ATMOSPHERIC DRY DEPOSITION OF PERSISTENT ORGANIC POLLUTANTS TO THE ATLANTIC AND INFERENCES FOR THE GLOBAL OCEANS

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This supplementary information contains 11 pages (including cover sheet) and 4 figures.

SUPPLEMENTARY MATERIAL

ANNEX I:

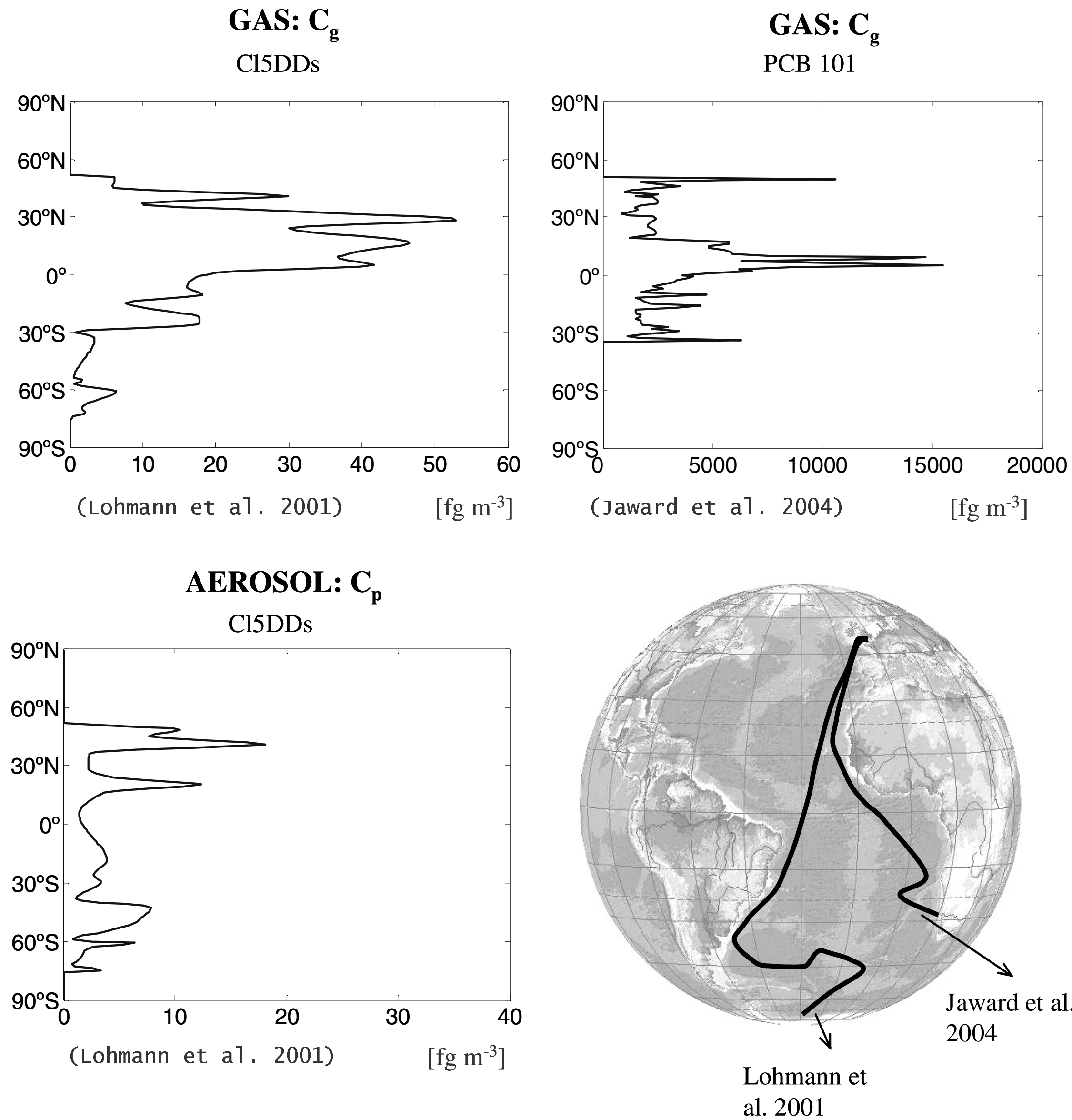

Figure A1.1: Information of the cruise data: Profiles of the measured gas and aerosol phase POP concentrations and sketch of the sampling routes.

ANNEX II:

Annex 2 aims to obtain the mass fraction of aerosols of size *i* (w_i) from parameters given by MODIS: r_{eff} and $\log(\sigma_{eff})$.

Pre-assumptions on the general structure of the size distribution are required in the inversion of MODIS data. The usual approach is to consider that the size distribution of the aerosol particles follows a lognormal distribution (1-3), which is the assumption behind MODIS dataset,

$$N(D) = \frac{N_{tot}}{\sqrt{2\pi}\, D \log(\sigma_{D,g})} \exp\left(-\frac{(\ln D - \ln D_g)^2}{2\log^2(\sigma_{D,g})} \right) \quad \text{[A.1]}$$

where N(D) (μm^{-1} m^{-3}) is the number distribution function, thus N(D)dD is the number concentration of particles having diameters in the range D to D+dD. N_{tot} is the total aerosol number concentration (m^{-3}), D_g (μm) is the median diameter, corresponding to 2 r_g,(μm) and $\log(\sigma_{D,g})$ (log μm) is the geometric standard deviation of the particle diameter, which corresponds to $\log(2)+\log(\sigma_{r,g})$. r_g and $\log(\sigma_{r,g})$ are derived from r_{eff} and $\log(\sigma_{eff})$, through equations 4 and 5 described in the paper. The effective radius, r_{eff}, is defined as the area weighted mean through the following equation (4):

$$r_{eff} = \frac{\int_{r_{min}}^{r_{max}} r^3 N(r)dr}{\int_{r_{min}}^{r_{max}} r^2 N(r)dr} \quad \text{[A.2]}$$

Through mathematical relationships, and assuming all particles as spheres, it is seen that the volume distribution is also a log-normal with the same geometric standard deviation as the number distribution, but with the volume median diameter D_{vg} (μm) given by (2):

$$D_{vg} = \exp(\ln D_g + 3\log^2(\sigma_{D,g})) \quad \text{[A.3]}$$

Thus,

$$V(D) = \frac{\pi}{6} D^3 N(D) = \frac{N_0}{\sqrt{2\pi}\ D \log(\sigma_{D,g})} \exp\left(-\frac{(\ln D - \ln D_{vg})^2}{2 \log^2(\sigma_{D,g})} \right) \qquad [A.4]$$

The volume of particles lying between an specific range of aerosol diameters (between D_{min} (µm) and D_{max} (µm)) is defined through the following relationship (2):

$$V(D_{min}, D_{max}) = \frac{N_0}{2} \left[\mathrm{erf}\left(\frac{\ln(D_{max} / D_{vg})}{\sqrt{2} \log(\sigma_{D,g})} \right) - \mathrm{erf}\left(\frac{\ln(D_{min} / D_{vg})}{\sqrt{2} \log(\sigma_{D,g})} \right) \right] \qquad [A.5]$$

where erf is the error function defined as:

$$\mathrm{erf} z = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\eta^2} d\eta \qquad [A.6]$$

Assuming equal density for all the size spectrum of aerosols (ρ_P= 2 g cm^{-3}), the mass fraction between a range of diameters (w_i) is equivalent to the volume fraction. Hence, if we account for the range of diameters retrieved by the MODIS satellite (0.1-20 µm):

$$w_i = \frac{V(D_{min}, D_{max})}{Vtot} = \frac{\left[erf\left(\frac{\ln(D_{max} / D_{vg})}{\sqrt{2} \log(\sigma_{D,g})} \right) - erf\left(\frac{\ln(D_{min} / D_{vg})}{\sqrt{2} \log(\sigma_{D,g})} \right) \right]}{\left[erf\left(\frac{\ln(20 / D_{vg})}{\sqrt{2} \log(\sigma_{D,g})} \right) - erf\left(\frac{\ln(0.1 / D_{vg})}{\sqrt{2} \log(\sigma_{D,g})} \right) \right]} \qquad [A.7]$$

ANNEX III:

This section includes the method used to model dry deposition velocity to natural water surfaces, performed through an adaptation from the Williams model (5). This model includes effects of spray formation during high wind speed periods, effects of particle growth due to high relative humidities, the variation of turbulent transport with wind speed, and surface roughness.

It separates the atmosphere below a reference height (10m) into two layers, as suggested by Slinn and Slinn (6). The model parameterizes transport through an upper layer to an underlying laminar sublayer and provides different paths for smooth water and water broken by whitecaps. Gravitational settling is superimposed on transport through both layers. The gravitational settling velocity v_S (cm s^{-1}) , either referred to dry particle diameter (then v_{S_dry}) or wet particle diameter (then v_{S_wet}), is given by Stokes Law as:

$$v_S = \frac{1}{18}\frac{\left(D_P 10^{-4}\right)^2 \rho_p g C_c}{\mu} \qquad \text{[A.8]}$$

where D_p is the particle diameter (μm) either in dry conditions (D_{dry}) or in humid conditions (D_{wet}), ρ_p the particle density (g cm^{-3}), assumed constant and equal to 2 g cm^{-3}, g is the acceleration due to gravity (9.8 m s^{-2}), C_C is the Cunningham correction factor (dimensionless), μ the dynamic viscosity of the air (g cm^{-1} s^{-1}).

The Cunningham correction factor is (2):

$$C_C = 1 + \frac{2\lambda}{D_P}\left[1.257 + 0.4\exp\left(-\frac{1.1 D_P}{2\lambda}\right)\right] \qquad \text{[A.9]}$$

where λ is the air mean free path ($7.63*10^{-6}$ cm at 298K).

Conversely, the dynamic viscosity of the air (μ, g cm^{-1} s^{-1}), for T> 273K is given by (4),

$$\mu = \left(1.718\times10^{-5} + 0.0049\times10^{-5}\times(T-273.15)\right)\times10 \qquad \text{[A10]}$$

The wet particle diameter (D_{wet} , μm) results from the increase of the dry particle diameter (D_{dry} , μm) due to humidity, and it is estimated according to Fitzgerald's formulation (7) , assuming a relative humidity around 80%:

$$D_{wet} = 2\left(2.3489\left(\frac{D_{dry}}{2}\right)^{1.00638}\right) \qquad \text{[A.11]}$$

Hygroscopic growth has been found to be an important factor (8); other factors such as waves (9) (not only white caps) can affect but they are not taken into account here by means of simplicity and restrained by the input and available parameters retrieved from remote sensing.

The aerodynamic or turbulent transfer coefficient (k_{ax}, cm s^{-1}) is used to characterize the turbulent transport in the overlying constant flux layer. Assuming neutral atmosphere, it is given by (2):

$$k_{ax} = \frac{\kappa u^*}{\ln\left(\frac{z}{z_{0x}}\right)} \qquad [A.12]$$

where the subscript x is either s (then k_{as}, smooth surface transfer coefficient) or b (then k_{ab}, broken surface transfer coefficient) , κ is von Karman's constant=0.4, u* the friction velocity (cm s^{-1}), z is the reference height (taken=1000 cm), z_{0x} is the roughness length (assumed equal to 0.1 cm for broken open sea and 0.01 cm for calm open sea (2)).

The friction velocity u* is parameterized versus the mean wind speed retrieved by the satellite (u10, cm s^{-1}) (6):

$$u^* = u_{10}\sqrt{C_D} \qquad [A.13]$$

where Cd=$1.3*10^{-3}$ is the drag coefficient in reference height of 10 m (6)

Transport through the sublayer (k_{xs}, cm s^{-1}) incorporates Brownian diffusion and inertial impaction. When referred to the smooth water surface it is characterized by the transfer coefficient k_{ss}, (cm s^{-1}):

$$k_{ss} = \left(\frac{(u^*)^2}{\kappa u_{10}}\right)\left[10^{(-3/St)} + Sc^{(-1/2)}\right] \qquad [A.14]$$

where St (dimensionless) is the Stokes number $=(u^*)^2 v_{s\_wet}/g\nu$, ν (cm^2 s^{-1}) is the kinematic viscosity $=10^4(\mu/\rho_{air})$, ρ_{air} (kg m^{-3}) the density of air and equals $(10*28.96*P)/(R*10^{-3}*T)$, R is the gas constant; Sc (dimensionless) is the Schmidt number ($Sc = \nu / D_c$) and D_c (cm^2 s^{-1}) is the diffusivity of the particles ≈ $(2.38*10^{-7}/D_{wet})(1+0.163/D_{wet}+0.0548\exp(-6.66D_{wet})/D_{wet}))$;

On the other hand when referred to the broken surface transfer coefficient ($k_{bs,}$), it is assumed to be 10 cm s^{-1} (5).

Since wind speeds estimations by remote sensing are monthly averages, it is important to account for the short-term variability and nonlinear influence of wind speed on St and k_{ss}. It has been assumed an oceanic Weibull distribution of wind speed with a shape parameter of 2, described in Livingstone and Imboden (10). Thus,

Cumulative 2-parameter Weibull distribution: $F(u_{10}) = \exp - \left(\frac{u_{10}}{\eta} \right)^2$ [A.15]

$F(u_{10})$ corresponds to the probability of a measured wind speed exceeding a given value u_{10}, with the scale parameter η

$$St_{\_weibull} = \frac{v_{s\_wet} C_D}{g \upsilon \Gamma\left(1 + \frac{1}{2}\right)} u_{10}{}^2 \Gamma\left(1 + \frac{2}{2}\right) \qquad [A.16]$$

$$k_{ss\_weibull} = \frac{u_{10}{}^2 C_D \Gamma(2) \Gamma(0.5)}{\kappa u_{10} \Gamma(1.5)} \left[10^{(-3/St\_weibull)} + Sc^{(-1/2)} \right] \qquad [A.17]$$

Finally, the dry deposition velocity (v_D, cm s^{-1}) is obtained through the following equation, obtained by applying the resistance method with the transfer coefficients described above (5):

$$v_D = \frac{A}{B} \left[(1-\alpha)(k_{ss} + v_{S\_wet}) + \frac{k_m \alpha (k_{bs} + v_{s\_wet})}{k_m \alpha (k_{ab} + k_{bs} + v_{s\_wet})} \right] + \frac{\alpha (k_{bs} + v_{s\_wet}) \alpha (k_{ab} + v_{s\_dry})}{k_m + \alpha (k_{ab} + k_{bs} + v_{s\_wet})}$$

[A.18]

where

$$A = k_m \left[(1-\alpha) k_{as} + \alpha k_{ab} + v_{s\_dry} \right] + (1-\alpha)(k_{as} + v_{s\_dry}) \alpha (k_{ab} + k_{bs} + v_{s\_wet}) \qquad [A.19]$$

$$B = k_m \left[(1-\alpha)(k_{as} + k_{ss\_Weibull}) + \alpha (k_{ab} + k_{bs}) + v_{s\_wet} \right] + (1-\alpha)(k_{as} + k_{ss\_Weibull} + v_{s\_wet}) \alpha (k_{ab} + k_{bs} + v_{s\_w}$$

[A.20]

The fraction of area that has a broken surface is represented by α. This value is strongly dependent on wind speed (u_{10}, cm s^{-1}) and can be calculated as (5):

$$\alpha = 1.7 \times 10^{-6} (u_{10} 10^{-2})^{3.75} \tag{A.21}$$

The lateral transfer coefficient (k_m, cm s^{-1}) is assumed equal k_{as} (5)

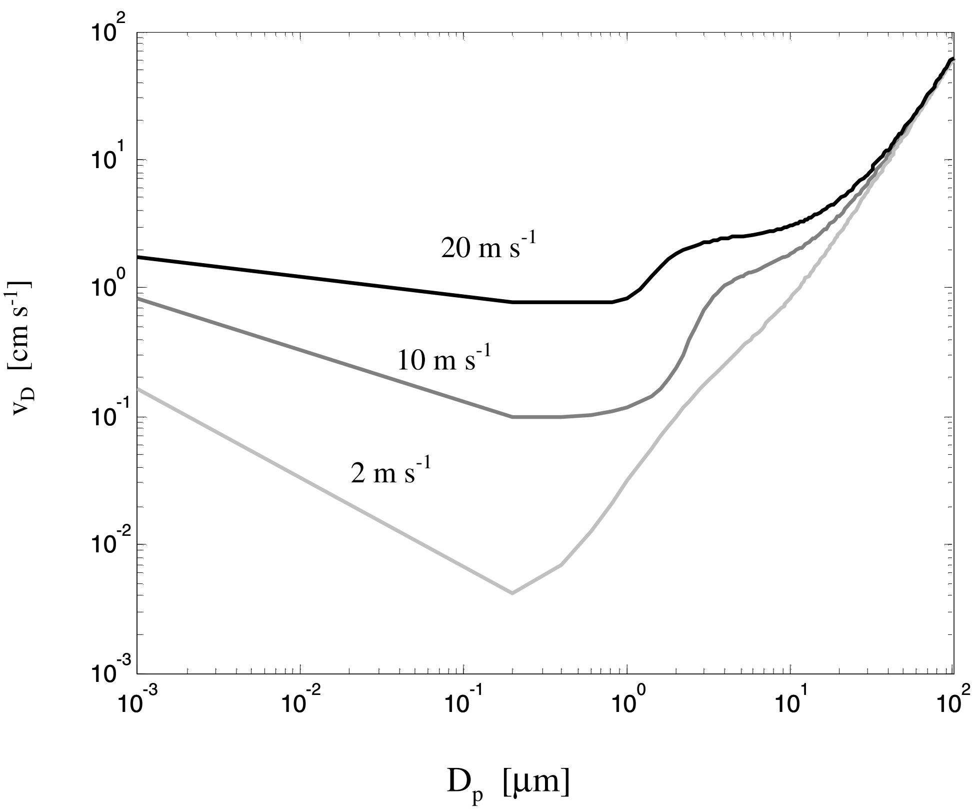

Figure A3.1: Dry deposition velocity versus aerosol diameter for different wind speeds. Assumptions for this figure are sea surface temperature of 298K, relative humidity about 80 %, and aerosol density of 2 g cm^{-3}.

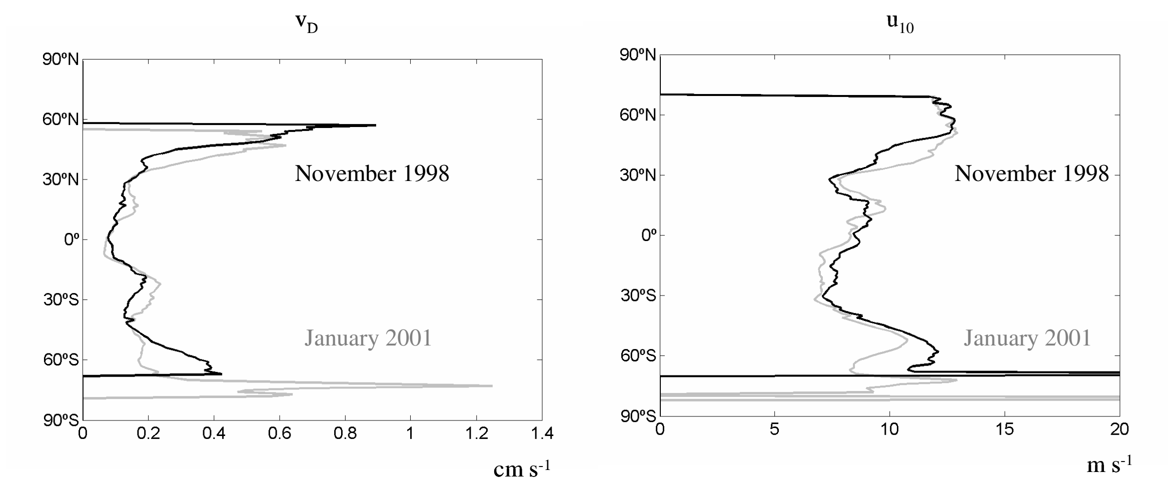

FIGURE A3.2: Latitudinally averaged profiles of dry deposition velocity and wind speed over the Atlantic Ocean.

ANNEX IV

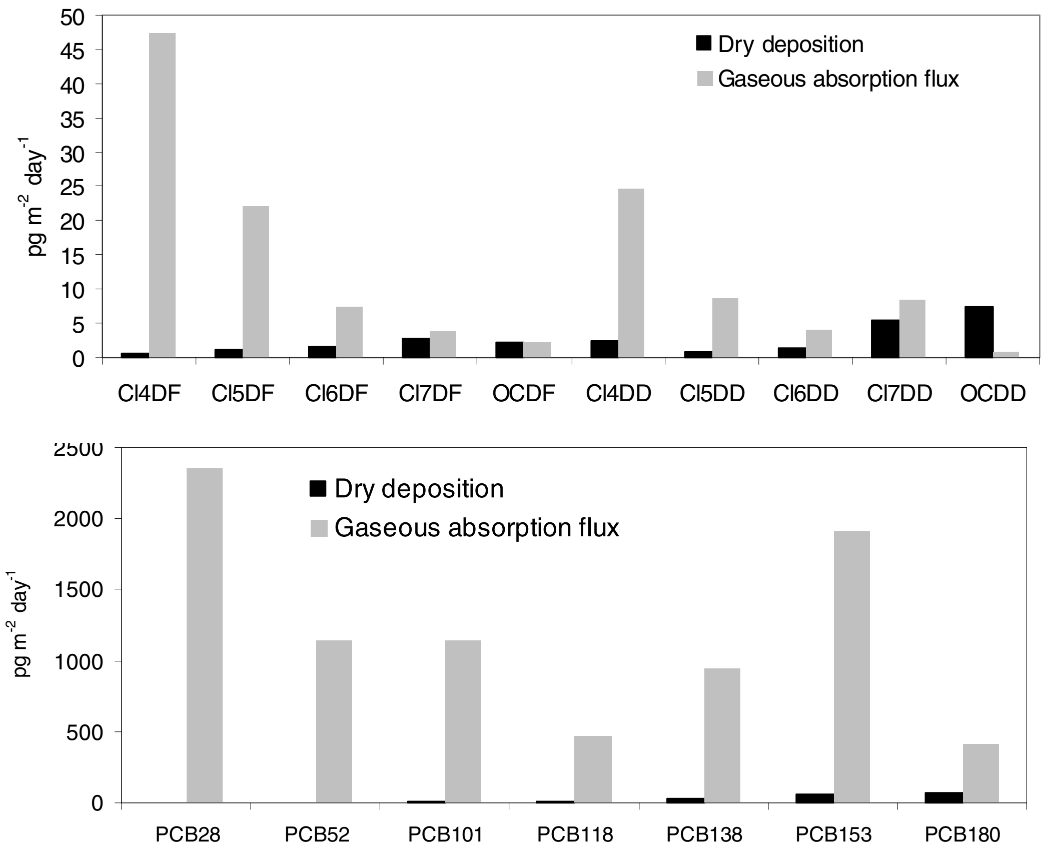

Figure A4.1: Comparison of gross absorption and dry aerosol deposition fluxes of PCBs and PCDD/Fs. Values correspond to averaged fluxes to the Atlantic Ocean.

REFERENCES

(1) Tanré, D.; Kaufman, Y. J.; Herman, M.; Mattoo, S. *J. Geophys. Res.* **1997**, *102*, 16971-16988.

(2) Seinfeld, J. H.; Pandis, S. N. *Atmospheric chemistry and physics: From air pollution to climate change*; Wiley-Interscience: New York, 1998.

(3) Kaufman, Y. J.; Tanré, D. "Algorithm for remote sensing of tropospheric aerosol from MODIS," MODIS Algorith Theoretical Basis Document No. ATBD-MOD-02, 1998.

(4) King, M. D.; Tsay, S.-C.; Platnik, S. E.; Wang, M.; Liou, K.-N. "Cloud retrieval Algorithms for MODIS: Optical Thicknee, Effective Particle Radius and Thermodynamic Phase," MODIS Algorith Theoretical Basis Document No. ATBD-MOD-05 MOD-06 Cloud product, 1997.

(5) Williams, R. M. *Atmos. Environ.* **1982**, *16*, 1933-1938.

(6) Slinn, S. A.; Slinn, W. G. N. *Atmos. Environ.* **1980**, *14*, 1013-1016.

(7) Fitzgerald, J. W. *J. Appl. Met.* **1975**, *14*, 1044-1049.

(8) Ondov, J. M.; Quinn, T. L.; Battel, G. F. Influence of temporal changes in relative humidity on size and dry depositional fluxes of aerosol particles bearing trace elements. In *Atmospheric deposition of contaminants to the great lakes and coastal waters. Preceedings from a session at the SETAC 15th Annual Meeting 30 October-4 November 1994*; Baker, J. E., Ed.; SETAC press: Denver, 1994; pp 17-34.

(9) J. Zufall, M.; Dai, W.; I. Davidson, C. *Atmos. Environ.* **1999**, *33*, 4283-4290.

(10) Livingstone, D. M.; Imboden, D. M. *Tellus* **1993**, *45B*, 275-295.