these groups informed of events, conferences, publications, and funding opportunities. These lists enable us to initiate and maintain frequent contact with stakeholder groups. We believe these lists are an excellent method of keeping the water-related public aware of NJWRRI, as well as informed about water-related news and information.

We also continue to participate in the New Jersey Water Monitoring Council, a statewide body representing both governmental and non-governmental organizations involved in water quality monitoring. We co-sponsored and helped organize the Sixth National Monitoring Conference in May 2008**.**

As part of a leadership role with the Climate and Environmental Change Initiative at Rutgers University, NJWRRI actively organized and planned a one-day symposium on climate change and water resources. "The Climate Ahead: Impacts of Climate Change on Water Resources Conference" was held on April 15, 2008 and was attended by approximately 175 members of state government, scientists and consultants from the public and private sectors, water managers, NGOs, and students.

We sponsored or co-sponsored several other events during this reporting period. We were a sponsor for the 2008 Mid-Atlantic Regional Water Resources Research Conference – The Water-Energy Nexus: A Necessary Synergy for the 21st Century, held November 17-19, 2008 in Shepherdstown, WV. We also co-sponsored the 2nd Passaic River Symposium held October 16, 2008 at Montclair State University. Finally, we were a sponsor with NJDEP and the USGS New Jersey Water Science Center on a workshop, Diurnal Cycling of Chemical Constituents in Surface Water and Related Media – Scientific and Regulatory Considerations, held December 12, 2008.

USGS Summer Intern Program

None.

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	4	0	0	0	4
Masters	1	0	0	0	1
Ph.D.	6	0	0	0	6
Post-Doc.	0	0	0	0	0
Total	11	0	0	0	11

Notable Awards and Achievements

The project 2008NJ156B "Process-based modeling of nitrogen removal dynamics in brownfield and intact remnant wetland systems" led to the development of an undergraduate research project at the same field site (titled “Carbon fractionation of an urban wetland soil”) that earned academic credit and an “A” for the undergraduate student. Since the final step of the project (i.e. the running of the process-based model) has not yet been completed, the data has not been formally presented or used for management. However, the results will be used to aid in the management of wetlands at Liberty State Park, New Jersey once they are finalized.

Project 2007NJ139B "Phosphate and Thermal Stabilization of Dredged Sediments for Reuse as Construction Material" was featured as a National Synchrotron Light Source Science Highlight: Environmental Science & Technology Journal paper, Ndiba et al. (2008), by Brookhaven National Laboratory, NY, USA, available at http://www.nsls.bnl.gov/newsroom/science/2008/pdfs/10-371.pdf

Publications from Prior Years

1. 2004NJ71B ("Soil Moisture Regimes and Nitrate Leaching in Urban Wetlands") - Articles in Refereed Scientific Journals - Stander, E. K. and J. G. Ehrenfeld. 2009. Rapid assessment of urban wetlands: functional assessment model development and evaluation. Wetlands 29(1): 261-276.
2. 2004NJ71B ("Soil Moisture Regimes and Nitrate Leaching in Urban Wetlands") - Articles in Refereed Scientific Journals - Stander, E. K. and J. G. Ehrenfeld. 2009. Rapid assessment of urban wetlands: do hydrogeomorphic classification and reference criteria work? Environmental Management. 43(4): 725-742.
3. 2004NJ73B ("Use of stable isotope ratios of mercury to track and differentiate between sources of mercury pollution") - Articles in Refereed Scientific Journals - Kritee K., Tamar Barkay and Joel D. Blum, 2009, Mass dependent stable isotope fractionation of mercury during mer mediated microbial degradation of monomethylmercury, Geochimica et Cosmochimica Acta, 73 (5): 1285-1296.
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5. 2004NJ73B ("Use of stable isotope ratios of mercury to track and differentiate between sources of mercury pollution") - Dissertations - Kritee, K. 2008. Mass dependent stable isotope fractionation of mercury during its microbial transformations. Ph.D. dissertation. Department of Biochemistry and Microbiology, Rutgers, The State University of New Jersey, New Brunswick, NJ. 167 pages.
6. 2004NJ73B ("Use of stable isotope ratios of mercury to track and differentiate between sources of mercury pollution") - Conference Proceedings - Kritee, K., T. Barkay and J.D. Blum, 2008, Mass dependent isotope fractionation of Hg during biotic degradation of methyl-Hg & reduction of Hg(II), Geochimica Et Cosmochimica Acta, 72, A499.
7. 2004NJ73B ("Use of stable isotope ratios of mercury to track and differentiate between sources of mercury pollution") - Conference Proceedings - Kritee K., Tamar Barkay and Joel D. Blum, 2008, Absence of magnetic isotope fractionation for Hg during dark biological processes: experimental evidence and theoretical considerations, Eos Trans. AGU, 89 (53), Fall Meet. Suppl., V52B-06. (Invited talk)
8. 2005NJ82B ("Examining Effects of Soil Compaction on Pollutant Removal Efficiency and Lifespan of a NJ Approved Stormwater Best Management Practice") - Dissertations - Moore, James. 2008. Effect of Compaction on Removal Efficiency of Lead, Copper, Zinc, Nitrate and Phosphate in a Bioretention System: A Column Study. M.S. Thesis. Department of Environmental Sciences, Rutgers, The State University of New Jersey, New Brunswick, NJ. 171 pages.
9. 2006NJ105B ("The Potential Impact of the Asian Isopod, Synidotea laevidorsalis (Miers 1881), on the Delaware Bay, USA") - Dissertations - Boyd, S. 2008. An Ecological Assessment of the Non-Indigenous Isopod, Synidotea laticada, in Delaware Bay. Masters Thesis, Dept. of Ecology and Evolution, Graduate Program, Rutgers University, New Brunswick, NJ. 82 pp.
10. 2006NJ98B ("Advancing the characterization of fractured bedrock aquifers using electrical geophysical methods: application to water resources evaluation in the New Jersey Highlands") - Articles in Refereed Scientific Journals - Wishart, D.N., L. Slater and A. Gates, 2008, Anisotropy characterization in fractured crystalline bedrock using field-scale azimuthal self potential gradient (ASPG), Journal of Hydrology, 358, 35-45.
11. 2006NJ98B ("Advancing the characterization of fractured bedrock aquifers using electrical geophysical methods: application to water resources evaluation in the New Jersey Highlands") - Articles in Refereed Scientific Journals - Wishart, D.N., L.D. Slater, D.L. Schnell, and G.C. Herman, 2009, Hydraulic anisotropy characterization of pneumatic-fractured sediments using azimuthal self potential gradient, Journal of Contaminant Hydrology, 103, 134–144.

12. 2006NJ98B ("Advancing the characterization of fractured bedrock aquifers using electrical geophysical methods: application to water resources evaluation in the New Jersey Highlands") - Conference Proceedings - Schnell, D. L, D. N. Wishart, L. D. Slater, and G. C. Herman, 2008. Non-Invasive Geophysical Method for Evaluating Fractures Induced By Pneumatic or Hydraulic Fracturing, The 2nd International Conference on Contaminated Fractured Rock: Characterization & Remediation CFR-2, September 22-25, 2008, San Diego, CA. (Oral presentation)
13. 2006NJ98B ("Advancing the characterization of fractured bedrock aquifers using electrical geophysical methods: application to water resources evaluation in the New Jersey Highlands") - Conference Proceedings - Slater, L., D. Wishart, D. Schnell, and G. Hermann, 2008, Hydraulic Anisotropy Characterization Using Azimuthal Self Potential Gradient [ASPG]: Results from Pneumatic Fracturing of Tight Clay Soils, Eos Trans. AGU, 89(53), Fall Meet. Suppl., Abstract NS41A-05
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15. 2006NJ118B ("Integrated Assessment of Economic and Water Quality Impacts of Agricultural Best Management Practices in Upper Cohansey River Watershed") - Conference Proceedings - Qiu, Z., C. Hall and K. Hale. 2008. Cost-effective Assessment of Alternative Conservation Buffer Restoration Strategies in Agricultural Lands. The 63rd Annual International Conference of Soil and Water Conservation Society, Tucson, AZ, July 26-30, 2008. (Oral Presentation)
16. 2006NJ118B ("Integrated Assessment of Economic and Water Quality Impacts of Agricultural Best Management Practices in Upper Cohansey River Watershed") - Conference Proceedings - Qiu, Z. 2008. Understanding Economics and Water Quality Impacts of Agricultural BMPs in a Suburban Watershed in New Jersey. The 63rd Annual International Conference of Soil and Water Conservation Society, Tucson, AZ, July 26-30, 2008. (Oral Presentation)
17. 2006NJ118B ("Integrated Assessment of Economic and Water Quality Impacts of Agricultural Best Management Practices in Upper Cohansey River Watershed") - Dissertations - Florencio C. Ballesteros Jr. 2008. Predicting Land Use Changes Using Parcel-level Data: Model Development and Application to Hunterdon County, New Jersey. Ph.D. Dissertation. Department of Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, NJ. 223 pages.
18. 2005NJ84B ("The Influence of Urbanization on Watershed Nitrogen Cycling Watersheds") - Articles in Refereed Scientific Journals - Rosenzweig, Bernice; Hee Sun Moon; James A. Smith; Mary Lynn Baeck; Peter R. Jaffe, 2008, Variation in the instream dissolved inorganic nitrogen response between and within rainstorm events in an urban watershed, Journal of Environmental Science and Health -Part A, 43(11), 1223-1233.
19. 2007NJ139B ("Phosphate and Thermal Stabilization of Dredged Sediments for Reuse as Construction Material") - Dissertations - Ndiba, Peter, 2009, Phosphate and Thermal Stabilization of Heavy Metals in Dredged Sediments, "Ph.D. Dissertation," Department of Civil and Environmental Engineering, Newark College of Engineering, New Jersey Institute of Technology, Newark, NJ, 125 pages.
20. 2007NJ139B ("Phosphate and Thermal Stabilization of Dredged Sediments for Reuse as Construction Material") - Book Chapters - Ndiba, Peter Kuria; Lisa Axe, 2009, Metal speciation in phosphate and thermal stabilization of contaminated dredged sediments. In Contemporary Topics in Ground Modification, Problem Soils, and Geo-Support (GSP 187); Iskander, M.; Laefer D. F.; Hussein, M. H. eds.; American Society of Civil Engineers, ISBN 13 #9780784410233, pp 512-519.
21. 2007NJ132B ("Development of Microscale Membrane Extraction for trace Monitoring of Pesticides and other Emerging Pollutants in Water") - Conference Proceedings - Hylton, Kamilah, S. Mitra, 2007, Comprehensive Microscale Membrane Extraction of Antibiotics. Eastern Analytical Symposium, Somerset, NJ. (oral presentation)
22. 2007NJ132B ("Development of Microscale Membrane Extraction for trace Monitoring of Pesticides and other Emerging Pollutants in Water") - Conference Proceedings - Hylton, Kamilah, S.Mitra,

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23. 2007NJ132B ("Development of Microscale Membrane Extraction for trace Monitoring of Pesticides and other Emerging Pollutants in Water") - Conference Proceedings - Hylton, Kamilah, S. Mitra, 2007, Trace Monitoring of New and Emerging Pollutants Via Microscale Membrane Extraction Techniques. Meadowlands Symposium II. Hackensack, NJ. (oral presentation)