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As early as 1974 it was suggested that certain organic chemicals may migrate through the global atmospheric environment and condense in low temperature regions (Rappe, 1974). Over the last 20 years this hypothesis has been restated and revised (Goldberg, 1975, Ottar, 1981, Rahn and Heidam, 1981) and was fully discussed in a review by Wania and Mackay in 1993, who suggested that a "global fractionation" process may occur in which persistent organic pollutants (POPs) may be fractionated during their journey towards the poles because of differing migration velocities. Although these velocities can not be measured there have been numerous measurements of concentrations of POPs in the global environment, particularly in oceanic and arctic regions, and substantial progress has been made towards understanding their global distribution. It is thus timely to evaluate, modify and extend some of these concepts, especially in the light of recently announced international intentions to control the use of such substances (UNEP, 1995, Johnson, 1995).

The Process of Global Fractionation and Condensation

The present concept of these processes derives from the belief that most POPs are sufficiently volatile that they evaporate and deposit, (i.e. cycle) between air, water and soils at temperatures encountered in the global environment. Warm temperatures at low latitudes favour evaporation from the Earth's surface, while low temperatures which prevail at higher latitudes favour deposition from the atmosphere (Wania and Mackay, 1993, Mackay and Wania, 1995). The lower temperatures result in "condensation" and accumulation in cold ecosystems because of

- a shift of partitioning from the atmosphere to the surface,
- an enhanced deposition due to greater adsorption to depositing particles,
- changes in the water-to-air diffusion resistances which slow evaporation,
- slowing of degrading reactions with a corresponding increase in persistence.

This is not truly condensation in the sense that the atmosphere becomes saturated or over-saturated with the contaminants. Conditions are always well below saturation limits, i.e. partial pressures are much less than vapour pressures. It is merely partitioning from a gaseous to a non-gaseous phase.

It was hypothesised that as a result steady net transfer of such contaminants from low to high latitudes should occur ("global distillation"). This migration to higher latitudes may occur, not as a single step, but as a series of steps (the grass-hopper effect) caused by the seasonal cycles of temperature in mid-latitudes. As will be pointed out in more detail later, the process is in

many respects analogous to gas chromatographic separation (Risebrough, 1990). This analogy further suggests that POPs of different volatility will migrate at different velocities. Indeed, a chemical may have a specific environmental condensation temperature or range of temperatures, and even a latitudinal range of condensation, dictated by the temperature-dependence of its atmosphere-to-surface partitioning. This “global fractionation” process will cause a shift in the relative composition of contaminant mixtures along a temperature or latitudinal gradient with more volatile constituents remaining more in the air phase and migrating faster, with less volatile chemicals partitioning more into the non-gaseous liquid or solid media of water, soils and vegetation.

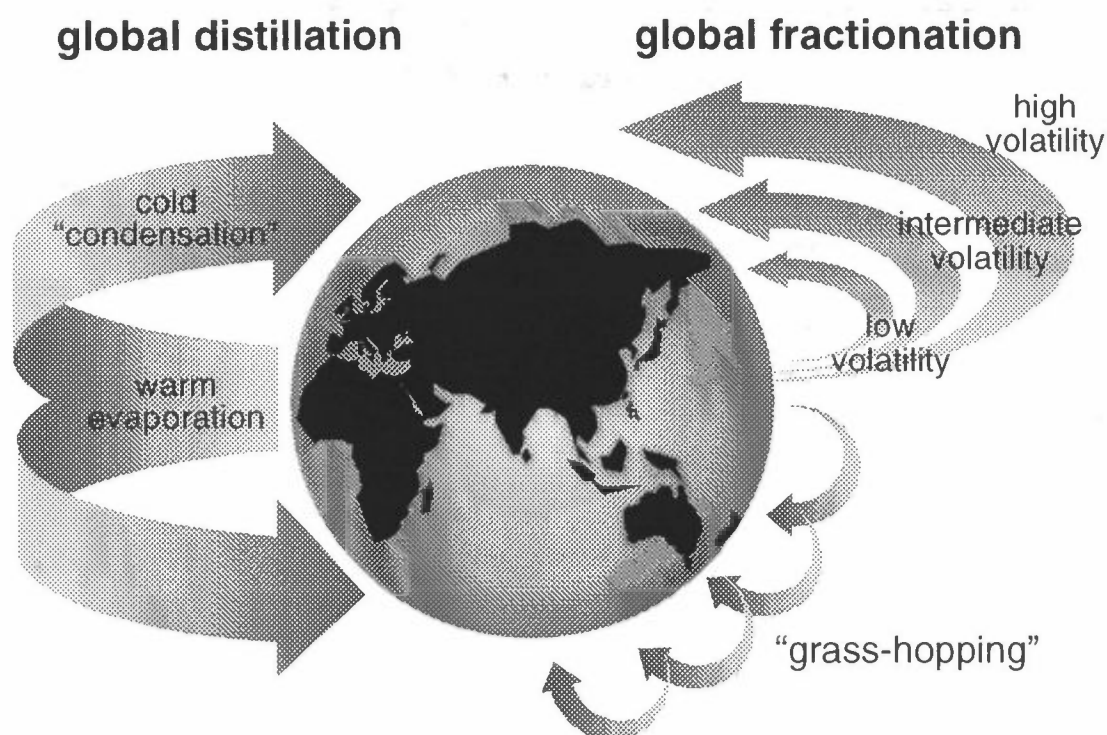


Figure 1 Schematic illustration of the concepts of global distillation, global fractionation and “grass-hopping”.

Predicted Latitudinal Concentration Gradients

An obvious test of these theoretically derived concepts is to measure and interpret concentration gradients along latitudes or climatic gradients, or as a function of height and thus temperature in mountains. But which latitudinal concentration gradients should be expected based on the global fractionation hypothesis? This is complicated by interacting factors such as physical-chemical properties, emission rates and locations, environmental factors (e.g. climatic parameters, or atmospheric and oceanic transport), and time. Ultimately it is likely that comprehensive models describing chemical fate and concentrations in the entire global environment will become available. Existing models such as those of Strand and Hov (1996) and Wania and Mackay (1995) are viewed as a step towards this goal, but there has not yet been adequate validation. A major problem is the lack of chemical usage and release data which are forcing functions in the model

and control concentrations. However, it is still illuminating to predict such gradients for simplified hypothetical scenarios as follows:

- 1) The steady-state condition which will be reached after prolonged discharge of chemical at a constant rate in a warm region of the globe, This provides insights into expected relative concentrations between locations, especially as a function of latitude.
- 2) The dynamic behaviour of a pulse input of chemical in a warm region, i.e. analogous to a GC injection, This provides insights into the velocity of travel and response times.

The first scenario assumes that a contaminant is released continuously at low latitudes and sufficient time is available for the establishment of a steady-state situation (Mackay and Wania, 1995). Atmosphere concentrations decrease from the source towards more cold and remote areas, and this decrease is steeper for the less volatile chemicals (Figure 2). In non-gaseous media (such as soils, vegetation, water and sediment) concentrations are determined by a steady-state non-gaseous phase-to-air partition coefficient. For reasons mentioned above, this coefficient increases at lower temperatures which is reflected in Figure 2 by the fact that the concentrations curves in air and non-gaseous phases are further apart at lower temperatures. As a result the latitudinal concentration profiles in non-gaseous media for the more volatile chemicals may not only be less steep than the one for less volatile chemicals, but may even be inverted, i.e. may be higher in areas further away from the source. For a contaminant mixture such as the polychlorinated biphenyls (PCBs) this implies that more volatile constituents should become relatively more important with increasing latitude. A more detailed deduction of these gradients is given in Mackay and Wania (1995).

The Influence of Time on Global Distribution Patterns

Due to the long distances and time scales involved and the comparably rapid changes in chemical release rate in time, a steady-state situation as assumed in the first scenario is unlikely to ever be established in the global environment. In the second scenario there is a pulse emission of a relatively mobile chemical (i.e. P_L between 1 and 0.0001 Pa) in a warm area (e.g. at the equator). Assuming that the chemical is neither degraded nor permanently retained in any non-gaseous medium, the temperature-dependent partitioning between atmosphere and Earth's surface will result in a gradual migration of the injected chemical amount from warm to cold climate comparable to the passage of a chromatographic peak (Figure 3A). The peak will widen and the maximum will decrease with time. "Snapshots" of latitudinal profiles at different points in time, will show a concentration maximum traveling to higher latitudes with time (Figure 3B). Within the intermediate volatility range (P_L is 0.0001 to 1 Pa), chemicals of different mobility will travel with different global transport velocities ("grass-hopper velocity"), with more volatile chemicals traveling faster.

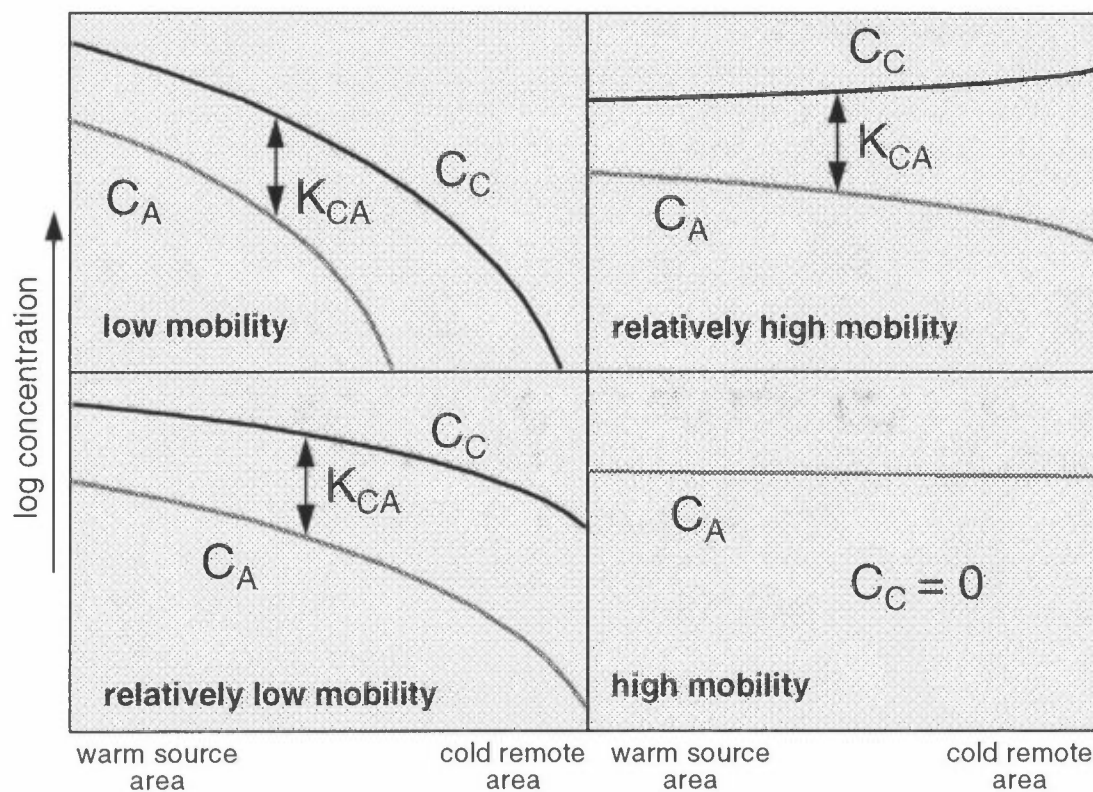


Figure 2 Predicted latitudinal concentration gradients in air C_A and non gaseous ("condensed") media C_C for the four chemical mobility classes at steady-state. K_{CA} is the steady-state non-gaseous phase-to-air partition coefficient, which increases with decreasing temperature. Low mobility chemicals will not be detected in the atmosphere and non-gaseous media of cold remote areas. High mobility chemicals will have uniform atmospheric concentrations but will not be found in non-gaseous media, even close to sources. Chemicals with intermediate mobility will show increasing, decreasing or uniform latitudinal gradients depending on their volatility and retention.

This implies that more remote regions can be expected to show a time delay in the establishment of peak concentrations, i.e. concentrations in the ecosystem may continue to rise even though the release in the source areas has decreased. Regions of past emission can continue to act as contaminant sources for decades due to slow release from accumulated chemical reservoirs. A delayed response of remote regions to emission reductions was observed in long term studies of the fate of persistent organic contaminants in the Japanese environment (Loganathan and Kannan, 1991 and 1994).

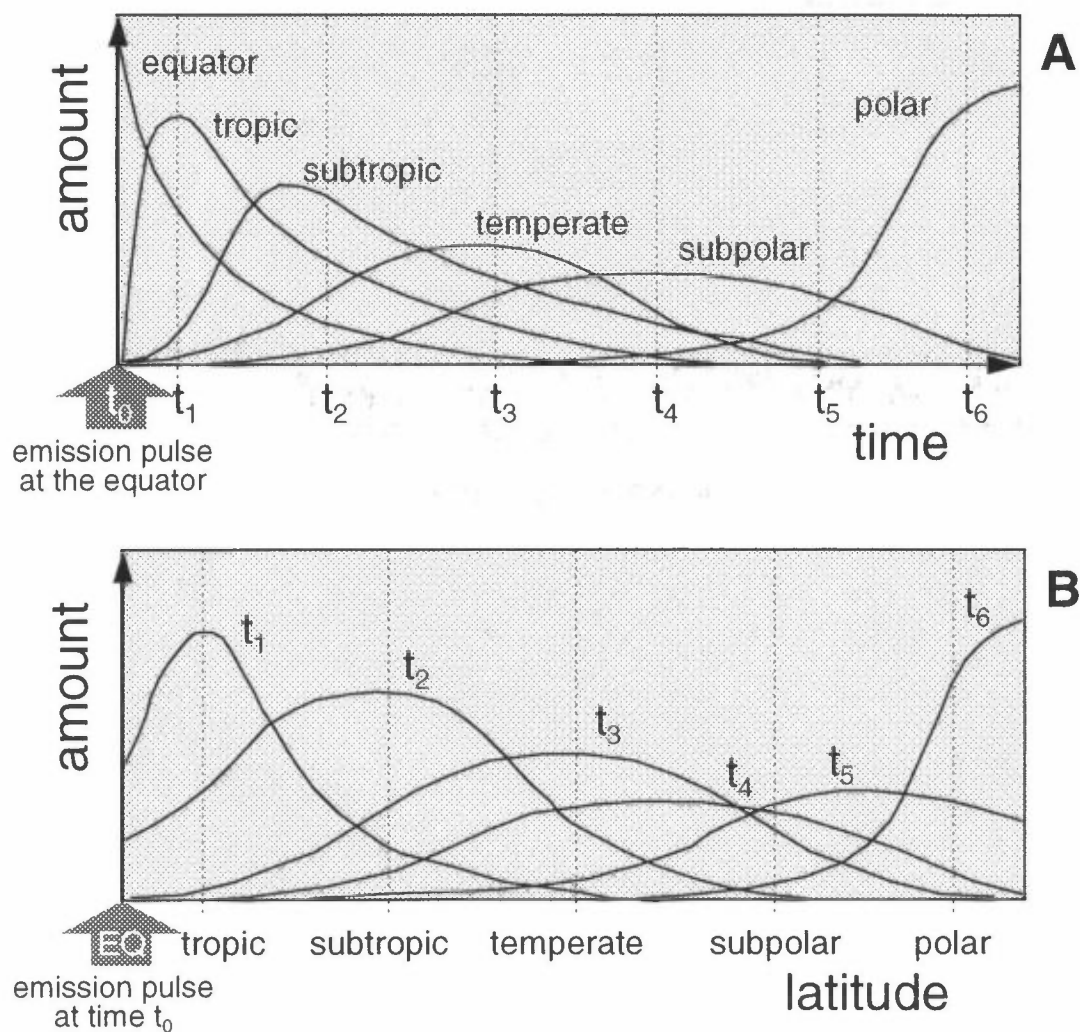


Figure 3 Predicted global fate of a single emission pulse of a relatively mobile chemical at the equator. It is assumed that the chemical is not degraded or permanently retained. The upper graph A shows the temporal change of the chemical amount in various climate zones. The lower graph B shows the latitudinal distribution of the total global amount at various points in time.

This concept of the fate of emission pulses into a particular location could serve as the basis for a modelling approach to the question of global distribution, which employs the principle of linear additivity (Stiver and Mackay, 1989). If it is possible to (i) derive concentration functions in time for "unit" emission pulses like the one presented for the equatorial pulse in Figure 3 and (ii) to define a matrix specifying time and location of global emissions, global concentrations in space and time can be calculated by simply adding emission-weighted concentration functions.

The steady-state scenario focuses on the differences between various chemicals, while the emission pulse scenario puts the main emphasis on the influence of time. The real global fate of persistent organic contaminants includes elements from both hypothetical scenarios. Although no persistent organic contaminant has been emitted to the global environment in a single

short pulse, the actual global usage for many contaminants has seen a steady rise followed by a period of declining usage following restrictions (e.g. Rapaport and Eisenreich 1988). Such a use pattern could be interpreted as a prolonged emission pulse which can vary in heights, widths and shapes in different regions of the world. For example, for many organochlorine pesticides such usage pattern occurred in several subtropical and tropical countries with a delay of approximately 20 years when compared to the industrialised nations of the northern temperate zone.

Observed Evidence for Cold Condensation and Global Fractionation

In the past few years several groups have reported measurements of persistent organic contaminants in samples taken along latitudinal profiles or all over the world. Non-gaseous media as diverse as sea water (e.g. Iwata et al. 1993, Schreitmüller and Ballschmiter 1995), vegetation (e.g. Simonich and Hites 1995, Lead et al. 1995), fresh water sediments (Muir et al. 1995a and b), and zooplankton (König et al. 1995) have been employed in these investigations. Did these environmental measurements supply any evidence for the predicted latitudinal patterns? Three related phenomena may be identified in monitored concentration data:

- “inverted” latitudinal concentration gradients of relatively mobile chemicals in non-gaseous media, i.e. concentrations increasing from warm source to cold destination.
- compositional changes of contaminant mixtures to the more volatile constituents at higher latitudes, and
- delayed maximum concentrations at higher latitudes when compared to areas close to the sources?

Inverted Latitudinal Concentration Gradients of Relatively Mobile Chemicals

Vegetation has been used extensively to investigate global distribution patterns. Calamari et al. (1991) were among the earliest to identify an inverted gradient in concentrations of hexachlorobenzene (HCB) in foliage. Recently, Simonich and Hites (1995) analysed tree bark samples from all over the world and found such a gradient for the four most volatile chemicals (HCB, α -hexachlorocyclohexane (α -HCH), γ -HCH, pentachloroanisol) in a set of 22 POPs. Less volatile compounds showed no significant latitudinal dependence. On a smaller scale similar patterns were also observed in lichen from Ontario, where samples from the northwestern part of the province were distinguished from most southern locations by higher proportions of more volatile organochlorine chemicals such as the HCH isomers, pentachloroanisol and chlorobenzenes (Muir et al. 1993)

A striking example of an inverted latitudinal concentration profile is the α -HCH concentration gradient in sea water from the Western Pacific extended towards the North with measurements in the Canadian Arctic. Figure 4, which gives most of the available data for the late 1980s and early 1990s from a variety of sources, reveals a strong inverted α -HCH concentration profile with very low concentrations in tropical seas (0.05 to 0.5 ng/L) and

increasing concentrations with increasing latitude - up to levels in the range of 5 ng/L in or close to the Canadian archipelago. Most use is believed to be on the southern fringe of this profile (Voldner and Li, 1995). The γ -HCH concentration profiles is more complex, which may be due to the continued use of large quantities of Lindane in that area, while the use of technical HCH is gradually eliminated. The very few measurements of HCHs which are available for the Atlantic Ocean (Iwata et al. 1993, Schreitmüller and Ballschmiter 1995) make it unfortunately impossible to generalise this pattern, but confirm the low levels at low latitudes.

In a study of organochlorine pesticides in surface sediments of eight Canadian lakes along a mid-continental transect from 49°N to 82°N, concentrations of Σ DDT were found to decline with increasing northern latitude, whereas levels of chlorobenzenes were generally higher in the surface sediments of the arctic lakes than in NW Ontario (Muir et al. 1995a). Toxaphene, chlordanes, dieldrin, and HCHs did not show consistent latitudinal gradients but had highest concentrations in lakes at 63°N and 75°N.

Compositional Changes of Contaminant Mixtures Along Latitudinal Gradients

The PCBs are ideal for detecting latitudinal, compositional changes of contaminant mixtures, because of their wide range of volatility. Such data for fish liver from lakes and rivers across Canada (Muir et al. 1990) were key for formulating the global fractionation hypothesis (Wania and Mackay 1993). Since then Muir et al. (1995b) presented additional evidence from Canadian lake sediments which cover an even wider latitudinal scale than the burbot data. Statistical analysis revealed that sediments from high arctic lakes could be distinguished by greater proportions of lower chlorinated PCBs (Muir et al. 1995b). Similar shifts in the composition of PCBs indicating a higher proportion of the tri- to pentachlorobiphenyls in the Arctic were reported by König et al. (1995) in zooplankton from Canadian lakes ranging from the Great Lakes region to Ellesmere Island. Finally, changes of PCB congener patterns with time and latitude, which agree with the cold condensation/global fractionation theory were observed in mosses sampled in Norway (Lead et al. 1996).

Changes in congener pattern with latitude were also reported for polychlorinated dibenzo-p-dioxins and furans. Surface sediment samples from the Barents Sea had a higher proportion of less chlorinated congeners of PCDDs and especially PCDFs than sediments from the North Sea (Oehme et al. 1993). While the PCDF profile was dominated by OCDF in the North Sea sediments, TCDF was the most abundant congener group in the Arctic samples.

Time Delay in Achieving Maximum Concentrations at Higher Latitudes

The Canadian sediment core data are also providing evidence for the time delay in concentration changes at higher latitudes. PCB concentrations peaked in the most recent slices in the high Arctic lakes, but in older slices (1960s/1970s) in more southerly locations (Muir et al. 1995b). The same was observed for some organochlorine pesticides, namely DDT (Muir et al. 1995a).

Difficulties of Interpretation

We emphasise that not all data support the concept of global fractionation. For example, a study of the geographical distribution of organochlorines on pine needles throughout Europe revealed inverted latitudinal profiles for pentachlorophenol with higher levels in northern Sweden, but did not find such gradients for the other more volatile compounds HCB, α -HCH and γ -HCH. (Jensen et al. 1992, Strachan et al. 1994). We suspect that it is unwise to over-interpret global distribution patterns using simple models.

- There is often poor sample comparability due to variations in sampled species, sampling time, analytical methods and environmental conditions.
- There have been many release locations and histories, which are often decades long. The “single pulse” or “steady emission” concept is thus excessively simplistic. Samples from non-background areas may be affected by chemical emissions in the vicinity and may distort latitudinal gradients (e.g. Calamari et al. 1994).
- Global dispersion processes may be slow because of the long distances (i.e. a steady state is unlikely to be established).
- The quantities of POPs traveling towards the poles decrease in time because of degradative losses and permanent retention in soils and sediments.

The Role of Retention and Degradation

This latter point deserves a more detailed discussion because we noticed that a misconception often develops that the bulk of the chemical inventory on the globe will eventually reach the polar regions. This misconception is possibly derived from the metaphor of a chromatographic peak moving towards the poles, and the observed dramatic decline of contaminant concentrations at lower latitudes, e.g. of PCBs in UK soils (Alcock et al. 1993) or of HCH pesticides in a tropical watershed (Takeoka et al. 1991). However, retention and degradation, both in source areas and en route are believed to ensure that most of the emitted amount will fail to make the long journey to the polar regions.

Very efficient retention of persistent organic contaminants in soils, sediments, and ocean water has been reported. Alexander (1995) recently reviewed the phenomenon of permanent retention of non-polar organic compounds, particularly pesticides, in soils. In New Zealand 40 % of DDT applied to agricultural fields in the 1950/60s could be found in the same soils 40 years later (Boul et al. 1994). Similarly, substantial residues of toxaphene

were detected in Canadian prairie lakes which had been treated 30 years ago (Miskimmin et al. 1995). The export of hydrophobic contaminants which are scavenged out of the surface oceans into the deep sea with settling particles constitutes another permanent sink.

It may be argued that these compounds are very persistent and degradation losses thus tend to be negligible. On a local or even regional scale degradation processes with half-lives in the range of many years to even decades may be insignificant, because transport processes are generally faster and export the chemical out of the area of question before substantial degradation can occur. With a global perspective, however (1) advective transport in atmosphere and ocean water does not contribute to a loss of chemical, but only leads to redistribution within the global environment, and (2) time scales become longer because of the great distances involved. Therefore, degradative loss becomes relatively more important with increasing size of the area under consideration.

Although only a part of the global inventory of a contaminant may migrate to polar regions, concentrations there can still be high. The polar regions are small in area when compared to the tropical and temperate zones. Areas North and South of 60° latitude constitute only 13.4 % of the global surface area, while 50 % lies in between 30 °N and 30 °S, i.e. tropical regions cover an area which is four times the area of polar regions. Even a minor share of the global inventory transferred to the polar regions can thus result in elevated concentrations.

The polar terrestrial environment also has a limited capacity to retain POPs, because of a low organic matter content in arctic and Antarctic soils. Contaminants are thus more readily transferred to the marine environment than in temperate ecosystems and may therefore have relatively higher concentrations in polar seas. Polar ecosystems may have features which enhance the potential for bioaccumulation, such as food web structure, the oligotrophy of arctic aquatic systems and the pronounced seasonal dynamics of lipids (Schindler et al. 1995, Wania 1996). Human residents rely more on locally obtained fish and wildlife for food.

Perhaps future global mass balance models may be able to estimate the percentage of the chemical introduced in certain regions (e.g. Southeast Asia) which will eventually reach the polar regions. This percentage may be quite small, e.g. one percent, but could be ecologically significant. Indeed, this percentage figure is possibly the single most useful quantity for characterising the desirability of international controls.

Chemical Classification According to Global Partitioning Behaviour

Clearly long range transport does occur and observations suggest that certain POPs such as HCB and the HCHs preferentially deposit in polar latitudes, while others such as DDT tend to deposit at lower latitudes (Wania and Mackay, 1993). Can we define more sharply the characteristics of chemicals subject to global transport and accumulation in cold climates? The obvious criteria are P_L , the vapour pressure of the sub-cooled liquid at 25 °C,

and K_{OA} , the dimensionless octanol-air partition coefficient (Figure 5 and Table 1).

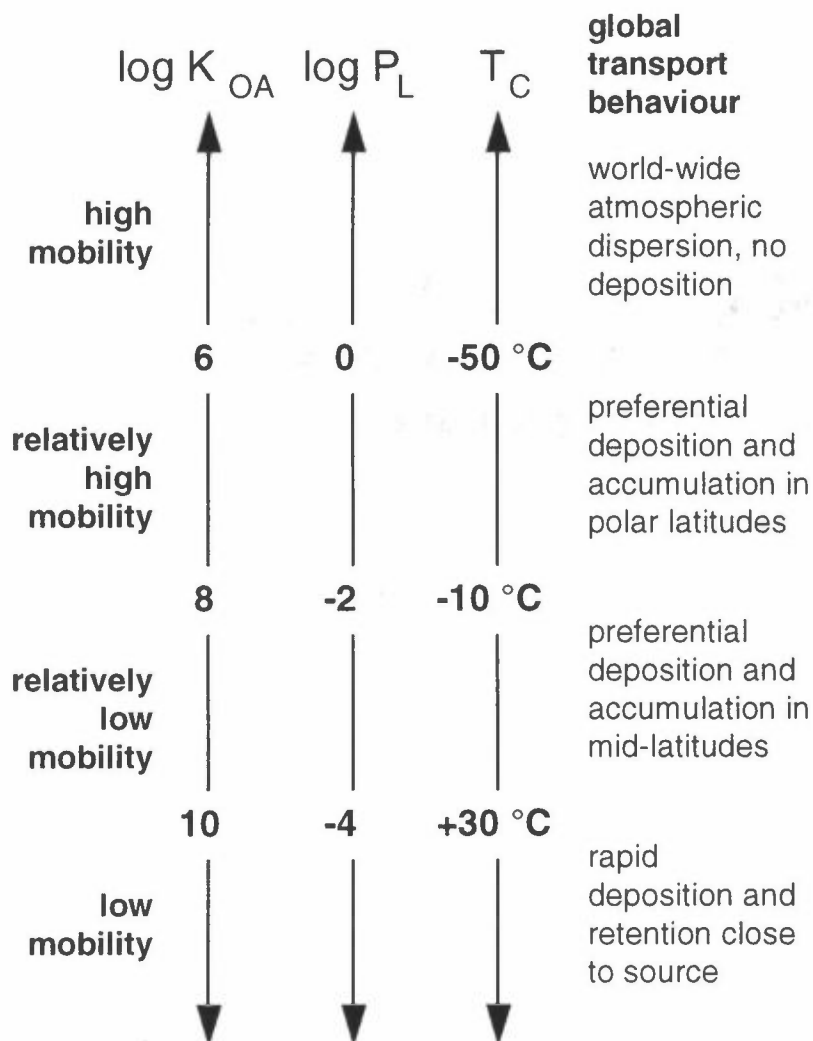


Figure 5 Suggested classification of contaminants according to their mobility in the global environment based on sub-cooled liquid vapour pressure, octanol-air partition coefficients and a contaminant-specific “condensation temperature” (for details see text).

We suggest four broad volatility classes. Contaminants with P_L above 1 Pa show little tendency to “condense” at temperatures encountered in the global environment. In the limit if a volatile POP partitions negligibly into soils or water, as may be approximated by chlorofluorocarbons, then the global atmospheric concentration may approach homogeneity, i.e. the chemical becomes well mixed throughout the entire planetary atmosphere. Compounds with P_L between 1 and 0.01 Pa “condense” at lower temperatures around -30 °C and thus are preferentially deposited in polar latitudes. Those between 0.01 and 0.0001 Pa “condense” appreciably at temperatures above 0 °C and tend to accumulate in mid-latitudes. The very involatile chemicals with $P_L < 0.0001$ Pa evaporate very slowly or not at all and tend to deposit and remain close to their sources.

A better criterion may be the octanol-air partition coefficient K_{OA} , because it also accounts for the potential of terrestrial surfaces such as soils and vegetation to retain a chemical. So far, experimentally determined K_{OA} exist for only very few chemicals (Harner and Mackay, 1995), but values can be estimated from the ratio of the octanol-water and air-water partition coefficients:

$$K_{OA} = \frac{K_{OW}}{K_{AW}} = \frac{K_{OW} \cdot S \cdot R \cdot T}{P_L}$$

where K_{OW}	octanol water partition coefficient
K_{AW}	air water partition coefficient (Henry's law constant)
S	aqueous solubility in mol/m ³
P_L	vapour pressure of the sub-cooled liquid in Pa
R	gas constant in J/(K·mol)
T	temperature in K.

Such calculations suggest that contaminants with relatively high mobility have a K_{OA} between 10^6 to 10^8 , while those with relatively low mobility a K_{OA} between 10^8 to 10^{10} . P_L and K_{OA} are of course highly correlated (see also Figure 6), since K_{AW} is a function of P_L . Perhaps K_{AW} is the best criterion for characterising partitioning to the oceans, while K_{OA} is best for partitioning to the terrestrial environment.

Aerosol-Vapour Partitioning

These properties also control the partitioning equilibrium between aerosols and the vapour phase, which may serve to illustrate the "condensation" of contaminants at low temperatures. As discussed by Bidleman (1988), the sorption of atmospheric contaminants to aerosols can be estimated by the Junge-Pankow relationship:

$$\Phi = \frac{c \cdot S_T}{P_L + c \cdot S_T}$$

where ϕ	adsorbed fraction
S_T	total surface area of aerosol in m ² /m ³
c	contaminant and aerosol specific parameter in units of Pa·m

The temperature dependence of P_L often is described by an Antoine-type equation:

$$\log P_L = \frac{m_L}{T} + b_L$$

where m_L and b_L empirical parameters

Because of the strong temperature dependence of vapour pressure, the aerosol adsorbed fraction ϕ is also a function of temperature.

$$\Phi = \frac{c \cdot S_T}{10^{\frac{m_L}{T} + b_L} + c \cdot S_T}$$

Figure 7 shows the fraction of atmospheric HCB and DDT adsorbed to aerosol within the environmental temperature range.

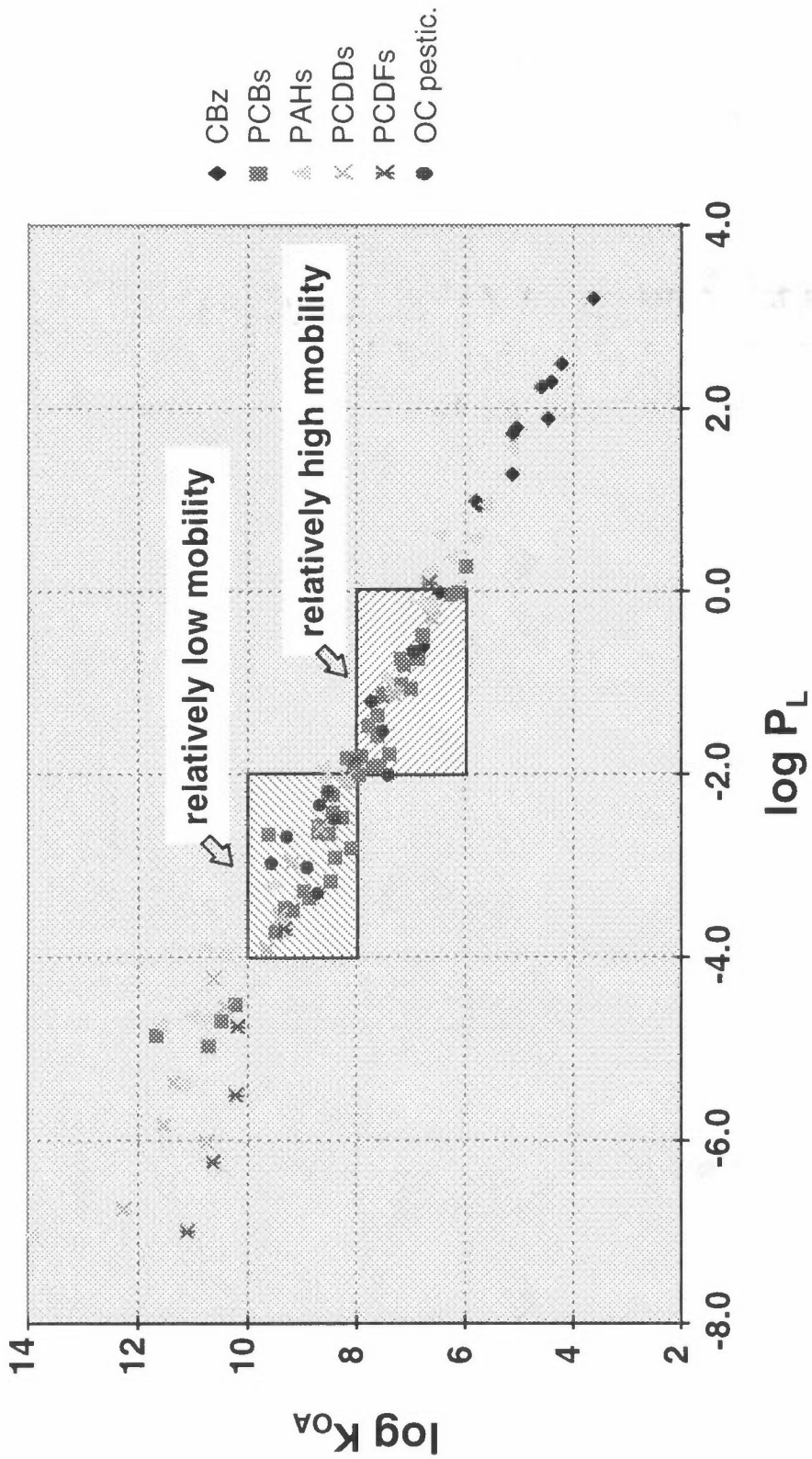


Figure 6 Regression of $\log P_L$ vs. calculated $\log K_{OA}$ and delineation of the global mobility categories.

Table 1		Vapour pressure of the sub-cooled liquid P_L , octanol-air partition coefficient K_{OA} and "temperature of condensation" T_C for selected persistent organic contaminants.		
		$\log(P_L/\text{Pa})^{(1)}$	$\log K_{OA}^{(2)}$	$T_C/^\circ\text{C}^{(3)}$
PAHs	naphthalene	1.6	5.1	
	anthracene	-1.1	7.3	-33
	pyrene	-1.9	8.6	-15
	flouranthene	-2.1	8.6	-10
	chrysene	-4.0	10.4	
	benz[a]anthracene	-3.2	9.5	+12
	benzo[a]pyrene	-4.7	10.8	+47
PCBs	2,4,4'-C ₃ B (#28)	-1.5	7.8	-22
	2,2',5,5'-C ₄ B (#52)	-1.8	7.9	-15
	2,2',4,5,5'-C ₅ B (#101)	-2.5	8.3	-2
	2,2',4,4',5,5'-C ₆ B (#153)	-3.2	8.5	+10
	2,2',3,3',4,4',6-C ₇ B (#171)	-3.7	9.5	+20
	2,2',3,3',4,4',5,5'-C ₈ B (#194)	-4.7	10.5	+37
CBzs	PC ₅ Bz	-0.0	6.5	
	HC ₆ Bz	-0.6	6.8	-36
PCDD/Fs	2,3,7,8-C ₄ DD	-3.9	9.7	
	1,2,3,4,7,8-C ₆ DD	-5.8	11.5	
	C ₈ DD	-6.0	10.8	
Pesticides	α -HCH	-0.7	6.9	-40
	γ -HCH	-1.2	7.7	-30
	p,p'-DDT	-3.3	8.7	+13
	p,p'-DDE	-2.5	8.4	-2
	p,p'-DDD	-3.0	8.9	+7
	cis-chlordane	-2.3	8.7	-6
	trans-chlordane	-2.2	8.5	-9
	dieldrin	-2.0	7.4	-11
⁽¹⁾		data from Mackay et al. 1992a and b, for PCBs from Falconer and Bidleman 1994		
⁽²⁾		calculated from K_{OW} , P_L and S_L , data from Mackay et al. 1992a and b		
⁽³⁾		temperature dependence of vapour pressure from Hinckley et al. 1990 and Falconer and Bidleman 1994, no value listed if such data missing		

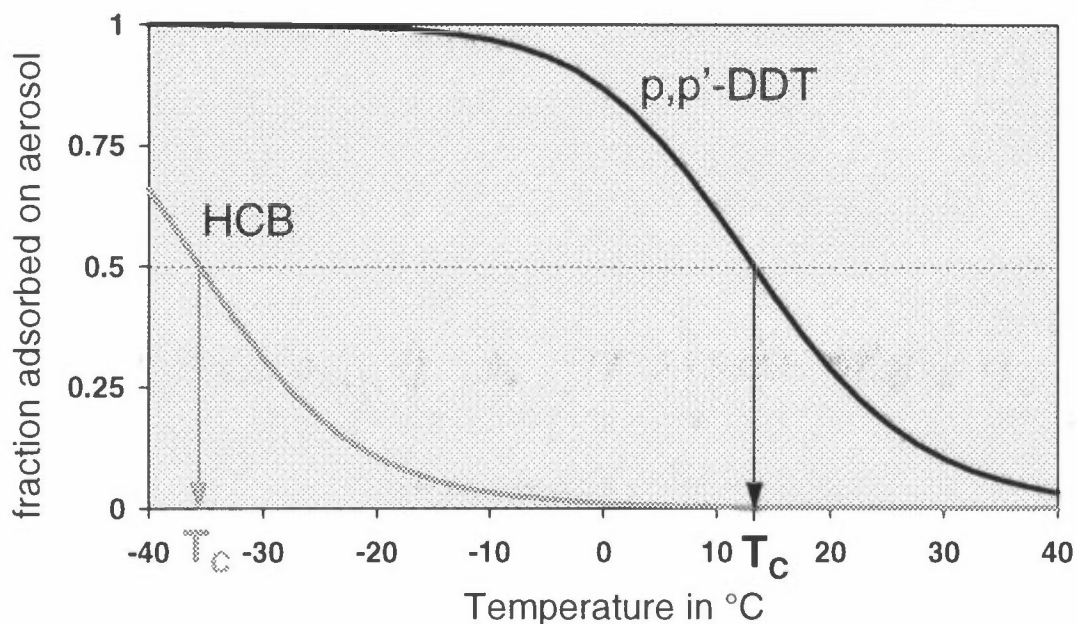


Figure 7 The fraction ϕ of HCB and p,p'-DDT adsorbed to aerosol as a function of temperature. It is assumed that the total aerosol surface area is $1.5 \cdot 10^{-4} \text{ m}^2/\text{m}^3$. The "temperature of condensation" T_C , at which half of the HCB and DDT is adsorbed to aerosols, is $-36 \text{ }^\circ\text{C}$ and $+13 \text{ }^\circ\text{C}$, respectively. Vapour pressures from Hinckley et al. 1990.

Significantly, the change in partitioning from mainly gas phase to mainly sorbed occurs within a fairly small temperature range of about 50 K. A characteristic "temperature of condensation" T_C can be defined when ϕ is 0.50, i.e. the chemical is equally partitioned between the gas phase and the aerosols under clean atmospheric conditions. From the previous two equations we derive:

$$T_C = \frac{m_L}{\log(c \cdot S_T) - b_L}$$

In a rough approximation c may be considered a constant of value 0.72 Pa·m and continental background air has on average a total aerosol surface area S_T of $1.5 \cdot 10^{-4} \text{ m}^2/\text{m}^3$ (Bidleman, 1988). Thus,

$$T_C = \frac{m_L}{-4 - b_L}$$

Using empirical P_L vs. T relationships reported in the literature (Falconer and Bidleman 1994, Hinckley et al. 1990, Mackay, Shiu and Ma 1992), values of T_C have been estimated and are given in Table 1. T_C is dependent on the concentration of aerosols, being higher at areas of high concentration. POPs which accumulate in arctic latitudes tend to have T_C 's between -50 and $-10 \text{ }^\circ\text{C}$, while for POPs preferentially depositing in temperate areas T_C is -10 to $+30 \text{ }^\circ\text{C}$. For a global contaminant, T_C and the average temperature in the zone of preferential deposition thus lie in the same range.

The PCBs homologues cover the entire volatility range which was identified as being relevant for global distillation phenomena. While mono- and unsubstituted biphenyls have a P_L greater than 1 Pa, the nona- and decachlorobiphenyls fall in the class of involatile chemicals with P_L smaller than 0.0001 Pa. The dividing line between PCBs which start to condense at temperatures above 0 °C and those which condense at temperatures well below 0 °C lies approximately at the tetrachlorobiphenyls. This implies that di- and trichlorobiphenyls will accumulate in polar latitudes, while PCBs with more than five chlorine substitutions tend to remain to a greater extent in mid-latitudes.

Some polycyclic aromatic hydrocarbons (PAHs) also have a volatility within this range. PAHs with three rings tend to fall in the category with preferential deposition in high latitudes, while four-ring PAHs already “condense” appreciably at temperatures above 0 °C. Within the global temperature range naphthalene is already too volatile for “condensation”, benzo[a]pyrene too involatile for evaporation.

Based on these arguments a number of organochlorinated compounds and PAHs are tentatively grouped into the four global mobility categories.

	low mobility	relatively low mobility	relatively high mobility	high mobility
Chlorobenzenes	-	-	5 to 6 Cl	0 to 4 Cl
PCBs	8 to 9 Cl	4 to 8 Cl	1 to 4 Cl	0 to 1 Cl
PCDD/DFs	4 to 8 Cl	2 to 4 Cl	0 to 1 Cl	-
PAHs	4+ rings	4 rings	3 rings	2 rings
Organochlorine pesticides	mirex	DDTs, PCCs, chlordanes	HCB, HCHs, dieldrin	-

The Factors Controlling Chemical Fate in the Global Environment

The emerging picture of the global fate of persistent organic contaminants is illustrated schematically in Figure 8. According to this picture global chemical fate is controlled by (1) the point of discharge into the global environment, (2) the movements of the atmosphere and the oceans, (3) the rate of exchange processes between the atmosphere and the Earth's surface, and (4) the rate of chemical loss from various environmental phases.

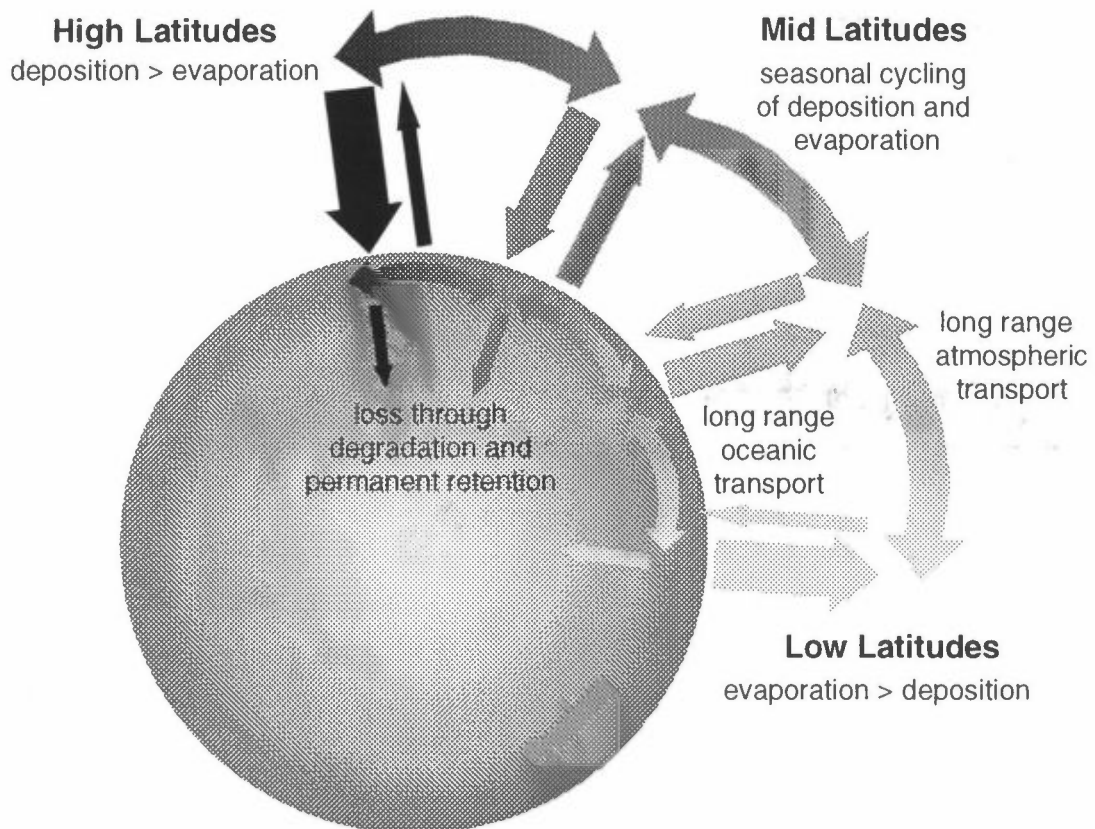


Figure 8 Sketch of the major processes controlling the global fate of persistent organic contaminants.

Discharge in the Global Environment

No matter how efficient the global translocation processes are in dispersing contaminants, concentrations in environmental sample will always be influenced by the history of chemical usage in the surroundings of the sampling site. This has to be accounted for in any attempt to understand and interpret global distribution patterns. Not surprisingly, several studies of global distribution patterns of persistent organic contaminants found a strong correlation with the use of a chemical in a country (Calamari et al. 1994, 1995, Tremolada et al. 1995, Simonich and Hites 1995). This is particularly true for less mobile chemical which tend to stay close to their point of release into the global environment.

Movement in the Atmosphere and Oceans

Chemicals are transported in the global environment as a result of the general circulation in the atmosphere and the oceans. The movement of these media is unaffected by the presence and absence of chemicals. In the atmosphere the transport occurs both in the vapour phase and associated with the aerosol particles. Similarly, in the oceans transport occurs in the dissolved phase and with suspended particulate matter.

Chemical transport in the atmosphere is fast and far-reaching. Zonal atmospheric mixing occurs in the time frame of days and even on a hemispheric scale mixing takes place within a few weeks. Inter-hemispheric

atmospheric mixing is somewhat slower. Although aerosol particles generally have shorter atmospheric residence times than a persistent chemical in the vapour phase, they are also transported rapidly on a hemispheric scale. Oceanic transport is considerably slower (years to decades), but nevertheless of global dimensions. Since the capacity of water to hold persistent organic chemicals is generally much higher than that of the atmosphere, the amounts transported in ocean currents may be very substantial. Vertical water exchange in the oceans is generally slow. However, settling particles constitute a short cut route for chemicals to deeper ocean layers.

Atmosphere-Surface Exchange Processes

The global environmental distribution of essentially non-volatile contaminants (heavy metals, soot particles, radionuclides, etc.) is controlled by the location of emission sources, preferred atmospheric pathways originating from these source regions and aerosol deposition processes. Persistent organic contaminants are fundamentally different because of their potential for re-evaporation after deposition. Key to the understanding of their global fate are thus the rates of exchange between the atmosphere and whatever constitutes the Earth's surface: ocean and fresh water, vegetation, soil and bedrock, ice and snow.

Deposition and evaporation processes of persistent organic contaminants are very complex and subject to many influencing factors related to both the chemical and the environment. Chemical-related factors are primarily the partition coefficients (air-water, air-aerosols, air-soil, air-foliage, air-snow, etc.), which in turn are derived from basic physical-chemical properties such as vapour pressure, aqueous solubility, octanol-air and octanol-water partition coefficients. Many of the environmental factors influencing air-surface exchange such as organic carbon content of soils, aerosol concentrations, precipitation rate are dependent on climate.

Chemical Loss

Degradation, sedimentation, transport to deeper ocean layers and permanent retention or percolation in soils can contribute to the disappearance of persistent organic contaminants from the surface layer capable of exchanging material with the atmosphere. The rate of loss is dependent on climatic conditions and likely to be higher in low latitudes than in polar regions.

Global Chromatography

With its interaction of transport and temperature-controlled partitioning between mobile and stationary phases, this picture of global chemical fate in many ways resembles a chromatographic process (Figure 9). The idea that the global environment can be understood as a gigantic, extremely complex chromatographic system was first formulated by Risebrough (1989) and later taken up by Ballschmiter (1992). The terrestrial surface, particularly soils and vegetation, constitute a non-polar stationary phase with a strong potential to retain the generally hydrophobic organic contaminants. The atmosphere serves as the mobile phase. The world oceans are both a polar

stationary phase with intermediate retention potential and a slowly moving mobile phase.

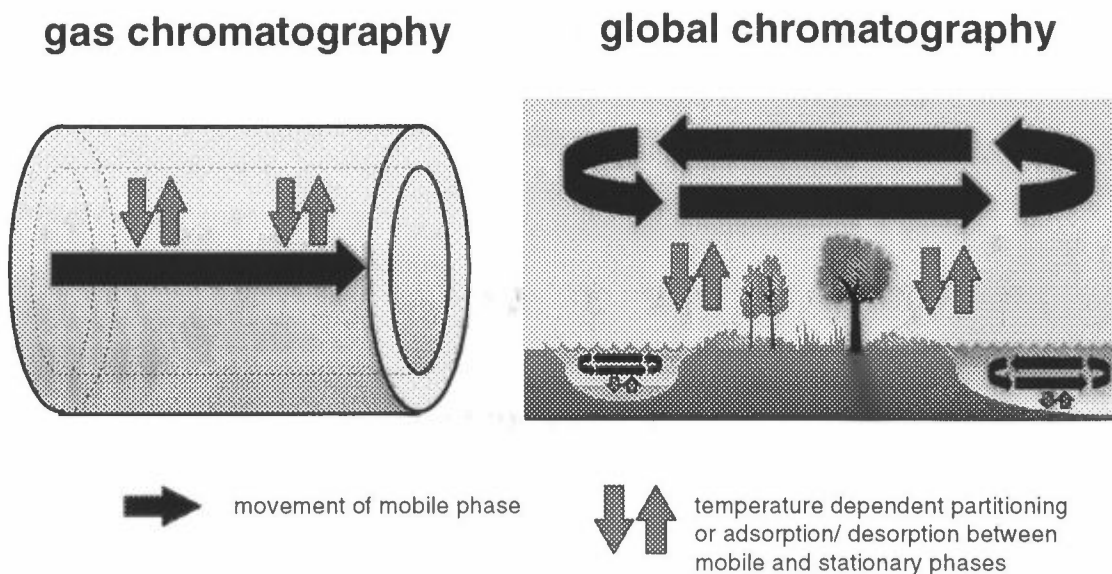


Figure 9 The interaction of transport and temperature-controlled partitioning between mobile and stationary phases is a feature common to both gas chromatography and the global dispersion process for persistent organic contaminants.

The differences in retention and mobility between chemicals lead to peak separation in laboratory chromatography and to what has been termed fractionation in the global environment. The concept of retention time relates to the global transport velocities or “grass-hopper” velocities mentioned above. It may even be possible to estimate relative and absolute values for the global transport velocity of various contaminants.

The global system, of course, is much more complex than any laboratory system:

- The injection of chemical into the global environment generally occurs not only in a single place (such as an injector), but at many locations.
- The phases in laboratory chromatography are homogeneous in both space and time, while the atmosphere, the oceans and especially the terrestrial environment are very heterogeneous in space and undergo pronounced short-term and long-term changes (e.g. seasonal change of climatic parameters (temperature) and surface coverage (snow and sea ice, annual vegetation)).
- In the global environment exchange between mobile and stationary phase is not just controlled by partitioning or adsorption equilibria, but can occur mediated by particles (e.g. wet deposition and dry particle deposition from the atmosphere, settling of particles in aquatic systems).
- The flow of mobile phases in laboratory chromatography is unidirectional, while atmosphere and oceans have very complex and variable flow patterns.

Temperature in Global and Gas Chromatographic Systems

Although in both, gas chromatography and the global environment, the influence of temperature on the partitioning equilibrium between mobile and stationary phases is important, the role of temperature is a different one: While temperature is used to influence retention times and thus analytical separation in gas chromatographic applications, temperature determines the net flow direction of chemical in the global environment. Spatial temperature differences thus substitute the uni-directional flow of the mobile phase in laboratory chromatography. Although in the global atmosphere contaminants may flow in any direction the wind blows, for reasons outlined earlier the net movement will be from warm to cold regions.

In gas chromatography the temperature can assume a very wide range of values (below 0 °C to several hundred °C), while in the global environment the temperatures are restricted to the range typically encountered at the Earth's surface and range between -50 °C and +45 °C. Global ambient temperatures thus tend to be low compared to temperatures used in gas chromatographic analysis. Correspondingly, what may be considered a fairly volatile and thus mobile chemical in standard gas chromatography, may be more or less involatile and strongly retained in the global environment. For example, highly chlorinated PCDD/DFs are still amenable to gas chromatographic analysis, but have to be considered fairly immobile in the global environment.

Therefore, temperature has to be accounted for when comparing the chromatographic behaviour of a chemical in a gas chromatograph and the global environment. When applying the previously used volatility classification for such a comparison, as is attempted in Table 3, the gas chromatography is assumed to be conducted at temperatures prevalent in the global environment.

Table 3 The four chemical mobility classes in terms of their behaviour in gas chromatography and the global environment.		
	gas chromatography	global chromatography
low volatility	no transport through column, remains in injector	minimal global transport, remains in source area
relatively low volatility	long retention time	slow global transport, tends to have higher levels in source areas
relatively high volatility	short retention time	readily transported globally, accumulates in cold remote areas
high volatility	not retained by stationary phases, behaves like carrier gas	no partitioning into Earth's surface, behaves like an air constituent

Table 4 summarises some of the correspondences between gas chromatography and the global chromatographic system.

Table 4 Comparison of several features of gas chromatography and the global environment as a complex chromatographic system.	
laboratory chromatography	global chromatography
one mobile phase (gas or liquid)	several mobile phases (atmosphere and world oceans)
one stationary phase (liquid or solid)	many stationary phases (terrestrial surfaces such as soils and vegetation, fresh and ocean water and sediments)
phases are uniform in space and time (temperature may change)	phases are heterogeneous in space and time
chemical separation	global fractionation
retention time	global transport velocity ("grasshopper velocity")
one chemical injection point	many chemical release locations
phase exchange by diffusive partitioning or sorption	phase exchange by diffusive partitioning or sorption, additionally "advective" phase exchange
unidirectional gas flow determines net flow direction of chemical	spatial temperature differences determine net flow direction of chemical
temperature range: below 0 °C to several 100 °C	temperature range: -50 °C to +45 °C

Recommendations

If we are to understand quantitatively the global distribution processes of POPs, more effort must be devoted to the study of emissions and climate dependent cycling processes. It is surprising how little is known about the amounts and use areas of organochlorine pesticides, which have been and are still being produced and discharged globally. Data on the magnitude and locations of the global use of POPs are thus critically important. We must also improve our knowledge of the influence of climatic characteristics of high latitudes such as snowfall and low temperatures on the cycling of POPs.

Ensuring absence of POPs in cold climate ecosystems requires reducing or eliminating the release of chemicals globally, which have the potential to preferentially accumulate in cold environments. We can now tentatively identify those properties which make a chemical susceptible to global long range transport and polar deposition. The Washington Declaration (UNEP, 1995) is heading in the right direction when it states the need to develop "a global, legally binding instrument for the reduction and/or elimination of emissions, discharges and, where appropriate, the elimination of the manufacture and use of persistent organic pollutants" To ensure that controlled POPs are not merely replaced with substances which have the same undesirable global distribution behaviour, a future protocol may refer

to a set of chemical properties such as ranges of P_L or K_{OA} and half lives rather than a specific list of chemicals. There is a clear need for the global scientific and regulations communities to work together to elucidate and solve this problem.

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