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Global Distillation in an Era of Climate Change

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1. Introduction

When a chemical enters the natural environment it undergoes change by several processes. It can be transported by the movement of the sector of the environment it enters, for example ocean currents and atmospheric movements, to a different geographical location. In addition as it is transported it is usually diluted so that its concentration is reduced. Chemical degradation processes take place which result in the production of more polar and water soluble products and leaving residual initial chemical. As all of these processes occur there is a distribution of the chemical between the phases in the environment. These processes have been described in a series of papers and books by Mackay as reported in Mackay et al. (2009).

The processes shown in Figure 1 illustrate the basic processes involved in the partitioning of a chemical into phases in the environment. All of the processes shown involve two phases and movement backwards and forwards of the chemical and thus can be characterised by a partition coefficient. The partition coefficient is the ratio of the chemical in the two phases at equilibrium and is often represented by the symbol, K. Thus the air – water partition coefficient is represented by $K_{AW}$ and is better known as the dimensionless Henrys Law constant (Shiu and Mackay, 1986), the fish – water partition coefficient is $K_B$ (Connell, 1990) the sediment – water coefficient is $K_D$ (Gobas and Maclean, 2003) and the other partition processes can be represented in a similar way. It is of interest to note that as a result of these partition processes a chemical can occur in very low concentrations in the atmosphere, low concentration in water but relatively high concentrations in fish and other aquatic biota. Most of these partition coefficients can be calculated from partition values arrived at by laboratory measurements. For example the Henrys Law constant and the octanol – water partition coefficient, $K_{OW}$, can be measured in the laboratory. The $K_{OW}$ can be used to calculate the fish – water partition coefficient, $K_B$ value and also the $K_D$ value and is extensively used to model chemical partitions in the environment. The octanol – air partition coefficient, $K_{OA}$, can be calculated or measured in the laboratory and can be used to evaluate the partitioning of a chemical into organisms as a result of concentrations in the atmosphere. The Persistent Organic Pollutants (POPs) are a group of mainly chlorinated hydrocarbon insecticides and dioxins which are often reported to undergo global distillation (Fernandez and Grimalt, 2003). These substances undergo the partition processes illustrated diagrammatically in Figure 1. However if they are discharged to the environment in the warmer zones of the planet a proportion will partition into the atmospheric phase according to the partition coefficient at that temperature. Movement in the atmosphere through winds
results in transport to different geographical regions which, with the polar zones, have a colder temperature. The partition coefficient values are displaced to favour the solid or liquid phase and not the atmospheric phase. Thus a transfer of chemical can occur from warmer to the polar zones of the planet by a process somewhat similar to distillation – global distillation. This can occur in a series of steps or hops (Ma, 2010).

Fig. 1. Pathways for Movement of Persistent Organic Pollutants within the Environment

1.1 Physicochemical properties of POPS
There is no direct evidence that all of the compounds which are currently classified as POPs (see Table 1) exhibit the property of global distillation. However the POPs which have been identified as exhibiting global distillation share a set of properties which lead to their long range transport to the polar zones in the Arctic and are presumed (rather than demonstrated to also do the same in the Antarctic). Firstly all of these compounds are chlorohydrocarbons which means there is a limited range of covalent bonds present in them. These bonds are mainly C-C, C=C aromatic, C=C, C-H, C-Cl which are resistant to oxidation and hydrolysis - the main degradation processes in the environment. This leads to environmental persistence with a half life of between 2 to 10 years in soil and 0.25 to 2.5 years in air. Aqueous solubility is low at 1 to 7 g/m³ with a correspondingly high solubility in lipid reflected in the KOW values from about 10² to 10⁶.
1.2 Climate change and long range transport of POPs

The effects of climate change on the global distillation process have been evaluated by several authors (e.g. Macdonald et al., 2003, Sadler et al., 2011). Macdonald et al., 2003 pointed out that while the partition process can be successfully modelled, the impact of other environmental processes such as altered rainfall and changes to the particulate content of the atmosphere are difficult to assess. In the years since this review, a great deal more has been learned regarding the processes that underlie global distillation and also the effects and severity of climate change. For this reason, an updated review of the literature has been undertaken with a view to providing a prediction of long range transport of POPs for both the Northern and Southern Hemispheres that is relevant to the current state of knowledge.

2. Evidence for global distillation

2.1 Northern Hemisphere

Since the process was first proposed by Wania and Mackay (1995), numerous studies (notably in the Northern Hemisphere) have provided evidence that would be supportive of a global distillation model in respect of global transport of persistent organic pollutants. Polychlorinated biphenyls (PCB) have been amongst the most heavily studied of pollutants in this regard and reports of PCB migration include those in Northern Hemisphere soils (Meijer et al., 2002), European high mountain lakes (Carera et al., 2002) levels observed in Norwegian mosses (Lead et al., 1996), deposition patterns in Canadian lakes (Muir et al., 1996) and Russian Lakes (McConnell et al., 1996). Studies universally point to enhanced retention of the more chlorinated PCB congeners at lower latitudes, probably reflecting a more facile volatilization of the simpler PCBs and their subsequent migration to the poles. It is clear that although overall distribution patterns are consistent with the theory of global distribution and transport, a number of other local factors have to be taken into consideration when ascribing differences to global transport. Regression plots generally show considerable scatter with regard to the trend line, particularly with octa-PCBs (Meijer et al., 2002). This may account for the fact that other studies have found only partial evidence in support of the expected global transport process.

Reports of similar distribution patterns have also been produced in respect of global distribution of PCBs and organochlorine pesticides in other media. For example Kalantzi et al., 2001, noted that the distribution of PCB congeners was highest in European and North American butter and lowest in butter samples from the southern hemisphere. But the authors rightly point out that there are a number of compounding factors, such as relative efficiency of uptake from air/foliage, history of use in the area, etc. A number of other POPs included in the study showed maximal levels in areas where they are still in use. Trapping of PCBs and organochlorine pesticides in pine needles in Canada has also been ascribed to their delivery via global transport processes (Davidson et al., 2003).

Additional evidence of POP migration in accordance with the global transport/distillation model has come from measurement of levels in air over an extended period of time. There are now a number of networks dedicated to this type of surveillance. The underlying premise is that with a decrease in evolution of POPs following withdrawal of their use in many countries, levels in air should decrease with increasing time. For example, Sweetman and Jones (2000) reported a decrease of this kind with respect to PCBs. Their study, which centered around Hazelrigg, UK, noted a significant downward trend in PCB congener levels with time. Similar results were also obtained as regards levels of PCB congeners around the
Great Lakes region (Slmck et al., 1999). In contrast, the situation in the Arctic is more complex, as there will be an ongoing input of POPs from the continuing use in certain countries and also in terms of completion of global migration which commenced in other areas when the pesticides were routinely employed. The levels observed in Arctic air will principally result from global transport and also to a lesser extent, from revolatilization of POPs already in the Arctic environment. Hung et al., 2001 observed a rather mixed response in terms of trends for PCB congeners in Arctic air with time. There was generally a lack in decline of temporal trend, particularly as regards the more chlorinated congeners. The authors considered this to be basically supportive of a global transport model. Nevertheless, there were some exceptions, notably PCB 180, which whilst polychlorinated, showed a distinctive downward temporal trend. It was postulated that the heavier congeners may be more subject to differential removal processes by snow and particulate scavenging, whereas the lighter PCBs may be more prone to attack by hydroxyl radicals.

There have also been a number of reports of global transport in respect of a variety of pollutants apart from PCB congeners. Several of these have been included in the discussion above, but pollutants for which similar patterns have been observed include endosulfan, HCB and HCH (Carrera et al., 2002), lindane (Zhang et al., 2008) and phthalates (Xie et al., 2007). Significant attention has been paid to α- and γ-HCH (lindane) as well as endosulfan, because of their relatively recent use. In 2002, γ-HCH was shown to have reached phase equilibrium in the North Atlantic as has α-HCH, but the surface waters of the tropical and southern Atlantic were strongly undersaturated with γ-HCH, especially between 30°N and 20 °S. It must be noted that the state of the air-sea equilibria of α-HCH and γ-HCH are very different. The sporadic occurrence of γ-HCH in air makes it difficult to obtain representative results from transect cruises (Lakaschus et al., 2002). Weber et al., (2006) collated data for these pesticides from a number of sampling expeditions over the past decade. Although all could be detected in the Arctic environment, different patterns of distribution were observed for each substance with α-endosulfan predominating in the western Arctic and γ-HCH in the central Arctic. It was concluded that coastal sources may be important as regards γ-HCH, whereas air exchange is the major pathway of input as regards α-endosulfan.

Hargrave et al., 1997 examined the Arctic air-seawater fluxes of a number of POPs in the Canadian Arctic Archipelago during 1993. All of the pesticides showed a bimodal seasonal distribution of concentrations with maxima in February-May and July-August separated by minimum values in June. Organochlorine levels in air increased sharply during April and May and decreased during June, coincident with the onset of the open water period. Volatilization losses for HCH isomers during the open water period were estimated to have been small, whilst those for HCB and dieldrin were significant. These workers obtained evidence for significant deposition of toxaphenes, chlordanes and α-endosulfan during the open water period. The former USSR and Eastern Europe were probable emission sources for atmospheric contaminants.

An alternative approach to demonstrating the operation of a global distillation process would be the demonstration of summer vs. winter differences as regards deposition of POPs. In theory, higher levels of POPs would be expected to be transported during the summer, as a result of increased volatilization. Although data of this kind have been demonstrated for a number of European sites (cf. Carrera et al., 2002), it is impossible to separate the processes of revolatilization resulting from summer temperatures and increased use patterns at this same period. Diel variations in polybrominated diphenyl ethers and chlordanes in air have also been
noted (Moeckel et al., 2008). The use of isotope tracers or more probably isotope ratios has also been advanced as a possible means of confirming the processes involved in long range transport of POPs (Dickhut et al., 2004).

There is also evidence that apart from global migration towards the poles, distillation phenomena can be invoked to explain the increasing concentrations of these pollutants with altitude. For example, Gallego et al., 2007 studied the distribution of PBDEs and PCBs in fish from high European mountain lakes (Pyrenees and Tatra Mountains respectively). PCB levels in fish muscle were found to be significant in both study areas, with higher levels being recorded in the Tatra Mountains. This would be expected as the latter region experiences lower minima than the former. As regards the recorded levels of PBDEs, there was a good correlation between their levels and those of the PCBs in samples from the lakes in the Pyrenees. The authors considered that this pointed to a predominance of temperature effects in this case, as would be predicted from the global distillation model. This relationship did not apply in the Tatra Mountains, probably reflecting the activity of other (unspecified) processes and also the fact that PBDEs are of later introduction than PCBs. One possibility would be the more recent and probably less restrained use of PCDEs during and immediately after the existence of the Eastern Bloc regimes (cf. Daly and Wania, 2005).

Similar conclusions were reached by Demers et al., (2007), in a study of PCB and other organochlorine levels in trout from lakes in British Columbia and Alberta. Although the results obtained were in keeping with overall global distillation, this process alone could not explain the levels of contaminants found in the trout. The authors considered that both the feeding behavior of the fish and the octanol-water partition coefficient of the contaminant in question were also important factors in determining the observed distribution.

However, Wania and Westgate (2008) have pointed to several important differences between so-called mountain cold trapping and polar cold trapping. Although the same families of pollutants, in particular the PCBs, have been shown to concentrate in both high latitude and high altitude locations, a detailed comparison of studies shows that different chemicals concentrate in high latitudes than at high elevations. The chemicals that become enriched in mountains tend to be less volatile than those preferentially accumulating in polar regions by about two orders of magnitude. Wania and Westgate (2008) hypothesized that the temperature dependence of the precipitation scavenging efficiency of organic chemicals underlies mountain cold-trapping. In both polar and mountain cold trapping, temperature gradients and their impact on gas phase/condensed phase partitioning play a crucial role. Nevertheless, these processes are controlled by different mechanisms and affect different chemicals. In the case of polar cold-trapping the temperature dependence of partitioning between the Earth’s surface and atmosphere is at the basis of the grass-hopper effect. In the case of mountain cold trapping the temperature dependence of partitioning between the various atmospheric components (gas phase vs. particles, rain droplets and snow flakes) is important. Franz and Eisenreich (1998) have pointed to the relative efficiency of snow as compared to rain for scavenging of PCBs and PAHs from the atmosphere, citing porosity differences as a major factor.

2.2 Southern Hemisphere

Evidence for operation of the process of global distillation in the Southern Hemisphere is generally more limited, albeit with at least some grounds for supporting the hypothesis (Corsolini et al., 2002; Noël et al., 2009). A major factor to be considered when comparing the
two processes is the relative differences in landforms between the two hemispheres. Whereas an extensive landmass extends towards the poles in the northern hemisphere, the Southern Hemisphere consists of large expanses of open ocean, with only South America extending close to the Antarctic. Consequently, it is not surprising that the few studies of POPs distribution in the Southern Hemisphere have not provided much evidence of global migration. Studies of seawater are subject to many compounding effects and thus a North-South transect that included a large number of sampling sites off the coast of Africa, failed to show any evidence of increased PCB content at southern latitudes (Nizzetto et al., 2008). The concentrations of HCHs in air and surface water of the Arctic have been shown to exceed those of the Antarctic by one to two orders of magnitude (Lakaschus et al., 2002). Soil and sediment samples from James Ross Island were shown to contain low levels of PCBs, PAHs, p,p'-DDT, DDE, and DDD, with generally lower levels being detected in the sediments. A prevalence of low-mass PAHs, less chlorinated PCBs, and more volatile chemicals was taken to indicate that the long-range atmospheric transport from populated areas of Africa, South America, and Australia as the most probable contamination source for the solid matrices in James Ross Island (Klánová et al., 2008).

Low levels of various organochlorine samples have been recorded in moss samples from high altitude southern hemisphere locations (Grimalt et al., 2004) and also from the Antarctic (Focardi et al., 1991). (Mosses are favoured for this type of observation because of their rather simple physiology compared to higher plants.) When compared to the levels of these pollutants found in similar locations within the northern hemisphere, the levels are small, with the Antarctic values being particularly low. As has already been explained, there are differences in the underlying principles of high altitude vs. polar deposition, even though there is some overall resemblance in the processes.

The general lack of supporting observations for operation of global distillation in the Southern Hemisphere is probably a reflection of a number of factors. As mentioned above, the Southern Hemisphere contains far larger expanses of ocean than does the Northern Hemisphere. There has to date been little evidence obtained to support the operation of global distillation in oceans, probably because of the susceptibility of deposited POPs to scavenging by water-borne particulates (notably those of phytoplankton origin), with subsequent benthic deposition (Dachs et al., 2002).

Moreover, it must be conceded that the overall shape of continents in the Southern Hemisphere differs markedly from that of their Northern Hemisphere counterparts. The two land masses that would provide a terrestrial pathway for POPs from the equator towards the poles (viz. South America and Africa) are both triangular in shape. Given that global distillation works best in terrestrial environments (Dachs et al., 2002), a persistent organic pollutant moving towards the Arctic in the Northern Hemisphere would have a relatively good chance of progressing via land. In contrast, movement southwards in Africa or South America would significantly increase the chance of a persistent organic pollutants’ entering the marine environment and hence being lost to the global distillation process. And although the southern tip of South America does lie close to Antarctica, southward migration would still require that the pollutant traverse a significant tract of the Southern Ocean. In the case of Africa, the migration distance across water would be so significant, as to probably relegate the global distillation process to a minor role. Interestingly, Gioia et al., 2008 noted that PCB levels in the North Atlantic appeared to be governed primarily by transport from source regions, whereas corresponding levels in the South Atlantic seemed to
be driven by temperature changes via air–water exchange with the ocean. This would be in keeping with the overall observations above. Finally, evidence of pollutant migration throughout the African and South American continents would probably be blurred by the ongoing/recent use of organochlorine pesticides in some of the countries. The relative differences in pollutant transport by global distillation in the two hemispheres are highlighted in the accompanying figure (Figure 2).

2.3 Alternative explanations
Reference has already been made to the fact that global distillation may, in certain circumstances provide only a partial explanation for the observed long-range transport of pollutants (Dachs et al., 2002). von Waldow et al., 2010 proposed an alternative differential removal hypothesis, which proposes that fractionation results from different loss rates from the atmosphere, acting along a gradient of remoteness from emission sources. They successfully applied the associated model to explain the observed differences in PCB concentrations in European air, using data from an ongoing study in which transects from England to Norway are monitored. From their data analysis, the observed concentrations were better correlated with distance from the source than with temperature. It must be emphasized that these data pertain only to a relatively limited transect within the Northern Hemisphere. Moreover, the authors point to possible anomalies in data collection using semipermeable membrane devices as a source of error in some calculations. The failure of this study to find evidence in support of global distillation does not negate the concept overall. Various other examples have been given above in which global distillation was shown to be of secondary importance to other processes. The two processes (viz. global distillation and differential removal) may be seen as competing and further discussion of their relative importance in terms of climate change is provided below.
Although multiple hops are involved in the global distillation process of POPs (Wania, 2003), only one is shown in these diagrams for simplicity.

Fig. 2. Global Distillation Processes in Northern and Southern Hemispheres

3. Processes involved in global distillation

Wania (2003) divided pollutants into:
- ‘Fliers’ which are very volatile pollutants and unlikely to deposit even at the poles.
- ‘Single hoppers’ which are volatile enough to be carried all the way to the poles, where they will ultimately deposit by condensation.
- ‘Multiple hoppers’ which will be carried toward the poles by repeated evaporation and condensation cycles.
- ‘Swimmers’, which are non-volatile and will be transported via the oceans.

Of these four groups, it is the multiple hoppers that will be subject to transport by global distillation. This group includes the persistent organic pollutants, which are enumerated in the Table below (Table 1).

3.1 Basic underlying processes

The ability of a substance to undergo long range transport via global distillation will be governed by three factors:
1. Its ability to enter the air compartment by volatilization, if it is not emitted directly to air.
2. Its ability to remain stable during the transport process.
3. Its ability to deposit in the Arctic region.

Thus the main physicochemical parameters that govern global distillation will be the Henry’s Law coefficient (H), the octanol-air partition coefficient (K_{OA}) and the air-water partition coefficient (K_{AW}).
<table>
<thead>
<tr>
<th>Chemical</th>
<th>$\log K_{OA}$</th>
<th>$\log k_{AW}$</th>
<th>$H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin</td>
<td>4.44</td>
<td>-2.23$^{11}$</td>
<td>$7.0669 \times 10^{-3}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Chlordane</td>
<td>9.21 (cis)$^4$</td>
<td>2.31$^{12}$</td>
<td>$4.105 \times 10^{-3}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>p,p'-Dichlorodiphenyltrichloroethane (DDT)</td>
<td>10.08$^4$</td>
<td>-2.48$^{11}$</td>
<td>$2.232 \times 10^{-3}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>8.54</td>
<td>-3.56$^{11}$</td>
<td>$1.1099 \times 10^{-4}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Endrin</td>
<td>10.15$^5$</td>
<td>-4.66$^{12}$</td>
<td>$3.08 \times 10^{-4}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>6.12$^4$</td>
<td>-0.02</td>
<td>$4.47 \times 10^{-2}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Hexachlorobenzene (HCB)</td>
<td>7.56$^2$</td>
<td>-1.64$^{11}$</td>
<td>$3.61 \times 10^{-2}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Mirex</td>
<td>10.7$^{12}$</td>
<td>-5.42$^{12}$</td>
<td>$8.28 \times 10^{-3}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Polychlorinated biphenyls</td>
<td>7.01 -10.75$^2$</td>
<td>0.349 - (-5.08)$^{12}$</td>
<td>$3.3x10^{-4}$ - $5x10^{-5}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Polychlorinated dibenzo-p-dioxins</td>
<td>8.564 – 11.66$^2$</td>
<td>-5.02 (TCDD)$^{12}$</td>
<td>$1.47 \times 10^{-3}$ (TCDD)</td>
</tr>
<tr>
<td>Polychlorinated dibenzofurans</td>
<td>10.28$^1$</td>
<td>(-2.511) - (-5.47)$^{12}$</td>
<td>$8.1 \times 10^{-5}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Toxaphene</td>
<td>7.6$^{12}$</td>
<td>-1.16$^{12}$</td>
<td>$6.0 \times 10^{-6}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Alpha hexachlorocyclohexane</td>
<td>7.26$^3$</td>
<td>-3.51$^{11}$</td>
<td>$6.9 \times 10^{-6}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Beta hexachlorocyclohexane</td>
<td>8.13$^5$</td>
<td>-5.32$^{11}$</td>
<td>$2.35 \times 10^{-9}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Chlordene</td>
<td>8.92$^{12}$</td>
<td>-6.9$^6$</td>
<td>$2.53 \times 10^{-3}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Technical endosulfan and its related isomers</td>
<td>6.00 (α-endosulfan$^5$)</td>
<td>-2.72 (α-endosulfan$^{11}$)</td>
<td>1.06</td>
</tr>
<tr>
<td>Hexabromobiphenyl</td>
<td>13.6$^{12}$</td>
<td>-4.62$^6$</td>
<td>$1.38 \times 10^{-6}$ to $5.7 \times 10^{-3}$</td>
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<tr>
<td>Hexabromodiphenyl ether and heptabromodiphenyl ether (commercial octabromodiphenyl ether)</td>
<td>12.113 – 12.273$^2$</td>
<td>-4.29$^{12}$</td>
<td>$1.88 \times 10^{-7}$ – $7.48 \times 10^{-8}$ atm-m$^3$/mole</td>
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<tr>
<td>Lindane</td>
<td>8.04$^4$</td>
<td>-3.96$^6$</td>
<td>$6.1 \times 10^{-5}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>6.539$^{2, 3}$</td>
<td>-7.03$^4$</td>
<td>$7.03 \times 10^{-4}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride</td>
<td>6.5 – 7.5$^9$</td>
<td>$&lt;2 \times 10^{-6}$</td>
<td>$3.09 \times 10^{-9}$ atm-m$^3$/mole</td>
</tr>
<tr>
<td>Tetrabromodiphenyl ether and pentabromodiphenyl ether (commercial pentabromodiphenyl ether)</td>
<td>10.04 (TBDE)$^8$</td>
<td>-3.67$^8$</td>
<td>$1.18 \times 10^{-6}$ – $3.54 \times 10^{-6}$ atm-m$^3$/mole</td>
</tr>
</tbody>
</table>

1 As defined by the Stockholm Convention (http://chm.pops.int/Home/tabid/2121/Default.aspx); 2 Data from Li et al., 2006, all values for 20°C unless otherwise stated. 3 Data for 18.7°C. 4 Data from Harner and Bidleman, 1998 (all data for 20°C). 5 Data from Shoeib and Harner, 2002 (all data for 25°C). 6 Data from Scheringer et al., 2006. 7 Data for BDE-99. 8 Data from Wania et al., 2002 (all data for 20°C). 9 Data from Shoeib et al., 2002 (all data for 20°C). 10 Data from POPRC, 2007. 11 Data for 25°C 12 Calculated according to the method of Meylan and Howard (2005)

Table 1. Persistent Organic Pollutants

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Using the above modelling parameters, Wania (2003) developed an averaged global distribution model (the Globo-POP model) to predict both intermediate term (1 year ongoing emissions) and long term (10 year ongoing emissions) Arctic Contamination Potential (ACP). The ACP of most chemicals is sensitive to the temperature dependence of the partition coefficients, temperature, atmospheric mixing coefficients, and sea ice cover. The substances with significant ACP were in the range elevated ACP overlap in the range $6.5 < \log K_{OA} < 10$ and $-0.5 > \log K_{AW} > -3$, corresponding to chemicals that have significant ability to bioaccumulate. From the modelling, a parameter $m_{ACP}$, representing the potential for relative enrichment in the Arctic was developed.

\[
m_{ACP} = \frac{m_{T1} - m_{A1}}{m_{TG}} \times 100\% \tag{1}
\]

where $m_{T1}$ and $m_{A1}$ are the mass of chemical in all compartments and in the four atmospheric compartments of zone 1 (N-Polar) of the Globo-POP model, respectively. $m_{TG}$ is the mass of chemicals in all model compartments. Wania (2006) later added a parameter for estimating absolute contamination of the Arctic environment ($e_{ACP}$):

\[
e_{ACP} = \frac{m_{T1} - m_{A1}}{e_{TG}} \times 100\% \tag{2}
\]

where $e_{TG}$ is the mass of chemical emitted cumulatively to the global environment. $m_{TG}$ will always be smaller than $e_{TG}$ because of chemical losses by degradation and loss processes such as transfer to the deep sea, with subsequent loss to deeper sediment layers.

### 3.2 Atmospheric sorption

During transport, a persistent organic pollutant will always be subject to loss processes. These could include sorption onto particles with subsequent deposition, either by wet or dry deposition processes. Little is known of the relative importance of wet vs. dry deposition fluxes for persistent organic pollutants, although in a study of a number of sites in Canada, Yao et al. (2008) demonstrated that wet deposition was more important than dry deposition for most organochlorine pesticides. Clearly, there is a need for similar studies in other geographic regions. Moreover, it cannot be assumed that all scavenging will take place via rain, particularly in higher latitudes, where a significant amount of precipitation takes place via snowfall. Snow has been demonstrated to be a more efficient scavenger of airborne particulates than normal rainfall, probably largely because of the larger size and surface area of snowflakes. Franz and Eisenreich (1998) studied the scavenging of PCBs and PAHs by snow in Minnesota. Although anomalous, gas scavenging of the two pollutant classes was a relatively minor contributor to the overall snow removal flux. Particle scavenging ratios ranged from $5 \times 10^4$ to $5 \times 10^7$ for the snow events, as compared to $10^3$ to $10^5$ for rainfall events. Snow particle scavenging was slightly greater for the more volatile PCBs and PAHs. The authors hypothesized that lower molecular weight semi-volatile organic carbon compounds are associated with a different particle size spectrum than their less volatile counterparts.

The characteristics of air-particulate sorption for POPs are somewhat obscure and it is almost certain that the sorption characteristics of particulates from different sources will not be the same (cf. Gustafason and Dickhut, 1997). Once sorbed to a particle and carried to the earth by some form of deposition, a pollutant can be considered to have been removed from the global distillation process, at least temporarily (cf. Scheringer et al., 2000). Such removal is particularly significant in the case of persistent organic pollutants, as a result of their
ability to sorb to particulates. Removal of this kind does not preclude the pollutant from undergoing desorption and revolatilization at some later stage although it will cause a temporary disruption to the global transport process.

3.3 Atmospheric destruction

Atmospheric destruction of POPs is obviously another competing process and one with the potential to permanently remove the molecules from global transport processes. The mechanisms are generally less well understood than are those of destruction of volatile organics in air, but hydroxyl radicals, nitrate radicals, and ozone are believed to be involved (Boethling et al., 2009). The potential for POPs to associate with atmospheric particles provides a further complication, although there is some evidence to suggest that sorbed POPs may still be subject to oxidation processes. In the case of atmospheric ozone and hydroxyl radical destruction, the half life ($t_{\text{½}}$) of a persistent organic pollutant is given by:

$$t_{\text{½}} = 0.693k_{\text{Oxidant}}[\text{Oxidant}]$$

where $k_{\text{Oxidant}}$ is the rate constant in units of cm$^3$ molecule$^{-1}$ s$^{-1}$, and [Oxidant] is the oxidant concentration in units of molecules (or radicals) cm$^{-3}$. On a global basis, the situation is complicated by the fact that the concentration of these oxidants vary from place to place and also exhibit seasonal as well as diel variation.

3.4 Aquatic sorption

When considering atmospheric volatilization and deposition processes, it is important to appreciate that the situation over water will differ from that over land. Over the oceans, the operative processes will be diffusive air-water exchange, as well as exchange involving wet and dry particulates. In terms of deposition, the latter terms will equate to wet and dry deposition. These processes will also be operative in the case of terrestrial systems but the situation will be complicated by air-soil exchange and air-vegetation exchange. Under normal circumstances in the oceans, air-water exchange is likely to be the dominant process (Dachs et al., 2002). The air-water partition coefficient is related to the Henry’s Law Coefficient by the following equation:

$$\frac{1}{k_{\text{AW}}} = \frac{1}{k_A H'} + \frac{1}{k_W}$$

where $k_{\text{AW}}$ is the air-water partition coefficient, $k_A$ and $k_W$ are the POP mass transfer coefficients (m d$^{-1}$) in the air and water films, respectively and $H'$ is the temperature corrected and dimensionless Henry’s law Constant. $k_{\text{AW}}$ is known to be very sensitive to temperature, because of its dependence on the Henry’s Law Constant, but it can also be affected by a number of other environmental variables such as wind speed. Therefore, the latitudinal variation of $k_{\text{AW}}$ will also be a function of prevailing winds. The air-water flux for a persistent organic pollutant will be described by the equation:

$$F_{\text{aw}} = k_{\text{aw}} \left[ \frac{C_A}{H'} - C_W \right]$$

where $C_A$ and $C_W$ are the concentrations in the air and water phases respectively.
Once a persistent organic pollutant lands on the water surface, it is unlikely to dissolve because of its low inherent solubility. The pollutant will however be subject to processes of aquatic sorption by suspended particles, notably plankton. As with atmospheric deposition (considered above), the pollutant could theoretically later desorb and revolatilize. This is however less likely in the case of phytoplankton sorption, as the phytoplankton cell will eventually senesce and deposit in the benthic layer. Dachs et al., (2002) modelled the phytoplankton uptake flux ($F_{WP}$) according to the equation:

$$ F_{WP} = k_{WP} \left( C_W - \frac{k_{dep}}{k_{up}} C_P \right) $$

where $k_{WP}$ is the water-phytoplankton mass transfer rate constant, $k_{dep}$ and $k_{up}$ are the depuration and uptake rate constants respectively and $C_P$ is the concentration in the phytoplankton. The overall sinking flux for a POP, associated with phytoplankton ($F_{sink}$) could be calculated from:

$$ \log F_{sink} = 1.8 \times F_{OC} \times C_P $$

where $\log F_{OC} = 2.09 + 0.81 \log \text{[Chlorophyll]}$

The authors suggested that the process would be of major significance in regions of ocean upwelling, where nutrient rich waters are brought to the surface, resulting in high primary productivity. In the overall transfer of POPs from the atmosphere to benthic sediment, the rate limiting processes will either be air-water transfer rate or the sinking rate. With POPs of $\log K_{OW} < 6.0$, the sinking process will provide the rate determinant step in most cases, whereas for more lipophilic compounds, sinking fluxes are probably rate limiting at lower latitudes and air-water exchange at higher latitudes. These biogeochemical processes have the ability to disrupt global distillation processes over the oceans and as has already been mentioned, are probably important in terms of explaining the differences in global distillation between the northern and southern hemisphere. Supporting evidence in respect of the role of these plankton mediated biogeochemical controls in the Mediterranean Sea has recently been produced by Berrojalbiz et al., (2011).

4. Climate change scenarios

Since 1990, considerable attention has been paid to climate change on an international basis, largely through the efforts of the Intergovernmental Panel on Climate Change (IPCC). To date, four assessment reports have been published, the most recent being in 2007 (IPCC, 2007a; IPCC 2007b; IPCC 2007c) and a fifth assessment report is expected to be published in due course. However, the topic of pollutant behaviour in response to climate change remains under-investigated. By far the most detailed studies of pollutant behaviour in response to climate change are those of MacDonald (MacDonald et al., 2002, MacDonald et al., 2003) which pertain to the Canadian Arctic. Although the majority of attention has been devoted to effects in the Northern Hemisphere, a recent review has considered possible climate change effects on pollutant behaviour in the Southern Hemisphere (Sadler et al., 2011). Further studies of the effects of selected climate change phenomena on behaviour of certain persistent organic pollutants have been carried out by some authors (Dalla Vale et al., 2007; Lamon et al., 2009, Ma and Cao, 2010).
When considering effects of a phenomenon such as climate change upon a complex process such as global transport, it is necessary to conduct the assessment with reference to as many variables as possible if a true picture is to be obtained. In a number of studies that have been conducted to date, there has been a tendency to consider temperature as the major driver associated with climate change. This is clearly not the case (cf. IPCC 2007a, IPCC 2007b). Climate change can be considered to consist of the following manifestations:

- Increases in land, water and air temperatures
- Increases in the intensity of extreme weather events
- Changes in salinization patterns within the oceans
- Rises in sea levels

In respect of temperature changes, it must be noted that although it is the most frequently discussed aspect of climate change, current predictions of global temperature rise are well below 10°C in 100 years. Most of these projections constitute relatively small changes and are unlikely on their own to have a major effect on pollutant behaviour. It is our view that more significant effects on pollutant behaviour (including ones mediated by temperature) will be occasioned by the increased intensity of extreme weather events. IPCC predictions point to significant changes in the intensity of heatwaves, tropical storms (whose range may well extend into areas currently free of such events). Such events have the potential to cause far greater changes in environmental parameters, notably temperature albeit over a shorter period. Hence, the modelling of climate change mediated effects becomes a far more complex process.

Another frequently neglected aspect of climate change is its potential to alter physical conditions leading to changes in both production environments and also receiving environments. This may be reflected in a number of ways, including patterns of use. Persistent organic pollutants such as DDT have been banned in many countries and hence their evolution rates declined significantly in the recent past. But the effects of warming have seen the occurrence of diseases such as Malaria increase in geographical scope in some countries (notably Africa). This has occasioned a reintroduction of these pesticides and hence a potential for increased evolution rates (cf. WHO 2009). Equally, the warming effects associated with retreat of the polar ice caps and glaciers have major potential to alter the scenarios as regards persistent organic pollutant sorption. The air-ice interface has been recognized as a major site of sorption for these pollutants and loss of this interface will almost certainly lead to a remobilization of pollutants both from polar and high altitude regions. Thus, even if global/mountain transport processes continue to operate at their present or some altered rate, persistent organic pollutants delivered to these sites cannot be expected to remain in their traditional niches.

Intense extreme weather events also have the potential to cause a significant export of nutrients from land and offering the potential for increased primary productivity in the oceans (Sadler et al., 2011). As has already been pointed out above and will be discussed more fully below, this too has significant ability to affect global transport phenomena. Glacial melt can also make a significant similar contribution in this type of area, with the potential to also transport persistent organic pollutants released from the ice.

It follows from the foregoing remarks that a detailed consideration of the processes involved in global transport of pollutants is required if a meaningful assessment of climate change effects is to be made. Whilst temperature will be an important driver for all these processes, it or any other factor cannot be considered in isolation.
4.1 Effects on modelling parameters

As has already been outlined, the most simple parameters associated with global distillation modelling are the octanol-air partition coefficient, the air-water partition coefficient and the Henry’s Law Constant. The octanol-air partition coefficient is known to vary log-linearly with temperature. Shoeib and Harner (2002) measured octanol-air partition coefficients for a range of persistent organic pollutants, over the range 278-308°C and plotted the response as log \( K_{OA} \) vs 1000/T (°K). From their data, they concluded that it was possible to calculate the variation in log \( K_{OA} \) from a simple regression equation. Using this equation, the variation in log \( K_{OA} \) for a 5°C and a 10°C temperature change as associated with global warming scenarios has been calculated for a number of persistent organic pollutants and is shown in Table 2.

<table>
<thead>
<tr>
<th>POP</th>
<th>293°C (20°C)</th>
<th>298°C (25°C)</th>
<th>303°C (30°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCB</td>
<td>7.55</td>
<td>7.38</td>
<td>7.23</td>
</tr>
<tr>
<td>( \alpha )-HCH</td>
<td>7.80</td>
<td>7.61</td>
<td>7.43</td>
</tr>
<tr>
<td>( \gamma )-HCH</td>
<td>8.04</td>
<td>7.85</td>
<td>7.66</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>7.84</td>
<td>7.64</td>
<td>7.45</td>
</tr>
<tr>
<td>Aldrin</td>
<td>8.29</td>
<td>8.08</td>
<td>7.87</td>
</tr>
<tr>
<td>\textit{trans}-Chlordane</td>
<td>9.16</td>
<td>8.87</td>
<td>8.59</td>
</tr>
<tr>
<td>\textit{cis}-Chlordane</td>
<td>9.21</td>
<td>8.92</td>
<td>8.63</td>
</tr>
<tr>
<td>( \alpha )-Endosulfan</td>
<td>8.88</td>
<td>8.64</td>
<td>8.40</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>9.11</td>
<td>8.90</td>
<td>8.69</td>
</tr>
<tr>
<td>Endrin</td>
<td>8.38</td>
<td>8.13</td>
<td>7.89</td>
</tr>
<tr>
<td>( p, p )-DDT</td>
<td>10.08</td>
<td>9.82</td>
<td>9.56</td>
</tr>
</tbody>
</table>

1Data calculated using the regression equation of Shoeib and Harner 2002.

Table 2. Variation in log \( K_{OA} \) values for Temperature Rises associated with Global Warming

It is readily seen that the temperature rises associated with climate change (and the values given in the above table are on the extreme side of predictions) cause relatively small changes in the octanol-air partition coefficient. In general, rising temperatures will tend to decrease sorption of persistent organic pollutants on particulates. But it must be remembered that the changes referred to above are also well within the range of uncertainty associated with determinations of octanol-air partition coefficients and temperature. It must also be remembered that the majority of observations, linking \( K_{OA} \) to particle sorption pertain to urban situations (cf. Radonić et al., 2011). The nature of the particles with which persistent organic pollutants will interact in non-urban situations may be entirely different, particularly in a climate change scenario and the subject may warrant some further specific consideration. Predictions of climate change scenarios generally include an increased frequency of intense dust storms and although currently, the majority of pollutants appear to exist in the gaseous phase, there have been contrary reports from some agricultural areas (cf. Yao et al., 2008). There is a need to obtain more information on the partitioning behaviour of pesticides with dust derived from agricultural soils, which will almost certainly form the majority of climate change associated dust.

Although it is possible to make theoretical estimates of log \( K_{AW} \) (cf. Table 1, Meylan and Howard, 2005), in the actual environment a number of parameters are known to affect the actual value of this parameter. Temperature plays an important role in affecting \( K_{AW} \) but
the parameter is also subject to other influences, notably wind speed and various
diffusion/transport variables (cf. Dachs et al., 2002). Prediction of future wind speed
changes with current state of computer power remains a difficult task and thus a subject
of active research. While definite trend changes in severe cyclonic wind intensity and
frequency have not yet established, preliminary research results suggest that significant
alteration in cyclonic wind intensity and frequency are possible. In terms of non-cyclonic
wind intensity, there appears good evidence to suggest significant increases, based upon
modelling using the IPCC A1F1 scenario (temperature change +2.4-6.4°C, best estimate
+4°C, over the final decade of the 21st century vs. the final decade of the 20th century)
(CSIRO 2007).
In terms of equation 2, it can be shown that both $k_A$ and $k_w$ are sensitive to wind speed. The
equation is clearly sensitive to changes in Henry’s Law Coefficient, which is known to
respond to temperature (see below). Obviously, climate change scenarios would be expected
to involve changes of temperature. But even in the absence of any temperature effect, it can
be shown that a 5% increase in wind speed (considered an upper best estimate by CSIRO
(2007) for the next 50 years) can have a noticeable effect on the value of $k_{AW}$. Later in the 21st
century, there may be greater increases in wind speed, depending on the forcings operative
at the time.
That temperature has a major effect on the value of the Henry’s Law Coefficient has been
demonstrated both experimentally and by calculation (Staudinger and Roberts, 2001). The
variation of Henry’s Law Coefficient with temperature is given by:

$$H' = \frac{H'_{293}}{1 + \frac{\Delta H_0}{R T}}$$

where $H'_{293}$ is the value of $H'$ at a given temperature, $T$, $\Delta H_0$ is the enthalpy of phase change
(J mol$^{-1}$) and $R$ is the universal gas constant (8.314 J mol K$^{-1}$).

The variation of $H'$ with temperature is not uniform for all environmental contaminants. On
the basis of an extensive literature survey, Staudinger and Roberts (2001) estimated the
average % rise in Henry’s Law Constant/10°C to be 60% in the case of hydrocarbons, 90% in
the case of miscellaneous substances and 140% in the case of chlorinated organic pesticides
and PCBs. Unfortunately, insufficient data of this kind are currently available in the case of
the more recent additions to the list of persistent organic pollutants. Kühne et al., (2005)
suggested that temperature variation of Henry’s Law Coefficient is maximal for compounds
that are polar or have significant hydrogen bond interaction capacity. In this case, it could be
expected that the temperature variation of the more recent additions to the POPs register
would be significant.
The effect of a 5°C temperature rise on the temperature corrected Henry’s Law constant for
a number of persistent organic pollutants is shown in Table 3. These values were derived
using the USEPA’s on-line calculator (USEPA 1996).
Because of its effects on modelling parameters, notably $k_{AW}$, the temperature effect on the
Henry’s Law Constant is probably the largest single effect that climate change is likely to
exert. From the data presented above and Equation 4, it can be seen that the difference
caused by even a 5°C rise of temperature would have a significant effect on the Henry’s Law
constant and also on dependent parameters such as $k_{AW}$. Although the temperature effect is
the most prominent influence of all on the Henry’s Law Constant, a number of other climate
change factors have the ability to affect this parameter as well. These have recently been discussed (Sadler et al., 2011) and although their effects will probably be secondary to the temperature perturbations associated with climate change, they may be of significant in some instances. Of special relevance to climate change scenarios is the effect of suspended particles, which would tend to offset the temperature increases in the Henry’s Law Constant. These will be further discussed below.

<table>
<thead>
<tr>
<th>POP</th>
<th>H’ at 20°C</th>
<th>H’ at 25°C</th>
<th>Ratio of H’ at 25°C/H’ at 20°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCB</td>
<td>0.0310</td>
<td>0.0540</td>
<td>174</td>
</tr>
<tr>
<td>α-HCH</td>
<td>0.000241</td>
<td>0.000433</td>
<td>237</td>
</tr>
<tr>
<td>γ-HCH</td>
<td>0.000319</td>
<td>0.000572</td>
<td>179</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>0.0268</td>
<td>0.0446</td>
<td>166</td>
</tr>
<tr>
<td>Aldrin</td>
<td>0.00384</td>
<td>0.00695</td>
<td>181</td>
</tr>
<tr>
<td>α-Endosulfan</td>
<td>0.000261</td>
<td>0.000458</td>
<td>198</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>0.000312</td>
<td>0.000617</td>
<td>198</td>
</tr>
<tr>
<td>Endrin</td>
<td>0.000165</td>
<td>0.000307</td>
<td>186</td>
</tr>
<tr>
<td>p, p-DDT</td>
<td>0.000139</td>
<td>0.000331</td>
<td>238</td>
</tr>
</tbody>
</table>

1Data obtained using on-line calculator (USEPA, 1996)

Table 3. Variation in H’ values for a 5°C Temperature Rise associated with Global Warming

4.2 Modelling studies relating to effects of climate change on global transport

To date, only a few specific studies relating climate change to effects on global transport have been published, although it is possible to make extrapolations from other published work. Lamon et al., (2009) examined the effects of climate change on global levels of PCBs. Using two IPCC scenarios, they were able to demonstrate that increased temperature would probably be the major driver as regards climate change effects on PCB transport. Higher temperatures were considered to drive increased primary and secondary volatilization emissions of PCBs and enhance transport from temperate regions to the Arctic. The largest relative increase in concentrations of both PCBs in air was predicted to occur in the high Arctic and the remote Pacific Ocean. Higher wind speeds were predicted to result in more efficient intercontinental transport of PCB congeners.

Ma and Cao (2010) developed a perturbed air-surface coupled to simulate and predict perturbations of POPs concentrations in various environmental media under given climate change scenarios. Their studies pertained to α- and γ-HCHs, HCB, PCB-28 and -153. The HCHs, HCB and OCB 153, showed strong perturbations as regards emissions under climate change scenarios. The largest perturbation was found in the soil-air system for all these chemicals with the exception of α-HCH, which showed a stronger perturbation in the water-air system. The study also included terms for degradation, as would be operative under climate change scenarios. As would be expected, climate change also has a significant effect on the degradative pathways for pollutants, potentially undergoing global transport. The scenarios investigated resulted in a maximum 12% increase of HCB and a 10% increase of α-HCH levels in air during the first year of disturbed conditions. Following the increases during the first several years, the perturbed atmospheric concentrations tend to result in decreased air levels due to degradation processes. It is clear from this study that simple
modelling of global transport cannot be undertaken, without a proper consideration of all factors that might be affected by climate forcings. As has already been noted in this review, the so-called global distillation is only one pathway available for transport and fate of persistent organic pollutants. Its relative importance may well change under some climate change scenarios.

### 4.3 A possible role for phytoplankton

All of the above studies pertain to Northern Hemisphere situations. As has already been pointed out above, the role of deposition on the oceans provides an important sink for persistent organic pollutants and is likely to be operative particularly in the Southern Hemisphere (cf. Dachs et al. 2002). Jurado et al., (2004) noted the importance of phytoplankton, especially in areas of high primary productivity as regards controlling levels of PCBs in the oceans. They stressed the need for further research, particularly as regards seasonal influences on phytoplankton populations and the associated biogeochemical cycles. The effect of climate change on phytoplankton levels has been the subject of a number of papers in recent years (Hayes et al., 2005; Hallegraeff et al., 2009; Sadler et al., 2011). All of these studies have identified the need for intense ongoing monitoring. There is a general belief that the effects of climate change will see an increase in the frequency and intensity of blooms, an expansion of the geographical range and seasonal window for warm water species. The general concern expressed by these studies has been a possible increase in toxic algae and the attendant public health problems. But it is equally true that these projected increases could translate into increased sinking fluxes of persistent organic pollutants, deposited on the ocean surface.

In order to appreciate the magnitude of what phytoplankton blooms could achieve in terms of removal of persistent organic pollutants, it is necessary to consider the magnitude of the $F_{\text{sink}}$ term (Equation 7). Dachs et al., (2002) calculated sinking fluxes on the basis of chlorophyll levels in oceans, as recorded by satellite imaging. Although chlorophyll concentrations are a less than satisfactory indicator of algal biomass, under the circumstances, it must be conceded that this was probably the best available indicator.

Seasonal growth of algae represents what is probably the normal situation at present, but given the fact that blooms will become more frequent with climate change, it is important to examine the relative ability of such occurrences in terms of capturing persistent organic pollutants. For comparison, therefore, data on two *Trichodesmium* bloom events are included. This organism has been chosen because of its adaptive abilities (cf. Bell et al., 2005) which make it an ideal candidate to successfully proliferate under climate change conditions. As is shown in the table below, bloom situations could effectively remove four to six times as much persistent organic pollutant than the relatively static situation reported by Dachs et al., (2002). This means that the phytoplankton blooms which are expected to result from climate change, particularly in the Southern Hemisphere provide an important and hitherto neglected contribution to the overall observed global transport of pollutants.

The possibility also exists that in the Arctic Region, with the retreat of the Arctic ice cover, phytoplankton blooms will occur in the resulting ocean, providing a sink for released pollutants (see next section). There is already evidence of earlier algal blooms in the Arctic Region (Kahru et al., 2010) but although considerable effort has been devoted to effects of climate change on higher vertebrates in the Arctic, there remains a significant gap of knowledge with respect to dynamics of phytoplankton (Wassmann et al., 2011).
Table 4. Phytoplankton and Organic Carbon Sinking Fluxes

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Reference</th>
<th>No of Phytoplankton Cellsx 10^3 L^-1</th>
<th>[Chlorophyll] mg m^-3</th>
<th>FOC ( calculated from number of trichomes, assuming 100 cells per trichome)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ocean at 60-75 S</td>
<td>Dachs et al (2002)</td>
<td>-</td>
<td>0.1-18</td>
<td>21-1068</td>
</tr>
<tr>
<td>Trichodesmium bloom, Arabian Sea</td>
<td>Desa et al., 2005</td>
<td>690.9</td>
<td>126.75</td>
<td>6214</td>
</tr>
<tr>
<td>Trichodesmium bloom Moreton Bay, Queensland</td>
<td>Queensland Department of Environment and Resource Management, unpublished Data</td>
<td>500</td>
<td>87</td>
<td>4581</td>
</tr>
</tbody>
</table>

\[ \log \text{FOC} = 2.09 + 0.81 \log \text{[Chlorophyll]} \]

The end product of this type of pollutant sink will almost certainly be an increase in the levels of persistent organic pollutants in benthic communities. Results such as those obtained by Berrojalbiz et al., (2011) tend to highlight the importance of phytoplankton processes as sinks for persistent organic pollutants. With regard to climate change phenomena, a full discussion of causal factors for algal blooms is given elsewhere (Hayes et al., 2005; Hallegraeff et al., 2009; Sadler et al., 2011). It will be particularly important to pinpoint sites of upwellings. Upwellings are of two kinds:
1. Upwellings caused by trade winds.
2. Upwellings caused by extreme weather events such as cyclones (hurricanes, typhoons). Both types have the potential to be affected by climate change. Upwellings caused by trade winds are known to decrease during El Niño events and increase during La Niña events. With the expected accentuation of these events as a result of climate change (IPCC 2007a) it could be expected that changes in the intensity and patterns of these upwellings would be observed. Similarly, the expected increase in intensity of cyclones (hurricanes, typhoons) with climate change will have an influence on the second type of upwelling. It is significant that some surveys of POPs in ocean transects have shown increased levels in waters off the west coast of Africa – a major site for ocean upwellings (Gioia et al., 2008).

4.4 Fate of transported pollutants
It is established that both Arctic cold trapping and mountain cold trapping lead to an accumulation of pollutants in the coldest regions, although the actual pattern of pollutant retention is different (Daly and Wania, 2005). To date however, there seems to have been a tacit assumption that climate change has the potential to alter these transport processes, but that any pollutants reaching the usual site of accumulation will be retained in the normal manner. Such a view is clearly untenable, particularly in respect of the Arctic, where significant ice melt has already taken place. It is known that the air-ice interface provides a particularly strong site for sorption of persistent organic pollutants (Hoff et al., 1995) and hence some examination of the fate of cold trapped pollutants is warranted. In fact, regions of the Arctic are particularly sensitive to changes in temperature as the Greenland Ice Sheet is normally only very close to freezing point (Archer and Rahmstorf, 2010).
Daly and Wania (2005) noted that concentrations of persistent organic pollutants in air and water increased during periods of melt activity. More recently, Stocker et al., (2007) modelled the effect of snow and ice on distribution of semivolatile organic compounds, with
particular reference to long range transport. It was concluded that polar ice receives most chemicals from snow precipitation, although HCH and PBDEs are largely brought to the Arctic region in a particle-bound form. The polar ice caps serve to prevent air-water exchange of gaseous pollutants and the major removal pathway of pollutants in surface ice is via transport to lower layers of the ice cap. Because of its open nature, snow offers a greater potential for both diffusion and revolatilization than does ice in the polar regions. Therefore, the loss of ice from both polar and mountain regions has the potential to bring about a redistribution of pollutants already in this layer. It can be expected that the pollutants will largely move to the aquatic phase in the first instance, although more severe warming could lead to increases in the air phase as well. In the case of the Arctic, the pollutants released to the aquatic compartment will have a significantly higher potential to enter food webs. Pollutants entering mountain meltwater will be carried downstream and it is noteworthy that a number of major river-systems throughout the world have a glacial origin.

![Fig. 3. Global Transport Processes for POPs as modified by Climate Change](image)

### 5. Overall conclusions

The topic of global distillation has been reviewed with respect to both Northern and Southern Hemispheres. It appears that the global distillation phenomenon is best suited for operation in the Northern Hemisphere, although even here, it may be subject to significant competition from other processes. It is hypothesized that climate change will bring about significant interference with the operation of global distillation in both hemispheres. Although the increased temperatures associated with climate change have the potential to result in increased volatilization of persistent organic pollutants, the altered conditions may lead to increased losses of pollutants from the atmosphere through increased availability of hydroxyl radicals and other species active in the destruction of these substances in the
atmosphere. There will be decreases in snow and rain scavenging in many areas, as a result of changes in precipitation patterns and a higher probability of particulate sorption in the atmosphere. The increase in phytoplankton blooms that is predicted to accompany climate change will provide a significant sink for persistent organic pollutants. Finally, the loss of ice at the poles will result in a redistribution of pollutants that have already been transported there, or those which subsequently arrive as a result of long range transport. The accompanying figure (Figure 3) provides a summary of the expected effects of climate change on global transport of persistent organic pollutants.

6. References


Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.

How to reference

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