Critical Review

Temperature Dependence of Atmospheric Concentrations of Semivolatile Organic Compounds

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Reported data on the temperature dependence of atmospheric concentrations of semivolatile organic compounds (SOCs) are compiled and expressed as linear regressions of the logarithm of the partial pressure in air versus reciprocal temperature: $\ln p_A = m/T + b$. Two simple models are introduced to explain the dependence of these air concentrations on temperature. The first assumes equilibrium between the atmosphere and the earth's surface. In the second, air concentrations are established as a result of chemical inflow and outflow in advected air and reversible exchange with a soil or water surface. The model equations are rearranged to express the partial pressure of the chemical as a function of temperature. On the basis of these models, it is shown that only under selected circumstances, namely, if surface contamination is high and atmospheric background concentration low, does the slope m of the $\ln p$ vs $1/T$ relationship reflect the thermodynamics of air−surface partitioning. Generally, however, m is a measure of the extent to which air concentrations are controlled by evaporation from surfaces close to the sampling location and by advection of air masses with global background concentrations. A shallow slope or low temperature dependence indicates that long-range transport controls atmospheric levels at a sampling site. Steeper slopes indicate high surface concentrations in the vicinity of the site. This hypothesis is applied to the observed temperature dependence of the compiled atmospheric concentration data and is found to be capable of explaining differences in slope m (i) between chemicals, (ii) between sampling sites, and (iii) at different seasons. Research efforts should be directed toward quantifying by measurements and predicting by models the kinetics of exchange of SOCs between the atmosphere and various surfaces.

Introduction

Cyclic fluctuations of concentrations of semivolatile organic compounds (SOCs) in the atmospheric environment are both interesting and important phenomena, the investigation of which may further the understanding of chemical fate in the environment. Such oscillations have been observed with both an annual (*1−5*) and a daily (*6, 7*) periodicity and are caused by the periodicity of both natural phenomena and human behavior (Table 1). Because temperature has a marked impact on the partitioning properties of organic chemicals (*8*), the following discussion will focus on this aspect of periodical concentration changes.

In this review, data on the observed temperature dependence of SOC concentrations in the atmosphere are compiled. Two approaches for quantifying temperature-driven cycles of air−surface exchange of SOCs are introduced. One is based on the assumption of a chemical equilibrium being established between the sampled atmosphere and surface; the other takes into account the kinetics of air−surface exchange. Equations describing the theoretically expected temperature dependence of air concentrations are derived and, equipped with these insights, the observed temperature relationships are reexamined and interpreted.

Measured Air Concentrations Regressed vs Reciprocal Temperature

In several instances, vapor phase concentrations of SOCs and corresponding temperatures have been measured at one location year-round, during several seasons, or at different times of the day. The logarithm of the gas-phase concentration (C_A) or preferably the partial pressure of the gas (p_A) can be regressed with reciprocal temperature $1/T$ with a slope m. Ideally, the temperature of the air−surface interface at the time of sampling should be used. However, interfacial temperatures are often not available, and temperatures can vary substantially during the time period it takes to sample air for SOC measurements. A time-averaged atmospheric temperature close to the ground is usually the only measurement available.

We compiled and analyzed all available data on temperature-dependent air concentrations of hexachorocyclohexanes (HCHs) and polychlorinated biphenyls (PCBs) and calculated (or culled and converted from the original papers) regressions of $\ln p_A$ vs $1/T$. Most of these studies regressed the logarithm of air concentrations (expressed on a pg/m^3 basis) and used the decadic instead of the natural logarithm. To make the data comparable, we either recalculated the temperature dependence from the original concentration data or converted the reported slopes.

Hexachlorocyclohexanes. Air concentrations of α- and γ-HCH as a function of temperature (Table 2) have been reported for cold temperate regions of central North America and northern Europe (*2, 5, 7, 9, 10*). Some studies (*11−13*) relied on a very limited data set and should be interpreted

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TABLE 1. Potential Driving Forces for Periodically Changing Concentrations of Contaminants in the Environment

driving force	examples
emissions and human behavior	pesticides with specific annual application period emission max of combustion-related contaminants during rush hour traffic or during winter work day/weekend differences for chemical emissions associated with manufacturing processes
degradation processes	degradation max during noon/summer, when OH radical concentrations are highest (e.g., ref *39*)
phase composition and surface properties	increase of particulate organic carbon content in water during phytoplankton blooms periodic changes in surface properties such as seasonal vegetation cover, snow/sea ice cover, or periodic flooding of tidal flats, drying of soils.
meteorological and climatic features	periodically changing temperatures: seasonally, daily periodically changing precipitation: wet vs dry seasons, noon rains in the tropics periodically changing wind patterns: valley/mountain and land/sea wind systems seasonally changing large-scale atmospheric transport patterns, e.g., arctic haze max during late winter associated with efficient meridional transport during that time period.

TABLE 2. Measured Temperature Dependence of α- and γ-HCHs Partial Pressure at Various Locations

	α-HCH				γ-HCH						
	m	*n*	r^2	*p*	*m*	*n*	r^2	p		*T* range	ref
Stockholm, Sweden[b]	−6192 ± 930	11	0.83	<0.001	−8187 ± 1651	11	0.73	<0.001	?	−11 to 11	11
Aspvretn, Sweden[b]	−4364 ± 433	10[c]	0.93	<0.001	−8338 ± 1763	11	0.71	<0.01	?	−7 to 18	11
Egbert, ON (all temps)[b]	−2252 ± 223	141[c]	0.42	<0.001	−5810 ± 284	142[c]	0.75	<0.001	G	−16 to 28	2
Egbert, ON (only $T > 0$ °C)[b]	−1179 ± 717	76[c]	0.04	ns	−7405 ± 906	77[c]	0.47	<0.001	G	0 to 28	2
Pt. Petre, ON[b]	−5468 ± 1704	9	0.60	<0.05	+63 ± 2263	9	0.00	ns	G	−5 to 11	12, 13
Turkey Lake, ON[b]	−3511 ± 636	12	0.75	<0.001	−2109 ± 1925	12	0.11	ns	G	1 to 18	12, 13
Villeroy, PQ[d]	−440	35	0.00	nr	−8293	32	0.49	nr	G	0 to 22	9
Marcell Bog, MN[d]	−5045	50	0.16	nr	−7304	44	0.65	nr	G	−5 to 30	7
Rörvik, Sweden[b,e]	−7715 ± 2810	23	0.26	<0.05	−8088 ± 4073	23	0.16	ns	T	−5 to 18	10
Gårdsjön, Sweden[b]	−2564 ± 1813	14	0.14	ns	−11556 ± 2600	14	0.62	<0.001	T	−1 to 19	10
Lista, Norway	−2290 ± 457	238	0.10	<0.001	−5493 ± 692	233	0.21	<0.001	T	−8 to 22	5
South Atlantic[b]	−6462 ± 1660	14	0.56	<0.01	−7423 ± 1440	14	0.69	<0.001	?	5 to 29	26

[a] Given is the slope *m* of the relationship $\ln(p_a/\mathrm{Pa}) = m/(T/K) + b$, the number of observations *n*, the regression coefficient r^2, the level of significance, and the temperature range during the measurements. In the third column from the right, G stands for gas-phase concentrations, and T stands for total atmospheric concentrations. ns, not significant; nr, not reported. [b] Temperature dependence calculated using concentration data reported in ref. [c] Extreme outlier was eliminated. [d] Slope m' given in ref converted using $m = 2.303m' - T$, where *T* is average temperature of sampling site, assumed to be 280 K. [e] Data from 1989 to 1992.

with caution. It is noteworthy that, in all studies of α-HCH involving a relatively large number of samples, temperature can explain none or only a very minor fraction of the variability in the air concentrations. The studies with a limited number of samples have much higher correlation coefficients but should be considered less reliable. Atmospheric γ-HCH (lindane) concentrations, on the other hand, tend to be more strongly correlated with temperature, and r^2 often exceeds 0.5. Most studies show a slope *m* of 7000−8500 K. The data from Lista in southern Norway are unique in that the slope is shallower (5500 K) and the r^2 is only 0.2 (*5*).

Polychlorinated Biphenyls. Atmospheric PCB concentrations as a function of temperature have been investigated at urban locations (*4*, *6*, *11*, *14*−*16*), rural sites in cold temperate regions (*2*, *7*, *10*, *11*, *17*, *18*), as well as very remote sites (*19*, *20*). Because the air−surface exchange is likely to be influenced by physical−chemical properties, it is more appropriate to analyze the temperature dependence for individual congeners rather than the sum of PCBs. Space limitations, however, allow us only to report the relationships for the sum of several PCB congeners (Table 3). Regression parameters for the most commonly reported congeners are provided in the Supporting Information (Table S1).

The temperature dependence for ∑PCBs is almost always highly significant ($p < 0.001$). Slopes are mostly in the range of 4500−7500 K. The exceptions are the Arctic sites, which have shallow slopes or show no temperature dependence. In North America there seems to be a clear decline in slope *m* with increasing distance from suspected PCB sources. For example, *m*(urban industrial/Bloomington) is 6000−7000 K and exceeds *m*(rural/Great Lakes, Minnesota) of 4000−5000 K, which further exceeds *m*(remote/Arctic Canada). In Europe no such differences can be observed, neither between urban and rural sites nor between coastal and terrestrial locations. The rural sites (Lista, Gårdsjön, and Rörvik) appear to have slightly steeper slopes than the urban locations (Augsburg, Manchester). The Arctic site (Ny Ålesund) has a very low slope.

In three studies (*7*, *10*, *17*) the slope *m* calculated for various PCB isomers is related to chemical characteristics; namely, it increases with an increasing number of chlorine atoms in the molecule—by about 1200−2000 K for each additional chlorine (Figure 1). No such relationships were found when analyzing the data measured in Egbert (*2*) and urban locations (*4*, *16*, *15*).

A feature first noted by Hoff et al. (*2*) is that whereas the concentrations of some SOCs increased strongly with temperature during summer, the temperature dependence vanished at lower temperatures. This results in nonlinear ln p_A vs $1/T$ plots as shown in Figure 2. The temperature below which the temperature dependence ceases is chemical-dependent. The concentrations of PCB-52 showed no temperature dependence below approximately 5 °C, but for those of γ-HCH, the corresponding temperature was approximately −5 °C (Figure 2). Tables 2, 3, and S1 thus report two slopes for the data from Egbert, one obtained using all measured values and one describing only those measurements conducted at temperatures above freezing. Other studies have failed to observe this behavior, but this may be

TABLE 3. Temperature Dependence of PCB Partial Pressure at Various Locations

	m	*n*	r^2	*p*		*T* range	ref
Stockholm, Sweden[b,c]	−6833 ± 1021	11	0.83	<0.001	?	−11 to 11	11
Bloomington, IN[b]						−8 to 35	
courthouse[c]	−7598 ± 1035	23	0.72	<0.001	G		14
batchelor[c]	−7787 ± 870	36	0.70	<0.001	G		14, 15
Sanders[c]	7556 ± 1853	18	0.51	<0.001	G		14
Bloomington, IN[b]							6
using *T* in soil	−6778 ± 1374	19	0.59	<0.001	T	14 to 26	
using *T* in air	−6974 ± 1212	19	0.66	<0.001	T	12 to 25	
Augsburg, Germany[b,d]	−5358 ± 669	8	0.91	<0.001	G	0 to 17.5	16
Manchester, U.K.[b]	−4766 ± 776	57	0.41	<0.001	G	1 to 21.5	4
Aspvreten, Sweden[b,c]	−12518 ± 906	10	0.96	<0.001	?	−7 to 18	11
Rörvik, Sweden[b,d]	−5724 ± 1498	32	0.33	<0.001	T	−5 to 18	10
Gårdsjön, Sweden[d]	−6775 ± 749	14	0.87	<0.001	T	−1 to 19	10
Lista, Norway[d]	−6746 ± 549	201	0.43	<0.001	T	−5 to 20	17
Egbert, ON (all temps)	−4596 ± 410	143	0.47	<0.001	G	−16 to 28	2
Egbert, ON (only $T > 0$ °C)	−9963 ± 1138	78	0.50	<0.001	G	0 to 28	2
north Wisconsin[b]	−4086 ± 506	14	0.84	<0.001	G	−13 to 22	1
Marcell Bog, MN[e]	−4886 ± ?	50	0.44	nr	G	−5 to 30	7
Great Lakes, IADN[f]							18
Eagle Harbor, MI	−4501 ± 450	nr	0.39	<0.001	G	−18 to 28	
Sleeping Bear, MI	−4471 ± 447	nr	0.41	<0.001	G	−12 to 27	
Sturgeon Pt., NY	−4603 ± 368	nr	0.50	<0.001	G	−11 to 28	
Ny-Ålesund, Svalbard[b,d]	−1383 ± 853	52	0.05	<0.2	T	−15 to 7	19

[a] Given is the slope *m* of the relationship $\ln(p_a/\text{Pa}) = m/(T/K) + b$, the number of observations *n*, the regression coefficient r^2, the level of significance, and the temperature range during the measurements. In the third column from the right, G stands for gas-phase concentrations, and *T* stands for total atmospheric concentrations. nr, not reported. [b] Temperature dependence calculated using concentration data reported in ref. [c] Assumed average molecular mass of 326.4 g/mol. [d] Total PCBs is only sum of a few selected isomers. [e] Slope *m*′ given in ref converted using $m = 2.303m' - T$, where *T* is average temperature of sampling site, assumed to be 280 K. [f] Slope *m* given in ref.

due to a narrow temperature range at the sampling site or an insufficient number of samples at low temperatures. As a result of this phenomenon, a slope based on measurements taken only during part of the year may be difficult to compare with slopes derived from year-round measurements or even from measurements taken at a different time of the year.

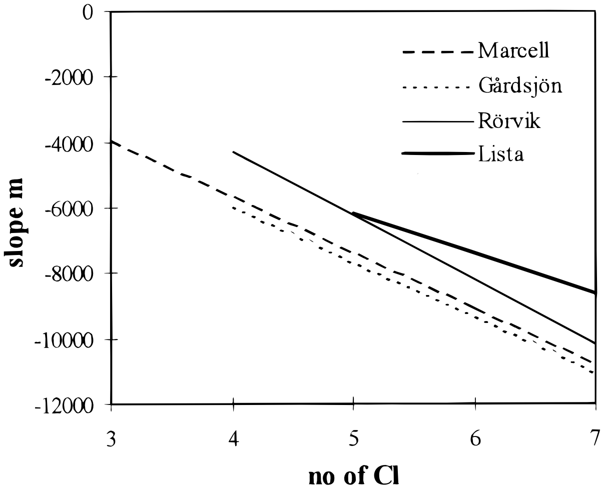
Modeling Concept of Atmosphere−Surface Exchange of SOCs

The variety of temperature relationships observed in the environment call for an explanation. What information is contained in the slope of these relationships? Why are slopes shallow in some places and steep at others? Why is there a reduced temperature dependence in the winter? Why do Arctic locations not show a temperature dependence? To provide insights into these issues, we derive two approaches for quatifying the temperature dependence of SOC vapor concentrations in the atmosphere.

An Approach Based on Atmosphere−Surface Equilibrium. The first approach assumes that surface phases and the atmosphere are in chemical equilibrium and is essentially a reformulation of the approach by Pankow (*21*). If the concentrations of a chemical in the gas phase, expressed as partial pressure p_A, and in any sorbing surface materials (suspended aerosol and whatever constitutes the earth's surface, e.g., plants, soils, water, snow, ice, bedrock) (C_S) are in equilibrium

$$\ln K_{AS} = \ln \frac{p_A}{C_S} = \ln p_A - \ln C_S \tag{1}$$

where K_{AS} is an equilibrium gas phase−sorbent surfaces partition coefficient (lumping together all sorbent surfaces participating in exchange with the gas phase). The temperature dependence of an equilibrium partition coefficient can be expressed as



$$\text{slope } m = x \cdot n_{Cl} + z$$

	n	x	r^2	sign.
Marcell	18	-1716	0.87	<0.001
Rörvik	6	-1968	0.89	<0.005
Gårdsjön	6	-1702	0.70	<0.05
Lista	7	-1244	0.85	<0.005

FIGURE 1. Dependence of the slope *m* of the ln p_A vs 1/*T* relationship for PCBs on the degree of chlorination. In some studies (*7*, *10*, *17*) *m* increased with increasing number of chlorine atoms in a PCB molecule (n_{Cl}), and the linear regression of *m* vs n_{Cl} was significant. (*n* is the number of PCB isomers used in these regressions. Only those isomers were used in this analysis that had a significant temperature dependence.)

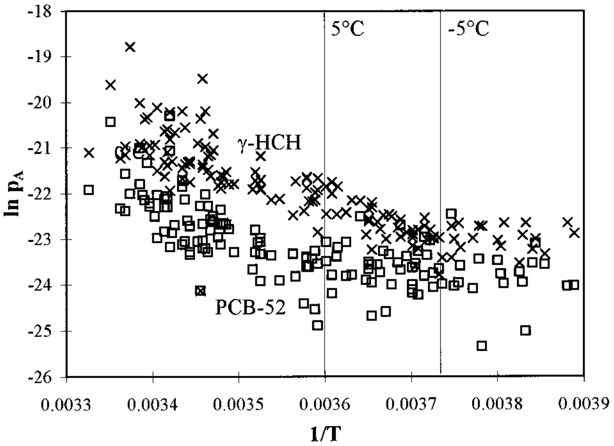


FIGURE 2. Temperature dependence of the atmospheric concentrations of PCB-52 and γ-HCH as measured in Egbert, ON, in 1988 by Hoff et al. (*2*). At low temperatures the concentrations of both chemicals show no dependence on temperature.

$$\frac{\mathrm{d} \ln K_{\mathrm{AS}}}{\mathrm{d}T} = -\frac{\Delta H_{\mathrm{AS}}}{RT^2} \qquad (2)$$

where ΔH_{AS} is the enthalpy of phase change between air and the sorbed state. If K_{AS} is known at a reference temperature T_{ref}, this can be integrated giving

$$\ln K_{\mathrm{AS}}(T) = \ln K_{\mathrm{AS}}(T_{\mathrm{ref}}) - \frac{\Delta H_{\mathrm{AS}}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right) = \ln K_{\mathrm{AS}}(T_{\mathrm{ref}}) - \frac{\Delta H_{\mathrm{AS}}}{RT} + \frac{\Delta H_{\mathrm{AS}}}{RT_{\mathrm{ref}}} \qquad (3)$$

Combining eqs 1 and 3 yields

$$\ln p_{\mathrm{A}} = \ln K_{\mathrm{AS}} + \ln C_{\mathrm{S}} = \left(\ln K_{\mathrm{AS}}(T_{\mathrm{ref}}) + \frac{\Delta H_{\mathrm{AS}}}{RT_{\mathrm{ref}}} + \ln C_{\mathrm{S}}\right) - \frac{\Delta H_{\mathrm{AS}}}{R}\frac{1}{T} = b + \frac{m}{T} \qquad (4)$$

Assuming that the concentration on the surface is so large that it is not changed by temperature-driven volatilization, the partial pressure in the gas phase should follow a log−linear relationship. Often the logarithm of atmospheric concentrations expressed on a mass per volume basis is regressed against $1/T$. The slope of these regressions yields internal energies of phase change, ΔU_{AS} rather than enthalpies ΔH_{AS}. These can be converted into each other since ΔH is $\Delta U - RT$ (*22*). If a decadic logarithm is used for the regressions the slope is $m = -\Delta H_{\mathrm{AS}}/(2.303R)$.

Dynamic Approach Including the Kinetics of Air−Surface Exchange

Model for Atmospheric Concentrations over a Soil Surface. The above assumption of atmosphere−surface equilibrium is not generally valid, and a more complex approach that takes into account the kinetics of air−surface exchange is warranted. We consider a simple, fugacity-based box model of atmosphere over a soil surface (Figure 3). Details on the concept and terminology of fugacity modeling, namely, the derivation of Z and *D* values can be found in ref *23*. At steady state, the input by advection and evaporation from the surface equals the output by advection and deposition to the surface:

$$D_{\mathrm{A}}f_{\mathrm{Ain}} + D_{\mathrm{V}}f_{\mathrm{S}} = (D_{\mathrm{A}} + D_{\mathrm{V}})f_{\mathrm{A}} \qquad (5)$$

where f_{Ain}, f_{S}, and f_{A} are the fugacities (or partial pressures) (in Pa) in the inflowing air, at the soil surface, and in the air compartment. D_{A} and D_{V} are *D* values (in mol/(Pa·h)) describing advection into and out of the air compartment and diffusive gas exchange between air and soil surface, respectively. Solving this equation for f_{A} yields

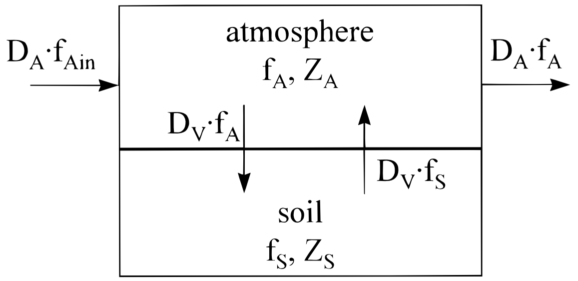


FIGURE 3. Steady-state two-compartment model used to describe the relative importance of advection and atmosphere surface exchange in controlling atmospheric concentrations.

$$f_{\mathrm{A}} = f_{\mathrm{Ain}}\frac{D_{\mathrm{A}}}{D_{\mathrm{A}} + D_{\mathrm{V}}} + f_{\mathrm{S}}\frac{D_{\mathrm{V}}}{D_{\mathrm{A}} + D_{\mathrm{V}}} \qquad (6)$$

The fugacity in the air is the sum of contributions from the fugacity in the inflowing air and the fugacity in the underlying surface. If the air side resistance controls, i.e., the rate of transport within the soil does not affect the rate of diffusive exchange with the atmosphere, the *D* value for diffusive exchange between soil surface and atmosphere can be expressed by

$$D_{\mathrm{V}} = kAZ_{\mathrm{A}} = kWLZ_{\mathrm{A}} \qquad (7)$$

where *k* is the mass transfer coefficient between atmosphere and soil surface (in m/h), *W* is the width of the atmospheric compartment (in m), *L* is the length of the atmospheric compartment (in m), Z_{A} is the *Z* value of air (in mol/(m^3·Pa)), and *A* is the soil surface area (in m^2).

The *D* value for atmospheric advection can be estimated from

$$D_{\mathrm{A}} = G_{\mathrm{A}}Z_{\mathrm{A}} = uWhZ_{\mathrm{A}} \qquad (8)$$

where *u* is the wind speed (in m/h), G_{A} is the atmospheric advection rate (in m^3/h), and *h* is the height (m) of the atmospheric compartment. Substituting eqs 7 and 8 into eq 6, we obtain

$$f_{\mathrm{A}} = f_{\mathrm{Ain}}\frac{\theta}{1 + \theta} + f_{\mathrm{S}}\frac{1}{1 + \theta}$$

where

$$\theta = \frac{uh}{kL} \qquad (9)$$

The parameter θ is dependent on geographical and meteorological conditions. Essentially, it expresses the ratio of the advective and surface contributions. It is smallest at lower wind speed *u*, lower atmospheric mixing height *h*, longer fetch *L*, and higher soil−air MTC *k*.

Assuming that sorption to soil organic matter is dominant, a fugacity in soil f_{S} can be estimated from a soil concentration (C'_{S} in mol/m^3 or C_{S} in ng/g of soil solids) using

$$f_{\mathrm{S}} = \frac{C'_{\mathrm{S}}}{Z_{\mathrm{S}}} = \frac{\dfrac{C_{\mathrm{S}}}{M_{\mathrm{M}}} \times 10^{-9}\rho}{f_{\mathrm{OC}}Z_{\mathrm{OC}}\rho \times 10^{-6}} = \frac{C_{\mathrm{S}}}{M_{\mathrm{M}}f_{\mathrm{OC}}Z_{\mathrm{OC}} \times 10^{3}} \qquad (10)$$

where Z_{S} is the *Z* value of soil (in mol/(Pa·m^3)), f_{OC} is the (mass) fraction of the soil solids that is organic carbon, ρ is the density of the soil particles (in g/m^3), and M_M is the molecular mass of the chemical (in g/mol). The Z value of soil organic carbon (Z_{OC}) can be estimated from the Henry's law constant H (in Pa·m^3/mol) and octanol water partition coefficient K_{OW} using $Z_{OC} = 0.41K_{OW}/H$ (*24*).

Similarly, a concentration in inflowing air (C'_{Ain} in mol/m^3 or C_{Ain} in pg/m^3) can be converted into a fugacity value f_{Ain} using

$$f_{Ain} = \frac{C'_{Ain}}{Z_A} = \frac{C_{Ain} \times 10^{-12} RT}{M_M} \qquad (11)$$

Illustrative Model Calculation: Fugacities in Air and Soil. We employed this simple model to calculate the fugacities of PCB-138 in air, incoming air, and soil using various combinations of C_{Ain} and C_S. For illustrative purposes, we assumed that u is 10 000 m/h (10 km/h), k is 5 m/h (assuming that the atmospheric boundary layer is controlling diffusive gas exchange and transport to the surface of soil or vegetation cover is not rate-limiting), L is 50 000 m (or 50 km), and h is 500 m. The parameter θ is then 20, and eq 9 becomes: $f_A = f_{Ain}0.95 + f_S0.05$. We further assumed that temperature fluctuated annually with a sinusoidal shape peaking in July at +30 °C and −10 °C in December. The fraction of organic carbon in soil was assumed to be 0.02. The results for three selected cases are shown in Figure 4. Both f_{Ain} and f_S are functions of temperature and undergo seasonal cycles. However, assuming that the concentrations in the inflowing air (C_{Ain}) and in the soil (C_S) are constant, f_S is more strongly influenced by temperature than f_{Ain} (see Figure 4).

Depending on the relative magnitude of the fugacities in inflowing air and soil surface, the resultant fugacity in air f_A (equivalent to air partial pressure p_A) can be essentially constant throughout the year, follow a strong seasonal cycle, or be constant during winter and show a temperature-dependent behavior in summer. The latter behavior is the result of the effect that the soil fugacity f_S will increase greatly at higher temperatures, whereas the fugacity in the inflowing air f_{Ain} is only weakly influenced by temperature. Thus, situations may exist where during winter inflowing air controls air concentrations, and during summer evaporation from soils is the decisive process.

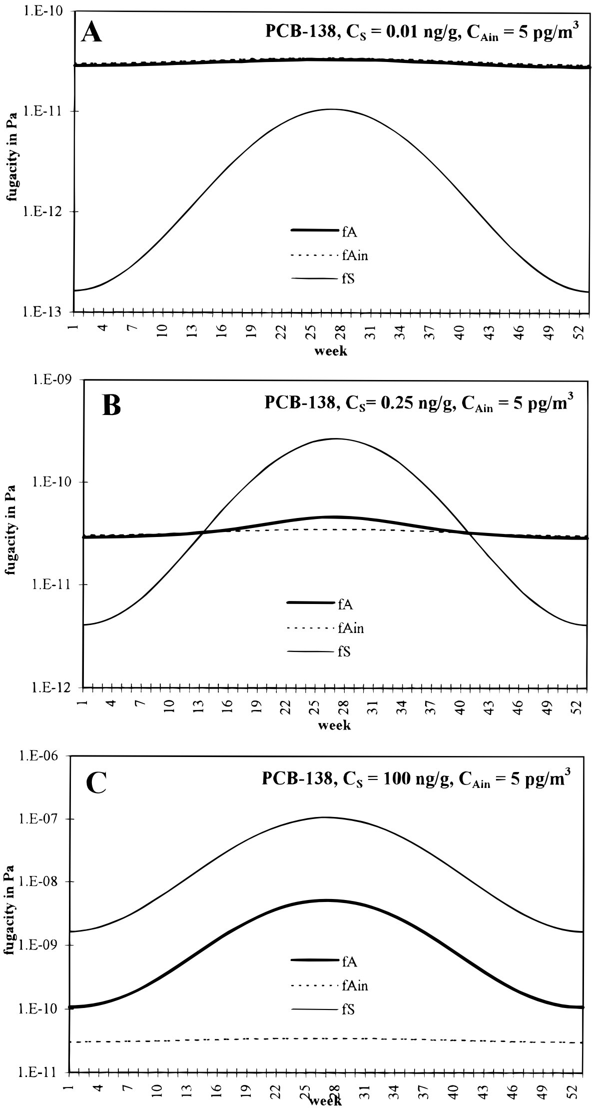


FIGURE 4. Fugacities in inflowing air, soil, and air over the soil calculated by the model over a 1-year time period. If the level in soil is low relative to the level in the inflowing air (A), the air fugacity is controlled entirely by the fugacity of the inflowing air. If the soil is relatively strongly contaminated relative to the background air concentration (C), the air fugacity follows closely the fugacity in the soil compartment. In an intermediate case, the air fugacity is controlled by the inflowing air at low temperatures, whereas at high temperatures f_S increases so strongly that it controls the air fugacity during the summer months (B).

Using the Model To Derive Equations for the Temperature Dependence of p_A. We can use the model to deduce the temperature dependence of the fugacity in air f_A (or partial pressure p_A). We first treat the two special cases, when either f_S or f_{Ain} determines f_A (termed $f_{A,Surf}$ and $f_{A,Adv}$). If volatilization of surface contamination alone is controlling the air concentrations, i.e., if f_{Ain} is negligibly small, eq 9 together with eq 10 gives

$$f_{A,Surf} = f_S \frac{1}{1+\theta} = \frac{C_S H}{M_M f_{OC} \times 0.41 K_{OW} \times 10^3} \frac{1}{1+\theta} \qquad (12)$$

$$\ln f_{A,Surf} = \ln H - \ln K_{OW} + \ln X$$

where

$$X = \frac{C_S}{M_M f_{OC} \times 0.41 \times 10^3} \frac{1}{1+\theta} \qquad (13)$$

Assuming that the soil concentration C_S and the parameter θ are not temperature dependent and that the temperature dependence of the partition coefficients can be expressed with a equation of the type $\ln K = m/T + b$, this can be rewritten as

$$\ln f_{A,Surf} = \ln X + \left(\frac{m_H}{T} + b_H\right) - \left(\frac{m_{K_{OW}}}{T} + b_{K_{OW}}\right) = \frac{m_H - m_{K_{OW}}}{T} + \ln X + b_H - b_{K_{OW}} \qquad (14)$$

or, in other words, the slope of the ln p_A vs $1/T$ relationship approximates the slope of the temperature dependence of H and K_{OW}, $m_H - m_{K_{ow}}$. If it is assumed that the temperature dependence of K_{OW} is negligible, the slope should approximate m_H.

In the other limiting case, i.e., air concentrations are influenced only by inflowing air and f_S is negligibly small, eq 9 becomes

$$f_{A,Adv} = f_{Ain} \frac{\theta}{1+\theta} = \frac{C_{Ain} \times 10^{-12} RT}{M_M} \frac{\theta}{1+\theta} \qquad (15)$$

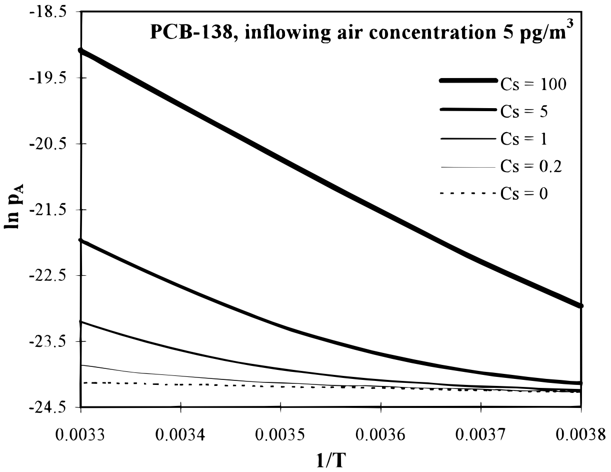


FIGURE 5. Plot of the logarithm of the calculated partial pressure of PCB-138 in air versus reciprocal absolute temperature for various combinations of C_{Ain} (in pg/m^3) and C_S (in ng/g).

If it is assumed that the inflowing air concentration and the parameter θ are constant, f_A is thus linearly related to absolute temperature and is thus relatively insensitive to temperature:

$$f_{A,Adv} = TX'$$

where

$$X' = \frac{C_{Ain} \times 10^{-12} R}{M_M} \frac{\theta}{1 + \theta} \tag{16}$$

Equations 14 and 16 can be combined to describe the general case, when inflowing air and evaporation from soils jointly control atmospheric concentrations:

$$\ln f_A = \ln f_{A,Surf} + \ln f_{A,Adv} = \ln T + \frac{m_H - m_{K_{OW}}}{T} + b_H - b_{K_{OW}} + \ln X + \ln X' \tag{17}$$

Illustrative Calculations of ln *p* vs 1/*T* Relationships. Using eq 17 and the model parameters from the illustrative example above, we calculated ln p_A vs $1/T$ profiles for various combination of C_{Ain} and C_S (see Figure 5). Obviously the shape and slope of the ln p_A vs $1/T$ relationship are governed by the relative magnitudes of C_S and C_{Ain}. If C_S is large as compared to C_{Ain}, the model predicts that ln p_A will show a linear relationship with $1/T$ and steep slopes. On the other hand, if C_{Ain} is large relative to C_S, the p_A will be essentially independent of temperature and the slope close to zero. If C_S and C_{Ain} have a comparable influence, the temperature dependence is linear at high temperatures, but vanishes at lower temperatures. The proportions, of course, depend on both the chemical's properties and the environmental conditions (soil properties and meteorology) of a site.

A Model for Atmospheric Concentrations over a Water Surface. If the air is in contact with a water surface rather than a terrestrial surface, eq 6 remains essentially identical except that f_S is replaced by the fugacity in the surface water (f_W). Whereas the calculation of the advective D value (D_A) is unchanged, the D value describing diffusive exchange (D_V) now also includes a water side resistance characterized by an additional mass transfer coefficient k_2:

$$D_V = \frac{WL}{\frac{1}{k_1 Z_A} + \frac{1}{k_2 Z_W}} = \frac{WL}{\frac{RT}{k_1} + \frac{H}{k_2}} \tag{18}$$

and the parameter θ in eq 9 is thus no longer independent of temperature, but is a function of T and H (which is also temperature dependent):

$$f_A = f_{Ain}\frac{\theta}{1 + \theta} + f_w\frac{1}{1 + \theta}$$

where

$$\theta = \frac{uh}{L}\left(\frac{1}{k_1} + \frac{H}{RTk_2}\right) \tag{19}$$

This implies that at lower temperature, θ increases, especially if the system is water side resistance controlled, i.e., $H/(RTk_2) > 1/k_1$. But f_W is also reduced at lower temperature, thus for water side resistant systems air–water exchange is relatively independent of temperature. For systems controlled by the air side resistance, θ remains constant and f_W is reduced at lower temperature, thus there is less evaporation.

Discussion

We suggest that important information may be gained from the slope of ln p_A vs $1/T$ relationships. On the basis of the above conceptual model, we hypothesize that the slope m is an indication of the relative importance of (a) advection of air masses from areas with surfaces with minor temperature fluctuations and (b) diffusive exchange with surfaces with major temperature fluctuations for determining atmospheric concentrations.

Concentration of SOCs in air masses that have moved large distances over the open ocean are likely to have a small or nonexistent seasonal signal, primarily because marine climates tend to experience minor annual temperature fluctuations. Atmospheric temperature and PCB levels measured in Bermuda show no discernible seasonal variability (*25*). The fugacities of SOCs in such air masses are likely to be close to the fugacities in the surface seawater, because there is enough time available for equilibrium to be established during the passage over the oceans and because there tend to be few or no point sources of SOCs in the oceans disrupting that equilibrium (*26*). The same should apply, although to a lesser extent, to air masses passing over enclosed seas and large lakes. When such air masses encounter land surfaces they receive SOCs from or deposit SOCs to, terrestrial surfaces depending on the fugacity difference between terrestrial surface and atmosphere (Figure 4).

The evaporation is substantial when the soil fugacity f_S is high, i.e., when surface concentrations are high and/or when terrestrial surface temperatures are high, e.g., during summer. Atmospheric concentrations should thus show strong seasonal variability, i.e., slopes m are high (case C in Figure 4), in or downwind from terrestrial areas with high surface levels and a pronounced temperature cycle resulting in hot summer temperatures.

When air passes over cold and/or uncontaminated terrestrial surfaces, SOCs are lost to the surface, resulting in low, stable levels in the air, i.e., slopes m are low or there is no temperature dependence (case A in Figure 4). It is conceivable that when such terrestrial surfaces heat up during summer and re-evaporate deposited material, temperature-driven concentration cycles may occur. However, slopes are likely to be small due to the small concentrations of SOC on the surface.

The slope of a ln p_A vs $1/T$ relationship at a sampling location is thus determined by the relative influence of (a) the advection of air masses with stable background concentrations created over large, more or less isothermal water bodies and (b) the temperature-controlled exchange with terrestrial surfaces. In the following, we attempt to illustrate how this concept can help in the interpretation of various aspects of the observed temperature relationships, which were presented above.

Why Does γ-HCH Show Consistently Steeper Slopes Than α-HCH? A peculiar observation was that whereas γ-HCH concentrations showed a strong temperature dependence in most studies, those for α-HCH did not. An interpretation based on equilibrium partitioning between atmosphere and surface is ineffectual, as the partitioning properties of both isomers are similar.

The world oceans tend to have higher levels of α-HCH than γ-HCH (e.g., ref 27), because much more of the α-isomer has been released globally (*28*) and possibly because α-HCH is more persistent. Accordingly, global atmospheric background concentrations are higher for α-HCH than for γ-HCH. Most sampling sites in Table 2 were in, or downwind of, western industrialized countries, which had used or are still using lindane (pure γ-HCH) but which had experienced little or no technical HCH usage (with a large fraction of α-HCH) in the recent past (*28*). Surveys of organochlorine levels in vegetation (*29, 30*) indeed confirm that in central western Europe γ-HCH concentrations in foliage and tree bark are always higher than α-HCH concentrations—often by an order of magnitude.

The reasons for the differences in the temperature relationships for α- and γ-HCH is that, at such sites, α-HCH levels are governed primarily by inflow of background air, whereas the γ-HCH levels are more influenced by temperature-driven evaporation from terrestrial surfaces. Haugen et al. (*5*) showed that advection of air with global background concentrations accounted for most of the presence of α-HCH at a sampling site in southern Norway, whereas γ-HCH was more strongly influenced by air mass transport from central western Europe.

This interpretation is supported by the indication that the slope for γ-HCH increases with increasing distance of a sampling site from the sea or large lakes (*9*). The slopes in continental locations are higher than the slope in Lista, the only coastal station. The highest slope for γ-HCH was found in the Swedish forest ecosystem in Gårdsjön. The Swedish sampling sites also show the strongest temperature dependence of α-HCH concentrations, particularly the study conducted in the early 1980s. This may be because these sites are closest to eastern Europe, an area known to have experienced technical HCH usage, especially in the 1980s (*28*).

Why Do SOCs Show No Temperature Dependence in the Arctic Atmosphere? The lack of a temperature dependence of SOC concentrations in Arctic air was first noted in the European Arctic (*19*) and later confirmed with observations in the Canadian and Siberian Arctic (*20*). The suggestion (*19*) of a temperature threshold for re-evaporation, which is not reached in the Arctic, is not sufficient to explain the phenomenon: (a) Even at Tagish, a site in the Yukon Territory with relatively high summer temperatures, PCB levels in air showed no temperature dependence (*20*). (b) A threshold would obviously have to be related to physical—chemical properties and thus be different for different SOCs (e.g., various PCB isomers). The lack of a temperature slope however seems to be nonspecific with respect to chemical characteristics.

The situation in the Arctic can be interpreted as an area of low surface contamination where atmospheric levels are dominated by the inflow of air with constant concentrations (Figure 4, case A). Ny-Ålesund, Alert, and Dunai are located on Arctic Islands, whereas Tagish, although further inland, is primarily influenced by air masses coming from the Pacific Ocean (*20*). Air must have reached these stations over either large stretches of ocean or relatively uncontaminated terrestrial/ice surfaces, and SOC concentrations in this air are thus likely to have only a minor seasonal signal. On the other hand, evaporation from terrestrial surfaces within the Arctic is unlikely to imprint a temperature-driven signal on atmospheric concentrations for several reasons:

(a) Levels of SOCs in Arctic terrestrial surfaces are likely to be small relative to the inflowing air concentrations, because of no or limited local usage and because of a low capacity of arctic soils to retain atmospherically deposited SOCs (lack of vegetation and the low organic content).

(b) Many surfaces from which evaporation could occur are snow and ice-covered for long periods of time, thus limiting or even preventing air—surface exchange.

(c) The temperatures are generally so low that the soil fugacities (f_S) do not increase appreciably in summer.

(d) Faster rates of air—water exchange at low temperatures can dampen temperature-driven oscillations of atmospheric concentrations.

Why Does the Temperature Dependence Sometimes Disappear during Winter? Related to the lack of a temperature dependence of SOCs in Arctic air is the observation of a decrease of the slope in the ln p_A vs $1/T$ relationships at lower temperatures (Figure 2; *2*). Air concentration profiles in time have a more “peaked” appearance than the temperature curves. With above model concept, namely, Figure 4 (Case B), such behavior is now explainable. During winter the advected background air in Egbert has relatively high and stable levels of SOCs by having been equilibrated with the waters of the Great Lakes, which are relatively warm and have a low-temperature variation relative to the terrestrial surfaces in the area (*2*). During summer, the soil fugacity increases dramatically as a result of high terrestrial temperatures and evaporation becomes controlling. The large water body with a low-temperature variation provides the advective background whereas evaporation from terrestrial surfaces creates the summer peaks.

What Is the Impact of Atmospheric Mixing on the Temperature Slopes *m*? In the model, the calculated slopes are very dependent on the selected parameters for wind speed and atmospheric mixing height, slopes being higher during periods of low wind speed, and low mixing height, i.e., stable atmospheric conditions. Honrath et al. (*31*) showed that periods of stable atmospheric conditions show the influence of temperature, whereas periods of rapid advection see a collapse of a relationship between temperature and air concentrations. The PCB data from southern Norway (*17*) show convincingly that the temperature dependence changes with wind speed (Table 4). The concentrations measured during relatively still days (wind speed <3 m/s) had the highest concentrations and the highest slopes *m*, and both these parameters decrease with increasing wind speed indicating a decreasing influence of local evaporation. At very high wind speeds (>9 m/s), the temperature relationship is lost completely.

Do the Temperature Slopes Change in Time, and If So, Why? Change of slope in time may occur when levels in terrestrial surfaces and in background air are changing at different rates. If a chemical (e.g., α-HCH) is banned in one location but is in continued (or increased) use elsewhere, the chemical may become depleted from local soils and plants as a result of outgassing to the atmosphere but may still be advected into the area with background air. This also occurs when the oceans constitute a long-term reservoir maintaining global background levels. In such cases, the slopes *m* should become more shallow with time. Unfortunately, very few time series of atmospheric concentrations span periods long enough to detect such a trend.

Why Does the Slope for PCB Isomers Change with the Degree of Chlorination? This effect was illustrated in Figure 1. An increase of slope with increasing number of chlorines (n_{Cl}) may reflect changes in the enthalpy of phase change (ΔH_{AS}). If the enthalpies of vaporization (*32*) and air—water

TABLE 4. Temperature Dependence of Partial Pressure of PCBs at Lista, Norway, if the Data Are Grouped According to (1) Wind Speed at the Time of Sampling and (2) Year of Sampling[a]

	C_{Air}	m	n	r^2	p
all data	115.1	−6746 ± 549	201	0.43	$<$0.001
windspeed $<$3 m/s	131.1	−7236 ± 1121	30	0.60	$<$0.001
windspeed between 3 and 6 m/s	123.1	−6840 ± 808	94	0.44	$<$0.001
windspeed between 6 and 9 m/s	109.6	−6244 ± 1070	53	0.40	$<$0.001
windspeed $>$9 m/s	83.9	(−1094 ± 3318)	23	0.01	ns
1992	160.7	−9590 ± 1145	46	0.61	$<$0.001
1993	107.2	−7481 ± 1138	52	0.46	$<$0.001
1994	100.9	−4352 ± 1119	51	0.24	$<$0.001
1995	104.6	−6035 ± 794	52	0.54	$<$0.001

[a] Given is the geometric mean concentration in pg/m^3, the slope m of the relationship $\ln(p_a/\mathrm{Pa}) = m/(T/K) + b$, number of observations n, and regression coefficient r^2. ns, not signficant.

exchange (*33*) are taken as an indication, ΔH_{AS} for PCBs decrease by approximately 2.5−4 kJ/mol with each additional chlorine. ΔH_{AS} is thus typically a factor of 4 less dependent on n_{Cl} than the observed slopes (Figure 1). An interpretation based on ΔH_{AS} also fails to explain why the slope changes with n_{Cl} in some places but not in other, primarily urban locations.

The effect of chemical properties is likely to be indirect in this case. At an urban "source" site PCBs of all degrees of chlorination should be available for evaporation from local surfaces, and advection of background air into the city environment should have a relatively minor influence. Slopes should accordingly be high for all isomers. At more distant locations far from sources, the amount of various PCB isomers on terrestrial surfaces, which is available for temperature-driven evaporation, is dependent on what has been deposited from the atmosphere in the past less that which has evaporated. Soils in rural areas may be more rapidly depleted in the lighter PCBs due to their higher volatility, whereas heavier, less volatile isomers are more likely to have maintained a high soil concentration (*34, 35*). Marine (or aquatic) atmospheric background concentrations of light PCBs, on the other hand, may have been maintained to a greater extent because surface waters are a reservoir for these more water-soluble PCBs (*36*). Heavy congeners are scavenged more efficiently from surface water by settling particles (*37*). This may explain why, in some locations in southern Scandinavia, light PCBs seem to be more dominated by advective background (low slopes) than the heavy PCBs, which are more influenced by temperature-driven exchange with terrestrial surfaces and show high slopes (Figure 1).

Identification of Research Needs

Many facets of the temperature dependence of SOCs in the atmosphere can be explained with a dynamic view of the processes involved in surface−air exchange, but not with an equilibrium partitioning approach between surface and atmosphere. The slope of the ln p_A vs $1/T$ relationship can thus only in exceptional circumstances, namely, in the case of high surface contamination and still conditions, be related to an enthalpy change associated with a surface−vapor transition. In most cases they are best interpreted as the result of a competing influence of surface evaporation and atmospheric advection. It may be possible to use the slope of the ln p_A vs $1/T$ relationship at a sampling site to assess qualitatively the relative magnitude of evaporation from sources close to the sampling locations vs advection of background air into the area.

Obviously factors other than those discussed in this approach have an impact on the slopes of ln p_A vs $1/T$ relationships, namely, many of those listed in Table 1. To illustrate this, Table 4 lists the temperature dependence of PCB ("sum of 7") concentrations in southern Norway (*17*) separately for 4 years of measurements (Table 4). A surprising year-to-year variability becomes apparent. During 1992, unusually high summertime concentrations resulted in a high annual average concentration and a steep slope however during the following years, in particular 1994, a far less pronounced temperature dependence was observed (*17*). These interannual differences cannot be explained with the present model and suggest that it is necessary to be cautious not to overinterpret data, particularly if they are based on a limited number of measurements or on measurements conducted only during parts of the year.

On the basis of the findings presented in this paper, we suggest a number of research priorities. The temperature dependence of atmospheric SOC concentrations generated in long-term monitoring networks such as IADN and CAMP should be analyzed within the framework of the presented models. Differences between ln p_A vs $1/T$ relationships from various locations and over time should be interpreted with an aim to distinguish the influence of long-range advection vs regional surface exchange. Measurements of the temperature dependence of SOC vapor concentrations in a variety of locations should be conducted while simultaneously measuring surface concentrations, i.e., concentrations in surface soils, foliage and surface waters. Ideally, surface fugacities should be determined instead of (or in addition to) concentrations, which may now be possible with "fugacity meters" (*38*). Only if data for both atmosphere and surface for one location are known will it be possible to develop models that are not just qualitative about the involved processes but that could potentially predict seasonal and diurnal atmospheric concentration cycles. The capability to quantify atmosphere surface exchange is crucial for many aspects of the environmental fate of SOCs. For example, only the fraction of chemical evaporating from surfaces is available for long-range atmospheric transport. More research is warranted into measuring in laboratory and field and quantifying with models the flux of SOCs between soils, plants, snow, and water surfaces and the atmosphere.

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Supporting Information Available

A table showing the temperature dependence of the partial pressure of individual PCB isomers at various locations (2 pp) will appear following these papers in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for $12.00 for photocopy ($14.00 foreign) or $12.00 for microfiche ($13.00 foreign), are required. Canadian residents should add 7% GST. Supporting Information is also available via the World Wide Web at URL http://www.chemcenter.org. Users should select Electronic Publications and then Environmental Science and Technology under Electronic Editions. Detailed instructions for using this service, along with a description of the file formats, are available at this site. To down-load the Supporting Information, enter the journal subscription number from your mailing label. For additional information on electronic access, send electronic mail to si-help@acs.org or phone (202) 872-6333.

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