Universitat Politècnica de Catalunya
Programa de Doctorat de Ciències del Mar

MODELLING THE OCEAN-ATMOSPHERE EXCHANGES OF PERSISTENT ORGANIC POLLUTANTS (POPs)

Tesi Doctoral
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Para comerse un elefante,
mejor hacerlo a rodajas

proverbio aleman

"There is, in Earth System Science, a growing infatuation with ever more complex models. It's gotten to the point where some models look as inscrutable as nature itself. With numerous adjustable parameters, these models are generally unfalsifiable, so that the opportunity to learn from a wrong prediction is shortcircuited."
(Harte, 2002)

AGRAÏMENTS

És estrany ja estar en aquest pas….el temps ha passat volant! 4 anys d'evolució i aprenentatge, i un acaba sent una persona diferent a la que va començar. Més sàvia.

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Agraeixo als membres del tribunal per acceptar ser part d'ell.

Sento que moltes persones del IIQAB-CSIC m'han marcat al llarg d'aquests 4 anys molt més enllà d'una estèril relació laboral. Sé que en un moment de la nostra vida hem crescut junts. Un especial record per persones que ja han marxat com la Sara, el Tirso, i l'Albert, he trobat a faltar els nostres cafes i converses quan ja no hi eren. Em sento afortunada d'haber treballat al costat de persones com la Naiara (i la seva ironia fina i el respecte pel medi ambient), el Sabino (i la seva amabilitat…titi mucha suerte, ya queda poco!) i l'Anna (una serietat admirable, sobretot en termes professionals), tots 3 del meu grup de recerca; m'han ajudat a entendre petits misteris de la química experimental, a més de desenvolupar noves tècniques de cooperativa alimentària. També un gràcies a la Sandra Meijer i el Matteo Dalla Valle. Un agraiment a la Marina i a la Jelena, per compartir estones molt divertides i amor per *eu brasiu*, la Sandra per la seva empenta contagiosa, la Rikke, l'Alain, el punt masculí necessari entre tanta dona química. Un salut des d'aquestes paraules al Daniel (al mate imaginario que nunca conseguimos tomar jeje), al Roger, al Roberto, a la Gemma, l'Eric (…m'he

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Per acabar un somriure especial amb ulls brillants a l'homegat que se'm va ficar dins de l'ànima ja fa un bon temps.

ABSTRACT

Persistent organic pollutants (POPs), such as PCB, PCDD/FS and PAHs, are a group of chemicals targeted for reduction, or already banned, because of their persistence, potential for long-range transport and their ability to bioaccumulate in food-webs. Atmospheric transport and subsequent deposition has been described as the major process by which they impact remote oceanic areas. Additionally in the air-water interface, which accounts about the 70% of the Earth surface, take place many vital processes that determine the role of the oceans as a sink and as a reservoir of POPs. However the interpretation of these processes encounters difficulties because of the lack of measurements in the remote oceanic areas, and the lack of understanding of the dominant mechanisms at different spatial and temporal scales.

This PhD-thesis focuses on the modelling of the transfer processes of POPs between the atmosphere and the oceans at regional and global scales. Satellite derived data has been coupled with multimedia box-contaminant models of level I-III for the first time, yielding estimations in agreement within a factor of two with measurements, in most cases. Moreover, it is shown the noteworthy variability of atmospheric depositional fluxes and the importance of considering large biogeochemical processes in the oceans when evaluating the dynamics of POPs. Global estimations of the dominant atmospheric depositional, sinking and subduction fluxes have been also performed. It is seen that diffusive air-water exchange is the predominant route of introduction of contaminants to the oceans for POPs predominantly in the gaseous phase. However, dry and wet deposition become dominant in certain ocean regions and for compounds that sorb strongly to aerosols. Furthermore the developed methodology has also been implemented to estimate the atmosphere-ocean exchanges of total organic carbon. Surprisingly, these estimations point to high fluxes which could help to close the carbon budgets in the global carbon models.

The fate of contaminants on the short-time scale and once they enter the water column has been investigated by means of a 0-D dynamic model and a 1-D dynamic coupled contaminant-hydrodynamic model. It is stressed the role of sediments recycling contaminants and the atmospheric based fluxes. The influence of sediments is especially important for shallow water columns (< 20 m). The extent to which they diffuse in the water column is explained by the interplay between sinking and turbulent fluxes. In this thesis and for the first time a novel and comprehensive analysis of the vertical turbulence to the dynamics of POPs has been performed.

All these results have been published in scientific literature, are in press for publication or under review.

The studies presented in this thesis are part of the project AMIGOS (Algorithms, models and global integrations for the study of the ocean surface and their role in the global change) (REN2001-3462/CLI), and the European Community research project "Thresholds of Environmental Sustainability" (European Commission FP6, SUST-DEV, IP Project 003933-2) (http://www.thresholds-eu.org/).

RESUM

Els Contaminants Organic Persistents (COPs), tals com PCB, PCDD/FS i PAHs, són un grup de compostos químics regulats per a la seva reducció o ja prohibits a causa de la seva persistència, potencial per a ser transportat llargues distàncies i la capacitat de bioacumular en xarxes tròfiques. El transport atmosfèric i la posterior deposició s'han descrit com els processos claus pels quals impacten àrees oceàniques remotes. Així mateix, en la interfície atmòsfera-oceà, que correspon al 70% de la superfície de la Terra, tenen lloc molts processos vitals que determinen el paper dels oceans com a dipòsit i reservori de COPs. La interpretació d'aquests processos no és senzilla a causa de la manca de mesures en àrees remotes de l'oceà i el desconeixement dels mecanismes dominants a diferents escales espacials i temporals.

Aquesta tesi doctoral està centrada en la modelització dels processos de transferència de COPs entre l'atmòsfera i els oceans a escales regionals i globals. Per primera vegada, dades derivades de satèl·lits s'han acoblat amb models multimèdia de contaminants i de caixes de nivell I-III, donant lloc a estimacions d'acord amb un factor de dos amb les measures en molts dels casos. Així mateix, s'ha mostrat la variabilitat dels processos de deposició i la importància de considerar processos biogeoquímics a gran escala quan s'avalua la dinàmica dels COPs. Estimacions globals del procés de deposició atmosfèrica dominant, i fluxes d'enfonsament i subducció també s'han dut a terme. S'ha vist que la difusió aire-aigua és la ruta predominant de introducció de contaminants a oceans per a COPs predominantment en la fase gas. En canvi, la deposició seca i humida és dominant per certes regions i per a contaminants que tendeixen a sorbir-se fortament a aerosols. D'altra banda, la metodologia desenvolupada s'ha implementat per a estimar els bescanvis atmosfera-oceà de carboni orgànic total. Sorprenentment aquestes estimacions apunten a fluxes elevats que podrien ajudar a tancar els balanços globals de carboni.

El destí dels contaminants a curta escala i un cop han entrat a la columna d'aigua s'ha investigat mitjançant un model dinàmic 0-D i un model acoblat hidrodinàmic-contaminant 1-D. S'ha recalcat el paper dels sediments en el reciclatge de contaminants i dels fluxes atmosfèrics. Així mateix s'ha vist que la influència dels sediments és especialment important per a aigües poc profundes (< 20 m) i la profunditat a la qual difonen en la columna d'aigua s'explica amb la interacció entre fluxes turbulents i d'enfonsament. Així doncs, en aquesta tesi i per primera vegada s'ha dut a terme un analisi exhaustiu de la turbulència vertical en la dinàmica dels COPs

Tots aquests resultats es presenten en forma d'articles científics que han estat ja publicats o en procés de publicació.

Els estudis presentats en aquesta tesi formen part del projecte AMIGOS (Algoritmes, models i integracions globals per a l'estudi de la superfície de l'oceà i el seu paper en el Canvi Global (REN2001-3462/CLI), i el projecte de recerca de la Comunitat Europea "Thresholds of Environmental Sustainability" (European Commission FP6, SUST-DEV, IP Project 003933-2) (http://www.thresholds-eu.org/)

CONTENTS

1 INTRODUCTION

1.1 General characteristics of POPs

Persistent Organic Pollutants (POPs), also termed by Persistent Bioaccumulable Toxic chemicals (PBTs), are bioaccumulable compounds of prolonged environmental persistence and susceptible to long-range atmospheric transport (LRAT). They have been detected in all the environmental compartments, even in remote areas like open ocean and polar regions, where POPs have been never manufactured or used (Iwata et al., 1993; Schulz-Bull et al., 1998; MacDonald et al., 2000; Wagrowski and Hites, 2000). Indeed, atmospheric transport has been suggested as the main route dispersing these semivolatile compounds thousands of km away from industrialized and densely populated areas (Eisenreich and Strachan, 1992; Iwata et al., 1993; Halsall et al., 2001; Shatalov et al., 2003). Furthermore, once in the environment they do not degrade, instead they recycle and partition between the major environmental media, being an environmental concern since toxic effects do not disappear and the control is difficult (Jones and de Voogt, 1999). In addition, they have low aqueous but high lipid/organic solubilities which result in their bioaccumulation in lipid-rich tissues and in their biomagnification through foodchains (Skei et al., 2000; Baker, 2002). Even at low concentrations they are toxic to humans and wildlife, with suspected effects including carcinogenesis, immune dysfunction, neurobiological disorders and reproductive and endocrine disruption.

POPs comprise man-made organohalogenated compounds and other chemicals that can in part be biogenic such as polycyclic aromatic hydrocarbons (PAHs). Organohalogenated compounds include: i) pesticide POPs: aldrin, chlordane, DDT and its metabolites DDD and DDE, dieldrin, endrin, heptachlor, mirex and toxaphene; ii) industrially produced POPs: hexachlorobenzenes (HCBs), hexachlorocyclohexanes (HCHs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs); iii) POPs that are unintended byproducts: polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs). PCBs, PCDD/Fs and PAHs have been largely studied and their physico-chemical properties are relatively well defined. In particular, PCBs are (or have been) used as dielectric fluids in capacitors or transformers, in plasticizers, adhesives, inks, sealants and surface coatings. Their basic structure is a biphenyl with one to ten chlorine substituents and a general structure of $C_{12}H_{10-n}Cl_n$ (n=1-10) (Figure 1).

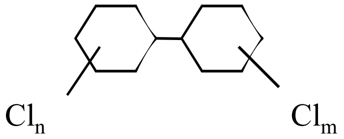

Figure 1 General molecular structures of PCBs

The 7 PCB congeners generally studied are PCB 28 (2,4,4'-triPCB), PCB 52 (2,2',5,5'-tetraCB), PCB 101 (2,2',4,5,5'-pentaCB), PCB 118 (2,3',4,4',5-heptaCB), PCB 138 (2,2',3,4,4',5-heptaCB), PCB 153 (2,2',4,4',5,5'-heptaCB), PCB 180 (2,2',3,4,4',5,5'-heptaCB), even though several dozens of them can be found in the environment. PCDD/Fs are released as by-products in a number of chemical, specially combustion, processes involving chlorine (waste incineration, chlorine bleaching of pulp and paper, manufacture of PVC, production of some pesticides, etc.). The basic structure comprises of two benzene rings joined either by a single (furan) or a double oxygen bride (dioxin). In Figure 2 is shown the 2,3,7,8-tetrachlorodibenzo-p-dioxin, the most toxic of the PCDD/Fs congeners.

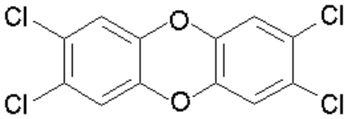

Figure 2 Structure of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)

It should be noted that the position of the number of chlorine atoms in the molecule is important for PCBs and PCDD/Fs toxicity. On the other hand, PAHs are compounds that consist of C and H atoms, grouped in the form of fused benzene rings. The PAH compound benzo(a)pyrene (Figure 3) is notable for being the first chemical carcinogen to be discovered. PAHs are formed by incomplete combustion of carbon-containing fuels and organic matter such as wood, coal, diesel, fat or tobacco and heavier congeners are more stable and more toxic than light ones. As well, as a general trend for PCBs. PCDD/Fs and PAHs, the increase of molecular weight is associated to a decrease of vapor pressure and solubility in water.

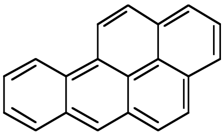

Figure 3 Structure of benzo(a)pyrene (BaP)

Man-made POPs started to be produced and used in the 1940s. The use of certain POPs in industry or as pesticides increased dramatically during the 1960s and 1970s. The first political regulations for the production and use of POPs date from the late 1970s. In 1995 UNEP Governing Council agreed on an international action plan to protect human health and the environment by the reduction or elimination of a list of 12 POPs, which lead to Stockholm Convention on Persistent Organic

Pollutants 2001 (http://www.pops.int/). The Stockholm Convention was the first global legally binding instrument of its kind with scientifically based criteria for potential POPs. Moreover, in 1998, under the auspices of the UN Economic Commission for Europe (UN/ECE), the Convention on Long-Range Transboundary Air Pollution (LRTAP) concluded negotiations for a protocol on 16 POPs in Aarhus (Denmark) (http://www.unece.org/env/lrtap/pops_h1.htm). The Parties committed to control, reduce or eliminate production and use of those pollutants and established criteria to propose new substances. In addition, the Oslo-Paris (OSPAR) Convention for the protection of the marine environment of the North-East Atlantic (http://www.ospar.org/) adopted a "Strategy with regard to Hazardous Substances" at Sintra in 1998 which aims at the cessation of discharges, emissions and losses of hazardous substances by 2020. On a European level it is noteworthy the EU Water Framework Directive (http://ec.europa.eu/environment/water/water-framework/index_en), established in 2000. Its objective is the protection of inland surface waters, coastal waters and groundwater and provides standards to establishing new hazardous chemicals by means of a prioritization mechanism. On the other hand, the European Commission has recently published a proposal for legislation concerning the Registration, Evaluation Authorisation of Chemicals (REACH) in which is developed the precautionary principle in the authorization and restriction in the use of hazardous substances.

The initial list of 12 POPs proposed in the Stokholm convention, the added under the Convention on Long-Range Transboundary Air Pollution and potential candidates are presented in the table below.

Banned substances in the Stockholm convention	**Banned substances in the LRTAP POPs protocol**	**Potential candidates[2]**	**Other dossiers in progress**
Aldrin	DDT	Hexachlorobutadiene (Netherlands)	Dicofol (Netherlands)
Chlordane	DDT in Dicofol	Pentabromodiphenyl ether (Finland/Sweden)	Short-chain Chlorinated parafins (Canada)
Toxaphene	Heptachlor	Pentachlorobenzene (Netherlands)	Pentachlorophenol (Poland)
Dieldrin	Lindane	Polychlorinated naphthalenes (Netherlands)	
Endrin	Polychlorinated Terphenyls (PCTs)		
Heptachlor	Ugilec		
Mirex			
PCBs			
HCBs			

PCDD/Fs
DDT[1]

[1] Severe restriction on use
[2] Rapporteur countries are given in brackets

Table 1 Priority and potential POP candidates

A large number of other chemicals exist, with comparable properties to the banned POPs. Thereby, an important aspect of the international protocols has been to establish scientific criteria for identifying additional POPs. The assessment of candidate POP chemicals for future additions in international protocols is based in a complex mixture of a number of criteria such as half life, bioconcentration, and potential for LRAT following guidelines as presented in Table 2, which is used by the United Nations Economic Commission for Europe (UN/ECE) working group in the identification and prioritization of POPs. However, as is noted later, broad guidelines as Table 2 should be used with caution.

Property	**Criteria for definition as POP**	
Potential for LRAT	Vapour pressure < 1000 Pa	and
	Half-life in air > 2 days	or
	Presence of the substance in remote regions	
Persistence	Half-life in water > 2 months	or
	Half-life in soil > 6 months	or
	Half-life in sediments > 6 months	
Bioaccumulation	logK_{OW} > 5 (K_{OW}: partition coefficient octanol-water)	or
	BCF > 5000 (BCF: Bioconcentration factor)	or
	evidence of high toxicity	

*LRAT: long range atmospheric transport

Table 2 UN/ECE criteria for identification of POPs (UN/ECE, 1998)

Equilibrium Partition coefficients such as the octanol-water K_{OW} and the bioconcentration factor BCF shown in Table 2 are explained in depth in the section 1.5.3. In short, K_{OW} of POPs refers to their hydrophobic and lipophilic nature, and the BCF refers to their tendency to bioaccumulate in the food-web. Conversely, the half-life, shown also in the previous table, gives insight into the time required to flush out the contaminant from an environmental compartment. It is not just related to the properties of the chemical, it also depends on the conditions of the surrounding media, the presence of other reactive compounds or the mode of entry of the compound in the compartment (Mackay, 2001). Indeed, using the half-life as an indicator of persistence (and of LRAT) and using a broad and simple classification as the one in Table 2 should be done with caution (OECD, 2004;

Klasmeier et al., 2006).

It is worth pointing out that LRAT and persistence cannot be measured properly by means of direct methods, as a result they have to be derived from models, as explained in detail in the section 1.4. Hence, multimedia models are the most appropriate way to assess the persistence and long-range atmospheric transport and to screen new chemicals. They have the advantage that they can consider the way of entry of the substance, partitioning properties and consider the hydrosphere, litosphere and biosphere as an integrated system. In this context, for example, there are some methods such as the internet-based "PBT Profiler" (http://www.pbtprofiler.net/) to provide screening level estimates of the Persistence-Bioaccumulation-Toxicity potential for organic substances. However it uses a simplified level III multimedia fugacity-based model.

1.2 Global occurrence of POPs

1.2.1 A global picture of POPs in the ocean-water system

The atmosphere is a critical compartment in the global distribution and cycling of POPs. As pointed before, atmospheric emissions and subsequent long-range transport provide a mechanism to distribute POPs widely through the global environment. Subsequently, atmospheric deposition of POPs may be the major process by which they impact remote oceans and other pristine environments (Bidleman, 1988; Iwata et al., 1993; Jeremiason et al., 1999; Blais et al., 2001). Oceans are also critical in the global cycling of those pollutants (Dachs et al., 2002b), their large volumes imply that they may represent an important inventory of POPs. Also the pathway air – deposition – water –phytoplankton – foodweb transfer – wildlife/human exposure is of key importance for these bioaccumulating compounds. Indeed studying the ocean-atmosphere exchanges of Persistent Organic Pollutants is fundamental. Figure 4 shows a diagram of the major processes affecting the transfers of POPs between the atmosphere and the ocean.

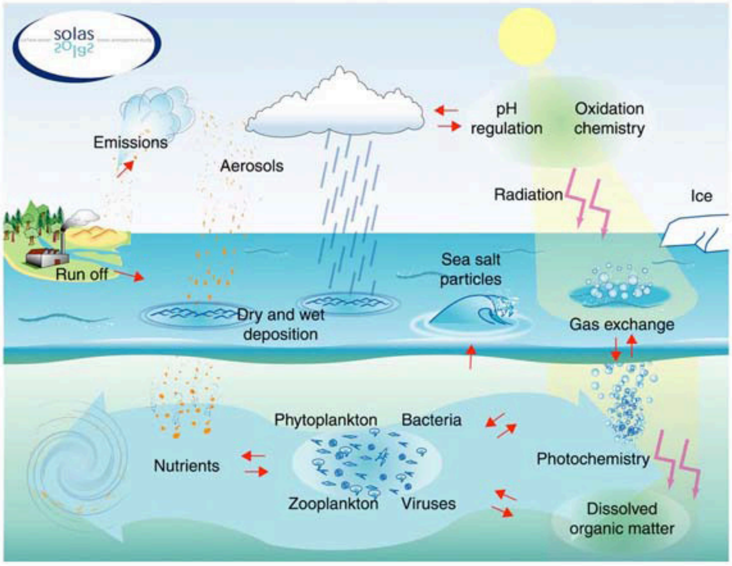

Figure 4 Major processes of POPs between atmosphere and water (adapted from SOLAS, 2004)

Summarizing, in the atmosphere POPs partition between the gas and aerosol phases and may then be removed by three main processes: dry deposition of particulate-bound pollutants, diffusive gas

exchange between the atmospheric and the surface ocean, and scavenging by rain (either from gas or particulate phases), the latter termed wet deposition. In the water column, POPs can be found either truly-dissolved, sorbed to colloids or sorbed to particles. They are affected by hydrodynamics of water masses such as turbulence and advection of water masses. Dissolved POPs can revolatilize back to the atmosphere. Furthermore, particle-bound compounds are subject to settling by gravity. Indeed, the oceans act as a source of POPs to the atmosphere, as a storage compartment or as a sink: sinks are in deep waters and sediments. In addition, sediments may exert an influence on the distribution of contaminants in the deeper water column through resuspension and diffusion from sediments porewater. The role of marine sediments should be accounted since they constitute an important inventory of POPs, favoured by their large organic-matter inventories (Jo_nsson et al., 2003). Furthermore, the influence of the sediments is noted on a major degree in coastal regions. There, the dynamics of contaminants are affected by the differential characteristics of coasts respect to the open sea, i.e. enhanced stratification due to freshwater input from rivers, influence of tides, greater human influence, enhanced interaction between the surface layer and the sea floor. Even though sediments are considered to be a long term storage compartment, there is no assessment of the capacity of the ocean as a contributor to the total inventory of POPs in the chemosphere.
Indeed an assessment of the ocean reservoir capacity has not yet been performed. The dominance of one or the other process at a global scale or the storage capacity of the surface ocean are poorly studied. It should be added the lack of knowledge of the role of the hydrodynamics of water masses to the distribution of POPs. On the other hand, the extent of the influence of the sediments in the water column and its relationship to other fluxes needs further research. A detailed examination of those processes is presented later, in chapter 1.5. What should be kept in mind here is that POPs are continuously seeking to equilibrate between the different reservoirs, therefore a permanent loss process of POPs occurring in any one reservoir will be reflected in the POP inventory of the others. It yields a global picture of POPs in the environment where they are continuously dynamically partitioning between the atmosphere-ocean-sediment/soil reservoirs.

1.2.2 Measurements of POPs in the environmental media

Sampling and analysis of POPs is time-consuming and expensive compared to many other contaminants, especially in the dissolved and gas phases and for the open ocean. It is noteworthy the scarcity of measurements, vertical profiles and time series of POPs in open ocean. The lack of data is a constraint when analyzing the distribution of POPs and when assessing the important processes that determine their fate. However, it is an incentive to develop models that help to predict and to understand their distribution.

A short summary of the occurrence and short-variability of contaminants in each medium is reported next. As pointed before, POPs are widespread in the environment. Generally the PAHs levels found in the environmental matrices are higher than the levels of PCBs and those higher than

PCDD/Fs. PCB air concentrations are in the pg m^{-3} to few ng m^{-3} range. Since they are dominated by secondary sources, i.e. not emitted directly, PCB concentrations in the atmosphere are mainly driven by temperature yielding higher gas-phase concentrations during warm periods (Brunciak et al., 2001; Van Drooge et al., 2002). This trend does not apply to PAHs, chemicals highly dominated by primary sources (Dachs et al., 2002a; Gigliotti et al., 2002). The short term variability in the atmosphere is major than in other environmental media and can be as high as a factor of 3-5 (Brunciak et al., 2001; Gigliotti et al., 2002). Reported concentrations in the oceans are lower (PCBs: at the pg L^{-1} level or even less). A considerable fraction of PCBs are sorbed to the suspended matter in the water column, and the vertical profiles exhibit a *surface enrichment - depth depleted – benthic layer enriched region* distribution with concentration maximums in phyto- and zooplankton zones (Schulz-Bull et al., 1988; Baker et al., 1991; Dachs et al., 1997a; Dachs et al., 1997b). Besides, data available on water column temporal variability is scarce and factors driving it largely unknown. Sediments and soils present raised amounts of POPs (Ockenden et al., 2003) and they remain relatively constant in these media on a long-term scale.

Spatial and long-term trends have been noted by monitoring networks of selected POPs, such as the Integrated Atmospheric Deposition Network (IADN) operating since 1990 in the Great Lakes (http://www.indiana.edu/~hiteslab/iadn/iadn.html) or the european EMEP database from ground stations (http://www.nilu.no/projects/ccc/emepdata.html). It has been noted a slight yearly decreasing trend, consistent with the introduction of regulatory restrictions on the use of these compounds and which agrees with studies elsewhere (MacDonald et al., 2000; Picer, 2000; Shatalov et al., 2003). However, this decrease may also be affected by improvements in analytical methodologies (Tolosa et al., 1997). On the other hand the IADN and EMEP monitoring networks have noted negative gradient of air concentrations away from the emission source and it agrees with the findings of lower reported concentrations in open-ocean than in the coast (Iwata et al., 1993; Tolosa et al., 1997; Lohmann et al., 2001; García-Flor et al., 2005). Additionally, samples from North-South latitudinal transects in the Atlantic (Baker and Hites, 1999; Lohmann et al., 2001; Jaward et al., 2004) have proven major concentrations in the Northern Hemisphere than in the Southern Hemisphere. This finding is reasonable as more than 80% of the industrialized regions act as sources for PCBs and PCDD/Fs are located in the Northern Hemisphere (Breivik et al., 2002). On the other hand, samples in background soils collected from a large number world-wide sites (Meijer et al., 2003; Ribes, 2003), have proven that soil PCBs are strongly influenced by proximity to source region and soil organic matter content. Finally, it should be noted again that monitoring networks in remote oceans are lacking. They are mostly found in ground or coastal sites. Since they involve large financial costs and it is unrealistic to assume that monitoring studies can cover the large number of POPs (and new appearing POPs) and geographic areas needed to assess the danger posed by these chemicals. Multimedia models are a more efficient way for doing this (Wania et al., 2006).

High concentrations of PCBs in the arctic wildlife and breast milk started to be reported in the late 1980s (Muir et al., 1988; Dewailly et al., 1989). It was of special concern not only because the finely balanced ecosystems in the Arctic and Antarctic, also because the distance from the sources that those pollutants were produced or used. Explaining such behaviour was decisive in the formulation of the "Global Fractionation" hypothesis, described next, and which has had a big impact on regulation and scientific community.

1.2.3 The Global Fractionation hypothesis

POPs tend to volatilize at rising ambient temperature rising and deposite as temperature declines. Hence, it has been proposed that on a regional or global scale, POPs can potentially migrate from warmer to colder areas and become "fractionated" on latitudinal or altitudinal gradients. This process has been named "Global Distillation", "Global Fractionation", "Cold Condensation" "Latitudinal Fractionation", "Selective Trapping" (Wania and Mackay, 1996). Hence, it results in the selective transport and enrichment of certain chemicals in cold environments with compounds that preferentially evaporate, thus having larger atmospheric mobility. Over the last 20 years there has been a significant interest in studying and testing this hypothesis of global fractionation (Bignert et al., 1998; Ockenden et al., 1998; Agrell et al., 1999; Grimalt et al., 2001; Wegmann et al., 2006). Meijer et al. (2003) who measured world-wide background soils didn't find clear evidence of cold condensation for PCBs, only in the samples north of 60ºN. It was suggested that it could be due to the fact that the lower latitude samples are more affected by local sources and by other removal processes not explained by temperature gradients. In addition it was found evidences that organic matter content in high-latitudes soils could explain better the latitudinal distribution. Simonich and Hites (1995) found increasing concentrations of the relatively volatile HCB and HCHs in tree bark with increasing latitude, whereas concentrations of the less volatile DDT do not correlate with latitude. Nevertheless, the cold condensation effect of substances at high latitudes is generally accepted, especially for terrestrial ecosystems. Therefore, POPs in the Northern polar environment is considered as "priority issue" by the Arctic Monitoring and Assessment Programme (AMAP, 1998, 2004, 2005).

The following figure shows a sketch of the movement of POPs by means of the "Global fractionation":

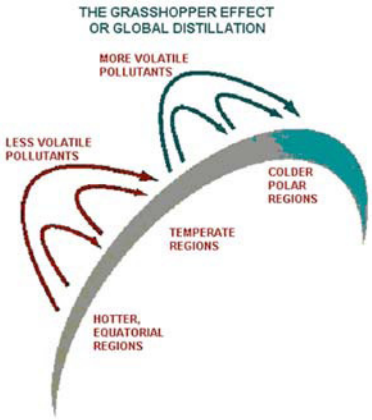

Figure 5 "Global Fractionation" hypothesis (Wania and Mackay 1996), from *Environment Canada*

1.2.4 Reality: away from the concept of "Global fractionation"

Obviously the analogy comparing the world with a chromatograph or a distiller, controlled by the temperature dependency of Henry's law constant alone, is a vast simplification of a very intricate set of processes. Certainly a chemical engineer's view of the earth ecosystem. For example in the real world input processes are much more complex and coupled with removal processes, which are not considered in the above paradigm. Furthermore, reality includes numerous processes that can deviate considerably from the chemical equilibrium, which is the assumption beneath the Global Fractionation Hypothesis. This is the case of sinking of particle-bound contaminants in the water column, wet and dry deposition, degradation processes, burial in sediments, etc. Indeed, a range of biogeophysical variables not considered traditionally such as the phytoplankton biomass, the extent of the Mixed Layer Depth, spatial and temporal differences in aerosol concentrations, ocean stratification, the turbulent diffusion coefficient, could also play an important role in the POPs dynamics in the oceans.

The work of Dachs et al. (1999; 2002b) proved the role of the phytoplankton uptake and settling of particulate matter as drivers of the oceanic sink of POPs such as polychlorinated biphenyls (PCBs) and dibenzo-*p*-dioxins and -furans (PCDD/Fs). Also it was suggested that the export to deep ocean affects the atmospheric residence time of POPs (Scheringer et al., 2004). Even though the modelling and measurements of POPs in settling particles is of great importance, it has not received much attention and measurements are still scarce. Other global studies have pointed to the significant role of wet atmospheric deposition, which may explain the altitudinal distribution of POPs in mountainous regions (Wegmann et al., 2006). Nevertheless, besides the role that organic matter/phytoplankton plays on the settling of POPs, no assessment exists of the potential influence of the spatial variability of other biogeophysical variables on the global distribution of those compounds. Also those variables are not generally accounted in multimedia models that explain the distribution of POPs to the global oceans, especially those that only account for fugacity driven processes. A different situation is found in models referred in terrestrial environments, where soil and vegetation organic matter, such as forested surfaces, have traditionally been considered (Eisenberg et al., 1998a; Wania and McLachlan, 2001). These studies have shown that terrestrial organic matter has an important influence on the dynamics and inventory of POPs.

1.3 Multimedia POP models

Concentration of POPs do show a significant spatial and temporal variability. However, there are few long-term data sets studies available for those compounds and a deficient understanding of the interactions of those chemicals with large scale biogeochemical processes. In addition, POP measurements lack sufficient geographical coverage, especially in the Southern Hemisphere remote oceans. Together, it yields to important gaps on the global distribution and on the dominant processes affecting POPs at large scales. Accounting their potential to travel considerable distances, it poses the need for developing global models to predict and understand their fate. On the other hand, global models can be used as a predictive tool: to estimate the persistence and potential for LRAT, and to screen and prioritize chemicals. On a more regional scale they can be give insights on the consistency of monitoring data or help to plan sampling campaigns.

Considerable advances have taken place in POPs multimedia model development over the last 10-15 years, among other reasons related to a major concern in contamination beyond political frontiers (Holloway et al., 2003). However, even if model complexity has increased in conjunction with improvements in computer architectures, some major essential features of these models have changed little. Most models are based on a mass balance approach, have a compartmental design and rely on similar empirical submodels to describe partitioning of chemicals between the different compartments. Multimedia POP models can be classified both in terms of model structure (from Level I to Level IV) and in terms of description of the environment (box models and chemistry transport models). Also one could distinguish between models of “real” and “evaluative” systems. In the first case there are data on chemical properties, inputs and concentrations in a well-identified region; in the second case the environment is fictitious, i.e. it does not correspond to a particular area but it is realistic. This latter approach is attractive for international regulation purposes because the assessment is not in a specific region, or for studying general trends of POPs.

The Levels I-IV of increasing structural complexity were suggested by Mackay (Mackay, 2001) and are summarized in Table 3. As one progresses from Level I to Level IV the fidelity of the calculation tends to increase at the cost of additional requirements for input data.

Type of compartment calculations	**Key assumptions**	**Information garnered**
Level I	• Equilibrium partitioning • Steady state • Closed system	Insights into the influence of chemical properties on environmental partitioning. Rapid assessment of the environmental media into which the chemical is likely to partition.

Level II	• Equilibrium partitioning • Steady state (can be extended to dynamic) • Open system	Relative importance of advection and degradation as removal pathways. Estimate overall persistence.
Level III	• Non-Equilibrium partitioning • Steady state • Open system	Influence of mode of emission on fate and transport. Refined assessment of overall persistence and loss pathways.
Level IV	• Non-Equilibrium partitioning • Dynamic • Open system	Time course of response of contaminant inventory to any time-varying conditions

*Steady-state: concentrations are constant with time, also referred to as a state of dynamic equilibrium where the rate of input equals the rate of removal

**Open system: includes advective inputs/outputs and degradation losses

Table 3 Summary of levels of structural complexity used to describe multimedia contaminants fate

It should be emphasized that equilibrium conditions establish the driving forces, since the system will always tend to move towards equilibrium. In a closed system the equilibrium conditions are easy to calculate and if such environment existed, it could eventually be reached. However, in open systems the equilibrium conditions may never meet everywhere in the system. More likely it will reach dynamic equilibrium, also referred to steady-state, or equilibrium conditions that will be broken by dissipative processes (non fugacity processes).

In terms of description of the environment multimedia models can broadly be classified between box models and chemistry transport models, as said before. The most fundamental assumption of box models is that well-mixed and interconnected compartments are used to represent the environmental media. The connected models can be set up as a series, a circular set, a two-dimensional network or using a nested configuration (Wania and Mackay, 1995; Scheringer, 1996). The term “compartment” refers to each phase in which the chemical may be present. It would correspond to Eulerian models, where the compartments are fixed in the space. A major utility of the box model approach is the application of the mass conservation principle in each compartment, i.e. dm/dt=input rate – output rate, where m is the mass in the compartment. A particular useful version applies when the inventory is fairly constant with time and thus dm/dt=0 and then the input rate equals the output rate. One method when writing mass balance equations is to use concentrations and a set of parameters, namely partition coefficients, transfer rates and degradation rates. This set-up is appropriate for non-polar organic chemicals, such as most POPs. It won’t be appropriate for chemicals that form different chemical species such as transformation products of the parent compound, the anions of acidic compounds or different form of metal complexes.

Another method when writing mass balances is to use fugacity as a surrogate for concentration. Fugacity is a criterion for equilibrium and it can be regarded as the “escaping tendency” of a chemical substance from a phase. It is essentially partial pressure in the case of a gas phase and it is assumed to be proportional to concentration. It was first applied by Mackay to environmental modelling (Mackay and Paterson, 1981), and it has been widely used after then. The advantage of fugacity is that in equilibrium between all the phases, the fugacities of the different phases are equal, and thus a single mass balance equation is written. Fugacity-based global models have been quite popular, especially during the end of the 90s. The simpler fugacity-based models assume chemical equilibrium between all media, whereas the more complex models allow for disequilibrium between media and may subdivide the environment into smaller compartments, thus introducing heterogeneity within a medium and reducing or eliminating assumptions of chemical equilibrium. However, level III-IV models usually require the consideration of non-fugacity processes.

Wania and Mackay introduced a multimedia global fugacity box model: the GloboPOP (Wania and Mackay, 1995), with nine connected climatic zones (see Figure 6A), Scheringer (1996) suggested a 1-D band around the globe with connected boxes (see Figure 6B). Other fugacity-based global models are the CliMoChem and ChemRange (Scheringer et al., 2000), and on a continental scale the BETR for North-America (MacLeod et al., 2001) and his European variant EVn-BETR (Prevedouros et al., 2004). Despite the simpler programming of fugacity-based models, their accuracy and reliability is questioned due to the intrinsic assumptions of equilibrium. Moreover, many of the originally developed fugacity-based models have evolved to complex multimedia dynamic models, as CoZMO-POP 2 (Wania et al., 2006). However, besides the conceptual simplicity relying in the fugacity approach, they are quite inscrutable and non-user friendly. In a more local basis, different interesting studies have used fugacity-box model approaches (Blais et al., 2001; Loizeau et al., 2001; Dalla Valle et al., 2003; Palm et al., 2004), and non-fugacity based dynamic box models (Farley et al., 1999; Dueri et al., 2005; Carafa et al., 2006). The major disadvantages of box models such as the fugacity-based presented before is the deficiencies in physical understanding of the system and a lack of information on contaminant distribution within the system limits.

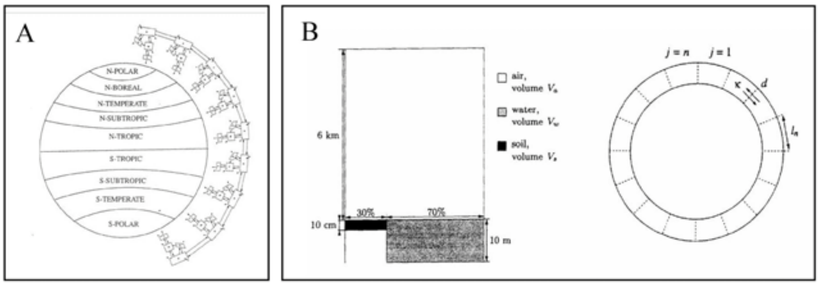

Figure 6 Global models by Wania and Mackay (1995) (A), in which “unit worlds” represent meridional segments arranged linearly; and global model by Scheringer (1996) (B) in which three-compartment “unit worlds” are arranged in a circular configuration.

An emerging area of research are the so-called chemistry global transport models, which estimate the spatio-temporal distribution of a contaminant combining emission data with global circulation models of the atmosphere and oceans. They are 3-D fully dynamic models. They can be seen as level IV models with a large number of boxes, based on the principle of conservation of mass and containing similar expressions for some mechanisms (e.g. gas/particle partitioning, atmospheric deposition, degradation). They do not apply fugacity equations to write mass balances. Examples of chemistry global transport models are the Danish Eulerian Hemispheric Model' (DEHM-POP) (Christensen, 1997; Hansen et al., 2004), initially developed for sulfur compounds, the global model developped by Lammel et al. (2001) and the MSCE–POP from EMEP (Shatalov et al., 2003; Malanichiev et al., 2006), among others. EUTREND (Van Jaarsveld et al., 1997), has been applied in the continental scale to model transport of γ-HCH and B(a)P (a PAH) in the European region, yielding results a factor of 3 lower than measurements in the case of levels of concentration in the precipitation. These models put a special emphasis on the atmospheric fate of the substance by including meteorological data at various locations (wind speed, temperature, precipitation, etc.). Compared to box models, chemistry transport models predict environmental concentrations with a higher spatial resolution and on shorter time scales, but have the drawback of requiring very high resolution input on emissions and other environmental parameters. They have, though, a poor understanding of the behaviour of pollutants in the water column, since they are more focused on estimate atmospheric dependent parameters such as the LRAT. To date, nearly no hydrodynamic models have been used to evaluate the distribution and transport of POPs. Besides MSCE-POP, which also includes hydrodynamic parameterizations, a pioneering work is the recently developed FANTOM model applied in the North-Sea and for γ-HCHs (Ilyna et al., 2006). However, a limitation of those models is the lack of an adequate coupling with ecological aquatic models. For example, in FANTOM is the omission of the colloidal phase to which contaminants can partition and use of a single partitioning coefficient to sorb to phytoplankton, bacteria, zooplankton and detritus.

Using a totally different method, inverse models have been used for compounds such as carbon monoxide, nitrogen dioxide, or methane using satellite measurements to provide the global coverage needed. Additionally atmospheric measurements of CO_2 fluxes have been combined with transport modelling to derive their surface fluxes (Fletcher et al., 2006). Inverse modelling can be viewed as simply the reverse of simulation or forward modelling. In simulation modelling the model is run forward in time from specified initial conditions and parameters. In inverse modelling, the observations are used to reconstruct the emissions necessary to account for current status or initial conditions of the parameters. Normally, inverse modelling is used because the emission inventories are often poorly known. However it requires a good knowledge of the spatial-temporal variability of the chemical, something that can be obtained for CO, CO_2 and other chemicals, but not for POPs. For relatively short-lived pollutants the inverse modelling technique has only limited use.

The choice of a suitable model essentially comes down to a matter of scales and applications. It is important to design the model according to the questions that one is trying to answer with the modelling work. A number of model inter-comparison studies have been published (AMAP Report 99:4 AMAP, 1999; OECD, 2002; OECD, 2004; Stroebe et al., 2004; Fenner et al., 2005; Hansen et al., 2006). For pollutants with atmospheric lifetimes larger than the order of a week it is recommended to use a global rather than regional or hemispheric models. On the other hand, semi-empirical models are preferred where necessary parameters cannot be adequately defined. Generally box models are well suited to modelling large areas over long time scales (hundreds to thousands of years), high resolution chemistry global transport models tend to be run over shorter periods (decades) due to computing power requirements. As pointed before, box models present the disadvantage of having a lack of information of the distribution of the contaminant within the system, and chemistry transport models require long computation times and are based on questionable emission inventories. Also in most of the chemistry transport models, a number of parameters are assumed to be constant (deposition velocities, washout ratios, etc.), which can be an important source of uncertainty. An optimum model would be the one that requires short computation time and yields high-resolution output data. This could be achieved for example using a box-modelling approach but with high-resolution real input data from satellites. However this approach is yet highly unexplored besides some pioneering studies of similar conceptual framework using spatially resolved data from geographical information system (GIS) data in regional areas (Coulibaly et al., 2004).

1.4 Measures of Persistence and Long-Range Atmospheric Transport

Persistence and long-range atmospheric transport (LRAT) are two essential properties for defining POPs. Their quantification cannot be done by direct methods and an accurate estimation is difficult due to the scarcity of concentration and emission data. For this reason global models as presented before are required.

It is surprising the amount of mathematical indicators that have been defined to quantify persistence and LRAT in multimedia models. A synthesis is presented next:

The *residence time* gives an indication of the average life expectancy of a pollutant in an environmental compartment, indeed it is an indicator of persistence and is best calculated at steady state. Using a mass balance approach it is the mass of chemical divided by the total rate of output (or input when steady state applies). When evaluating the residence time of a chemical in a single compartment which is affected by output fluxes such as diffusive transport to other media ($F_{transport}$=V C k_T), advective outflow ($F_{outflow}$=V C k_O) and degrading reactions (F_{degr}=V C k_{degr}), the formulation of the residence time (τ [T]) is:

$$\tau = \frac{\text{Inventory}}{\text{Output rate}} = \frac{m}{VC\left(k_T + k_O + k_{degr}\right)} = \frac{1}{k_T + k_O + k_{degr}} \qquad [1]$$

where k [T^{-1}] are the decay rates of each of the fluxes, V is the volume of the compartment, m the mass and C the concentration. As for most substances transformation rates follow the order: air >> water > sediment/soil, persistence is greatest for substances that predominantly reside in sediment and soil, which is the case for many hydrophobic POPs. It should be pointed that the consideration of a process as a loss processes depends on a number of factors and can be highly variable from model to model. For example some models consider loss processes other than reactions as irreversible losses, e.g. sediment burial or transport to the stratosphere. In a multimedia system, with multiple compartments, the overall residence time is a weighted average of the individual residence times, and the weighting is dependent on the mode of entry and the partitioning characteristics of the chemical.

Using a different approach Junge (1974) postulated that there is an inverse relationship between tropospheric residence time and variability in concentration of the concentration; bringing together field data he found an empirical relationship between residence time and standard spatial variation in concentration (RSD):

$$\tau = \frac{0.14}{RSD} \qquad [2]$$