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Persistent organic pollutants (POPs): state of the science

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Abstract

The environmental chemistry and ecotoxicology of persistent organic pollutants (POPs) are fascinating areas of scientific research. Our objective in this paper is to provide a brief, focussed overview of what constitutes a POP, highlight the harmful effects they may have on biota, make some comments on their environmental sources and analysis, their environmental trends and processes, their movement through foodchains and highlight some important regional-and global-scale environmental transport issues. Finally, we offer some personal thoughts on some current and future areas of scientific enquiry on POPs. © 1999 Elsevier Science Ltd. All rights reserved.

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1. What are Persistent Organic Pollutants (POPs) and their properties?

There are many thousands of POP chemicals, often coming from certain series or 'families' of chemicals (e.g there are theoretically 209 different polychlorinated biphenyls, differing from each other by level of chlorination and substitution position). POPs are persistent in the environment, having long half-lives in soils, sediments, air or biota. There seems to be no consensus of opinion about how long the half-life in a given media should be for the term 'persistent' to be conferred; however, in practice a POP could have a half-life of years or decades in soil/sediment and several days in the atmosphere.

A recent approach has considered defining 'persistence in the environment' operationally from a model-calculated overall residence time at steady state in a multimedia environment (Webster et al., 1998).

POPs are typically 'water-hating' and 'fat-loving' chemicals, i.e. hydrophobic and lipophilic. In aquatic systems and soils they partition strongly to solids, notably organic matter, avoiding the aqueous phase. They also partition into lipids in organisms rather than entering the aqueous milieu of cells and become stored in fatty tissue. This confers persistence on the chemical in biota since metabolism is slow and POPs may therefore accumulate in foodchains.

Importantly, POPs have the propensity to enter the gas phase under environmental temperatures. Hence, they may volatilise from soils, vegetation and water bodies into the atmosphere and—because of their resistance to breakdown reactions in air—travel long distances before being re-deposited. The cycle of volatilisation and deposition may be repeated many times, with the result that POPs could accumulate in an area far removed from where they were used or emitted. In the atmosphere itself, POPs can partition between particles and aerosols depending on ambient temperature and the physico-chemical properties of the chemical.

In summary, then, the combination of stability and propensity to form a gas under appropriate environmental conditions means that POPs are subject to long-range atmospheric transport (see later). The combination of resistance to metabolism and lipophilicity means that POPs will accumulate in foodchains.

Amongst the important classes of POP chemicals are many families of chlorinated (and brominated) aromatics, including polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and-furans (PCDD/

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Fs), polybrominated diphenyl ethers (PBDEs) and different organochlorine pesticides (eg. DDT and it's metabolites, toxaphene, chlordane, etc.) Some are accidental byproducts of combustion or the industrial synthesis of other chemicals (e.g. the PCDD/Fs) not produced deliberately. Many have been synthesised for industrial uses (eg. PCBs, chlorinated paraffins, PBDEs) or as agrochemicals (e.g. DDT, Lindane, chlordane). Examples of more polar POPs are phenols (e.g. polyethoxylated alkylphenols which are nonionic surfactants), and chlorinated phenols.

Certain key properties of chemicals control their fate in the environment and, if these are known, environmental chemists can make predictions about their fate and behaviour. These properties include aqueous solubility, vapour pressure, partition coefficients between water:solid (analogous to the measured octanol:water partition coefficient, K_{OW}) and air:solid or liquid (analogous to the measured octanol:air partition coefficient, K_{OA}; and Henry's law constants, K_{AW}), and half-lives in air, soil and water. These properties have been compiled for many POPs in various databases, e.g. those of Mackay and co-workers (Mackay et al. 1992) the United States Enviromental Protection Agency (US EPA) and the Dutch AQUAPOL system (Krop et al., 1995), either from direct measurements made in the laboratory or field, or calculated from theory. However, there are often wide variations in the values reported and their quality, conferring uncertainty on the precise behaviour of the POPs, and these databases are constantly being revised and improved.

2. Some comments on persistence

Given a defined rate of release of a chemical into the environment, concentrations in air, water and soil are controlled by various chemical properties, including its persistence, and properties of the environment. Persistent chemicals last longer in the environment. Two aspects of this need to be considered.

2.1. Persistent chemicals have higher concentrations

If emissions are more or less constant over a sufficiently long period of time, concentrations will build up to a steady state, where releases are balanced by losses. For extremely persistent chemicals decades are usually 'sufficiently long'. At steady state, the amounts present in the environment are inversely proportional to the overall transformation rate constant (proportional to the overall residence time and overall half-life) in the environment. The overall transformation rate constant in the environment is a composite of transformation rate constants for air, water, and soil, the weightings being dependent on the relative amount of chemical dispersed among these media.

2.2. Persistent chemicals are eliminated more slowly

If, after a certain period of use, emissions drop to near-zero, the amount of chemical in the environment will decrease exponentially. The rate of elimination is characterised by the overall transformation rate constant in the environment. Initially, this is the rate constant at steady state. As elimination proceeds, the relative amounts of chemical in air, water and soil will generally change. This will be more pronounced if the differences in transformation rates are great, intermedia mass transfer is slow, and significant amounts are present in a 'slow' compartment. As a result, the effective transformation rate constant will decrease with time. Generally, the time necessary for near-complete (e.g. 95%) elimination will be significantly longer than estimated on the basis of the initial overall rate constant at steady state (van de Meent et al., 1992; 1999).

3. What are the harmful effects of POPs?

Because POPs can bioaccumulate and magnify in the foodchain, concern centres around their impact on top predator species, including humans. Probably the best documented and clearest evidence of effects have been in birds and marine mammals. Indeed, Rachel Carson drew attention to declining bird populations in her classic book "*Silent Spring*" and this topic was addressed in the very first paper in *Environmental Pollution* in 1970 (Prest et al., 1970). Various papers have documented and reviewed how organochlorines (OCs), notably DDE—a metabolic breakdown product of DDT, can affect eggshell thickness in birds of prey (Ratcliffe, 1967, 1970; Pearce et al., 1979). These are amongst the classic ecotoxicological studies. Numerous subtle but far-reaching effects on the reproductive potential of fish-eating birds continue to be reported in the Great Lakes (Giesy et al., 1994) and in Europe (Bosveld and Van den Berg, 1994). It is re-assuring to see how, as POP residues have declined in certain top predators in certain areas, populations have increased again. Examples include harbour seals in the Southeast North Sea (Reijnders et al., 1997), white-tailed eagles in the Baltic and piscivorous birds in the Great Lakes (Munro et al., 1994). Reproductive impairment has also been shown for seals in the Baltic Sea (Bergman and Olsson, 1985) and the Dutch Wadden Sea (Reijnders, 1986) and for Beluga whales in the St. Lawrence seaway, Canada (Béland et al. 1993) and linked to POPs, principally PCBs. However, because an extensive array of POPs occur and accumulate simultaneously in biota it is very difficult to say conclusively that an effect is due to one particular chemical, a family of chemicals, their metabolites or indeed several families of chemicals acting synergistically. This makes control of the problem difficult, because scientists and policy makers have been unsure which POP(s) require restriction/regulation. POPs are also amongst the many chemicals implicated in the current concerns over 'sex hormone' *or* endocrine disruption in humans and wildlife (Harrison et al, 1995; Kelce et al. 1995; Kavlock et al., 1996). In addition to reproductive effects, many POPs are known or suspected carcinogens. Polynuclear aromatic hydrocarbons (PAHs) and PCDD/Fs are perhaps the most obvious examples. The health effects of PCDD/Fs have been the subject of a huge research and review effort, costing in excess of $1 billion, by the USEPA and various European government agencies. These compounds present particular challenges because they occur in mixtures and the 17 individual 2,3,7,8-substituted congeners act collectively on a range of biological end-points (Safe, 1994) and together with other compound classes (e.g. certain PCBs; polychlorinated naphthalenes, PCNs). These end-points include in vivo and in vitro effects. Current toxicological thinking is that the effects of these compounds are arylhydrocarbon receptor-mediated and additive, so that toxicity equivalent factors and concentration data should be combined to determine the total toxicity equivalent (ΣTEQ) loading present in the exposed tissue/target organism (Safe, 1994). These issues have led to a massive research effort from toxicologists over recent years, which will no doubt continue.

Purported POP effects also extend to damage to the immune system of top-predator species (Safe, 1994, Ross et al. 1995), enhancing their susceptibility to disease and effects on patterns of behaviour (De Swart et al, 1994; Leonards, 1997).

Clearly, the concerns over adverse health effects in humans and wildlife provide the impetus for research on their sources, environmental fate and foodchain transfer.

4. Sources, measurement and trends of POPs

4.1. Sources

For agrochemical POPs the source is clear—the deliberate application to crops and soils. However, despite their *deliberate* manufacture, data on the total amount entering the environment and regional/global usage patterns of agrochemical POPs is highly uncertain and often poorly known (Wania and Mackay, 1999).

Other POPs have been deliberately manufactured but have multiple diverse and diffuse uses. PCBs, for example, were first synthesised in the late 1920s and have been used in many tens of 'open' and 'closed' applications. It has been estimated that the global production since that time is of the order of 10^6 tonnes (de Voogt and Brinkman, 1989), but information on the breakdown of usage is very limited, making it very difficult to derive estimates for the historical and contemporary source term.

This issue is compounded in the case of *accidentally* formed and released POPs, such as PCDD/Fs. PCDD/Fs enter the environment from a whole host of combustion sources, from metal refining and as impurities in other, deliberately manufactured chlorinated compounds, such as pentachlorophenol (PCP) and PCBs. It is clearly of fundamental importance to identify the dominant sources to the environment, if source reduction measures are to be effective. National efforts have therefore been directed towards detailed PCDD/F source inventories. However, at the present time these are still highly uncertain, being difficult and costly to measure, highly variable from source to source and based on very limited information. At the present time, there is a lack of consensus on whether primary (combustion) or secondary (e.g. volatilisation from soil; chemical usage) sources dominate atmospheric emissions (e.g. Duarte-Davidson et al., 1997) and discrepancies between the national/regional emission and deposition estimates. An interesting approach in this case has been the use of 'fingerprint' techniques, looking at the characteristic mixture or pattern of PCDD/F compounds emitted from different types of source (Hagenmaier et al., 1994) and matching these to the typical mixture present in ambient air or soils (e.g. Evers et al., 1993; McDonald et al., 1998). To be effective, this required knowledge of their atmospheric/environmental processing and reactivity—an area of active research at the present time (Atkinson, 1996).

In summary then, reliable estimates of the historical/contemporary emissions/sources of POPs are very difficult (and in some cases, almost impossible) to achieve. They are, of course, of fundamental importance for effective source reduction measures and for national/regional/global environmental inventories, budgets and models. Quite basic information is sometimes still lacking; e.g. there is a lack of consensus at the present time over whether there are natural formation mechanisms for PCDD/Fs, giving rise to a pre-industrial environmental burden of the compounds (Alcock et al., 1998), or whether their occurrence in the contemporary environment results purely from industrial activities through this century (Alcock et al., 1999; Baker and Hites, 1999). This section highlights, then, that much research remains to be done in developing and refining our understanding and quantification of POPs sources.

4.2. Measurements

Environmental organic chemists now have incredibly sensitive and selective analytical methods at their disposal. To illustrate this point, PCDD/Fs are released into the environment in ultratrace amounts; their national atmospheric emission to the UK is only ~0.5 kg ΣTEQ annually. If this were dispersed evenly throughout the UK atmosphere (volume ~10^{14} m^3), air concentrations would be of the order of fg m^{-3}. Current high resolution gas chromatography–high resolution mass spectometry (HRGC–HRMS) techniques allow detection of a few fg on column. Consequently, if air samples of just ~500 m^3 are taken then a wide array of compounds can be detected. Sensitivity at this level can also give problems because samples can readily become contaminated by residues in glassware, solvents or laboratory air that come into contact with the sample. Modern methods of analysis benefit greatly from the availability of ^{13}C and deuterated (eg. for PAHs) analogues of the POPs, making possible precise and sensitive quantitation by isotope dilution—MS techniques.

Because of the great sensitivity of electron capture and MS detectors, POPs can now be routinely detected in the full array of environmental media at trace levels; they are ubiquitous in the modern environment even in areas far removed from sources. However, detection needs to be considered in the context of the amount emitted and the persistence of the POP; in other words, detection does not automatically signal that there is a 'POPs problem'. A couple of further points should be noted in this section. Firstly, instrument manufacturers have now found effective ways of coupling high pressure liquid chromatography (HPLC) with MS, opening up the possibility of very sensitive analysis of more polar, water soluble classes of chemicals for future research (Barcelo, 1996). Secondly, the sampling and analysis of POPs is time-consuming and expensive compared to many other contaminants. This has focussed efforts by some researchers into development and validation of models to predict residue concentrations, fate and behaviour (Wania and Mackay, 1999, this issue).

4.3. *Trends and environmental re-cycling of POPs*

As noted earlier, there are numerous types of POPs chemicals and it is therefore difficult to generalise as to their inputs and detailed behaviour in the environment. However, many classes of POPs are subject to a similar broad trend in usage/emission to the environment (e.g. PCBs, OC pesticides, chlorobenzenes). This is shown in Fig. 1(a) and basically consists of the following:

1. synthesis and development for use earlier in this century, e.g. in the 1930s/40s;
2. increasingly widespread use in Europe/North America and other industrialised regions through the 1950s and 1960s;
3. concerns over environmental persistence and foodchain accumulation in the late 1960s/early 1970s, resulting in restrictions in usage in Europe and North America; and
4. reductions in emissions in Europe, North America and other industrialised regions arising from the bans/controls in the 1970s through the 1980s and 1990s.

It should be noted, however, that this general pattern may be unrepresentative of the *global* emission profile when the chemical is used extensively outside of Europe and North America (i.e. in the tropics or following a global shift in the place of manufacture). For some 'newer' POPs a similar 'pattern' may have been observed, but have been more compressed in time. Examples are the brominated flame retardants, used extensively in insulating materials for electrical equipment (De Boer, 1989; Jansson et al. 1993; Pijnenburg et al., 1995), and the chlorinated benzyltoluenes used as PCB substitutes (Friege et al. 1989; Van Haelst et al. 1996; Wester and Van der Valk, 1990).

These trends in emission have had fundamental implications for concentration trends in air, soil, water and sediments and for the magnitude and direction of fluxes between these compartments for those POPs capable of dynamic, multimedia exchange. As Fig. 1(b) shows, a likely response to the emission phase represented in Fig. 1(a) has been deposition from the atmosphere to greatly exceed volatilisation to it in the 1940–60/70s and for the reverse to have applied in the more recent past. Fig. 1(c) therefore shows the hypothetical responses of the air and the soil compartments to the emission pulse. Air concentrations can be expected to respond rapidly to the increasing emission (1940–60s) and to reflect it. However, as the primary sources became controlled/reduced air concentrations initially reduced, but in more recent times may actually have been 'maintained' by volatilisation ('outgassing') of recyclable POPs from the terrestrial and aquatic compartments. The time over which they are maintained will be dependent on a number of factors, such as the size of the 'reservoir' of compound in the soil/sediment/water compartments, persistence in the soil/sediment compartments, physico-chemical properties of the compound and whether there is free exchange of the POP which has been deposited in the past (i.e. is adsorption/desorption of the POP completely reversible?; e.g. see Pignatello and Xing, 1996). For some POPs, which may have entered the soil or water body primarily associated with particulate deposition, outgassing will be limited and concentrations/burdens in these compartments will tend to remain high/increase [Fig. 1(c)]. For others, which readily enter the gas phase, outgassing will result in the soil/water body concentration/burden declining [Fig. 1(c)]. Research in the Great Lakes area provides powerful evidence for these long-term trends and reversals of the air-surface exchange flux (Swackhamer et al., 1988; Baker and Eisenreich, 1990; Jeremiason et al., 1994; Hornbuckle et al., 1995; Pearson et al., 1996; Honrath et al., 1997). Sediment cores show deposition of PCBs, DDT, toxaphene etc. to the lakes reflecting the hypothetical input curve of Fig. 1 (Beurskens et al., 1993), whilst mass balance calculations, analysis of paired air–water samples and monitoring of air

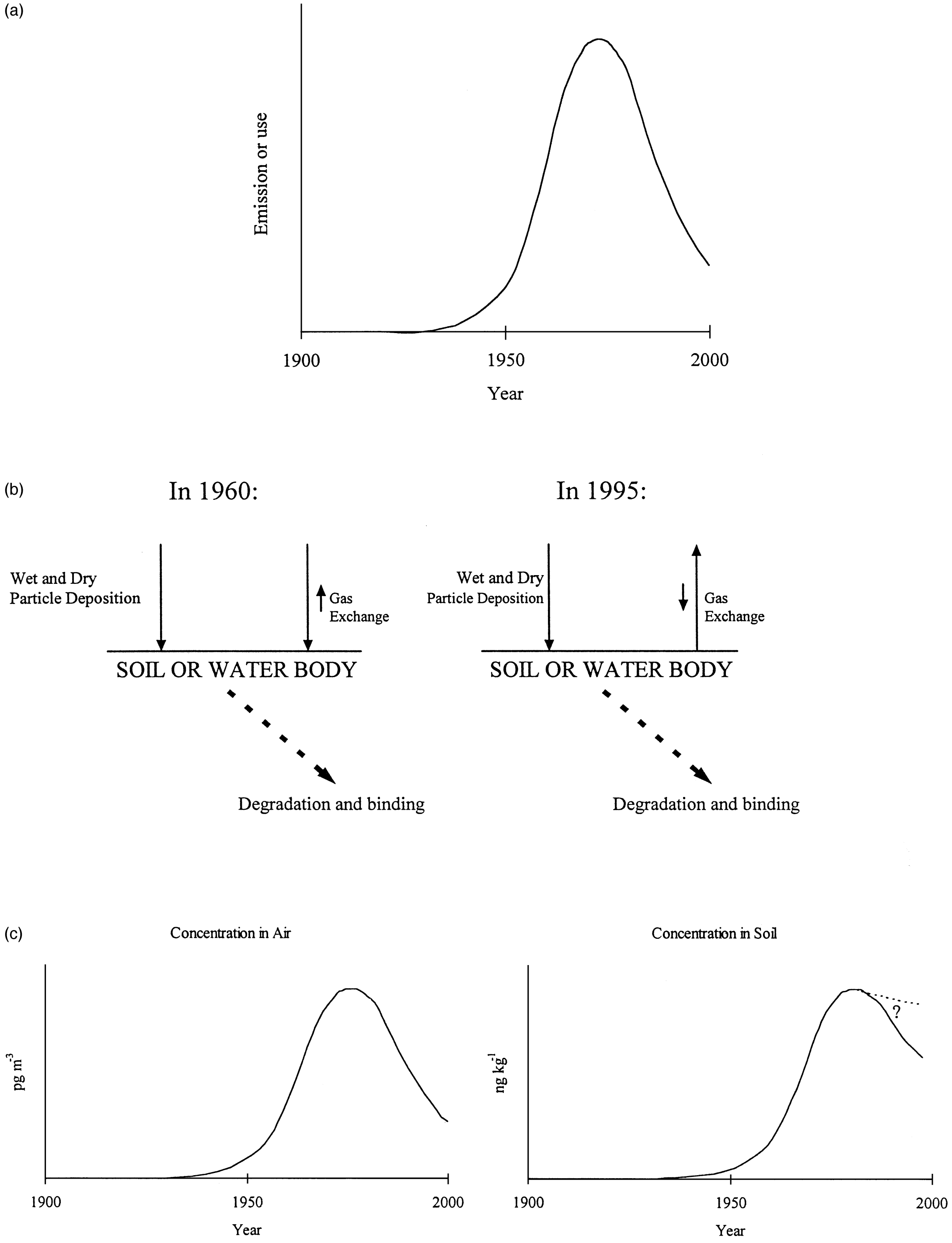

Fig. 1. (a) Typical persistent organic pollutants time trend, (b) air–soil exchange processes and (c) soil residues.

concentrations all provide evidence that volatilisation now exceeds deposition, i.e. the water bodies now act as sources to atmosphere, rather than as sinks. Historical reconstructions of soil and air concentrations for PCBs in the UK also suggest a reversal in the long-term net flux (Harner et al., 1995), as do studies on the air–sea exchange of hexachlorocyclohexane, (HCH) in the Canadian Arctic (Bidleman et al., 1995; Jantunen and Bidleman, 1995). Several researchers have shown atmospheric concentrations of re-cyclable POPs respond to seasonal or diurnal changes in temperature (Halsall et al., 1995; Hillery et al, 1997; Lee et al., 1998). When this happens, it suggests that the air concentration is 'controlled by' secondary re-cycling rather than fresh/ongoing primary emissions (e.g. as for PCBs and HCHs). In contrast, PCDD/F air concentrations are generally higher in the winter than the summer—probably indicating that primary combustion sources are still the principal source to air (see Lohmann and Jones, 1998, for a review).

Some key points from the above discussion are therefore:

1. primary and secondary sources may both be supplying POPs to the atmosphere;
2. dynamic temperature-controlled exchange of the POP can occur between gas and particle phases in the atmosphere;
3. dry gaseous, dry particulate and wet deposition processes deliver the POP to vegetation, soil and water bodies;
4. the rates of exchange and net flux across air–surface interfaces can vary spatially and temporally and with compound physico-chemical properties;
5. because POP chemicals 'have time' in the environment, they strive to approach multi media equilibrium status; and
6. net losses from the system can occur due to degradation/burial/occlusion in the soil/water body and atmospheric reactions (i.e. photolysis; OH radical reaction), shifting the air–surface equilibrium status.

5. POPs in soils and sediments

The bulk of the burden of POPs in the environment resides in soils and sediments where they primarily partition into organic matter. Small changes in the mass of soils/sediments would have a major impact on concentrations in 'adjacent' media, such as air or water. A number of processes influence POPs concentrations/burdens in soils and sediments, including biodegradation, volatilisation and 'ageing' effects which can produce less or non-extractable residues over time. Substantial research efforts have been and continue to be directed towards understanding these processes (Pignatello and Xing, 1996) and clearly the formation of 'bound' or non-extractable residues will remove the proportion of the POP available for environmental re-cycling and—potentially—for transfer into foodchains. Fig. 2 is a conceptual diagram of the possible 'forms' of a POP in the soil, illustrating the idea of changing proportions of readily extractable, poorly extractable and non-extractable fractions over time. The presence of a non-extractable residue, which may be the parent compound (as shown in Fig. 2) or a breakdown product, can be determined with a radiolabelled compound after sample oxidation. Alexander and co-workers drew attention to an extremely important observation, that compound bioavailability can decline during compound ageing (Hatzinger and Alexander, 1995). At the present time, numerous important papers are appearing in the literature applying techniques to investigate POP soil/sediment binding processes and mechanisms and bioavailability (Pignatello et al., 1993; Cornelissen et al., 1997), often motivated by the desire to enhance compound solubilisation, bioavailability and degradation for clean-up/remediation purposes (Luthy et al., 1997). However, relatively few are addressing: (1) how or whether enhanced biodegradation which can be induced under laboratory conditions can be achieved under field conditions with contaminated soils/sediments; and (2) whether techniques that encourage ageing and increased compound recalcitrance over time may actually be a more effective alternative to the treatment of contaminated sites, by lowering extractability and bioavailability over time.

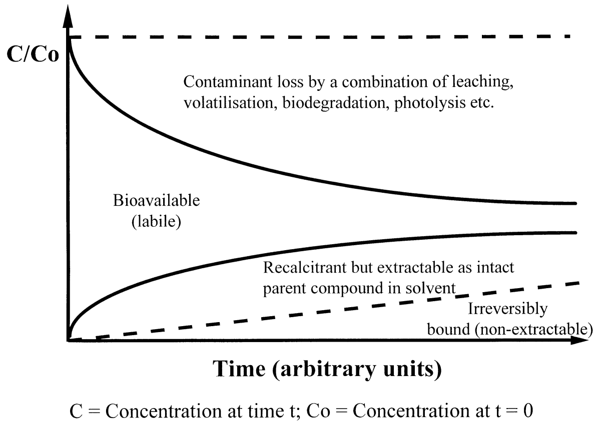

Fig. 2. Conceptual diagram of the possible forms of a persistent organic pollutant in soil or sediment. C, concentration at time *t*; Co, concentration at *t* = o.

5.1. Foodchain transfer

Because of their bioaccumulatory properties, the transfer of POPs through some foodchains has been quite thoroughly studied. The balance of this research has been on aquatic ecosystems, with research in the Great Lakes again to the fore, rather than terrestrial ecosystems. Work on the algae–plankton–fish–fish–birds pathway in the Great Lakes has been at the forefront in North America (Skoglund et al, 1996; Herbert et al., 1997). The recent developments in which the detailed dynamics and trophic status of ecosystems is characterised by stable isotope techniques and combined with POPs analysis has been particularly powerful (Kidd et al., 1998), allowing the development of a detailed understanding of the dynamics of transfer through a knowledge of 'who eats what' and modelling approaches. Campfens and Mackay (1997) illustrate the level of complexity now achieved in a foodchain model of Lake Ontario, for example.

Research on terrestrial ecosystems has focussed on a pathway of importance for human exposure: air–grass–grazing animals–milk/meat–human (McLachlan, 1996; Welsch-Pausch and McLachlan, 1998) and on some specific wildlife species of interest/concern. The approaches taken have largely focussed on PCBs, PCDD/Fs and OC pesticides, where the physico-chemical properties are relatively well defined, with a key objective being to investigate whether it is valid to assume equilibrium–partitioning between 'compartments'/foodchain components (Welsch-Pausch et al., 1995; Thomas et al., 1998), the dominant pathways of uptake (e.g. in fish, gill uptake versus dietary uptake, the principal deposition pathways to plants), the role of metabolism (Thomas et al., 1999) and the formation of stable intermediate by-products which may themselves be of toxicological concern (Kato et al., 1995; Letcher et al., 1998). Fig. 3 illustrates differences in the fluxes, pathways and susceptibility to metabolism of two PCB congeners in cows. Absorption efficiency across the gastro-intestinal tract has been the subject of attention in several species (e.g. earthworms, fish, cows, humans) as well as in laboratory studies with specific cell lines (Dulfer et al., 1998), with a common trend of absorption efficiency with increasing K_{OW} being noted in these disparate organisms (McLachlan, 1993). Because of their lipophilicity, the storage and release dynamics of POPs is intimately linked to that of fat storage and metabolism. In some organisms, such as lactating cows, for example, conditions approaching steady state may apply and a fairly constant flux of compound from feed through blood to milk being maintained and buffered slightly by the fat storage pool (Sweetman et al., 1999). In others, such as seals and other marine mammals and migrating birds and fish, there are dramatic changes in POP body burdens and dynamics over short periods of time as the body fat depot is re-mobilised (Abarnou et al., 1986; Borrell, 1993; Tanabe et al. 1994). Female grey seals, for example, can excrete around 15–20% of their body burden (which will have been accumulated over several years until they reach sexual maturity) in milk in the space of ~20 days (Green, 1997). This, of course, provides cross-generational transfer of POPs to the developing offspring and raises concerns over the potential impacts of large doses of POPs on the developing infant of humans and some wildlife species.

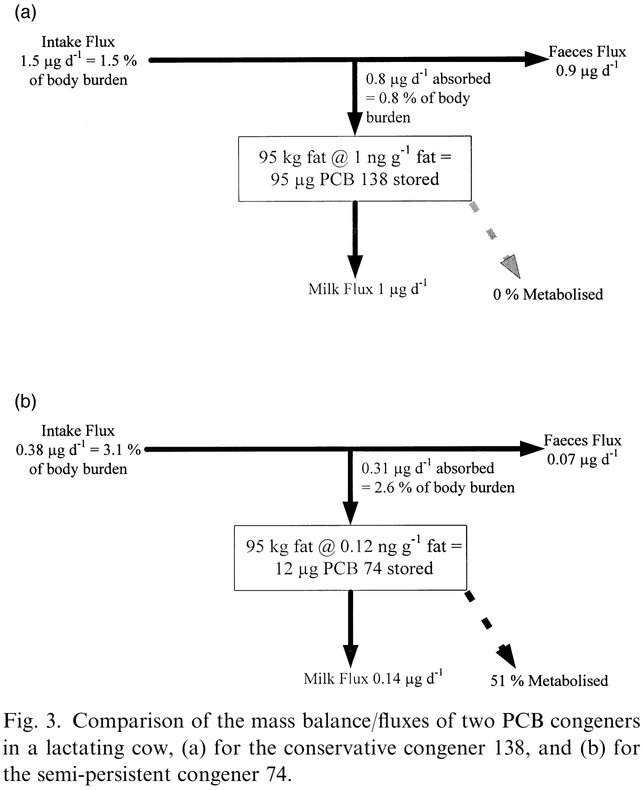

Fig. 3. Comparison of the mass balance/fluxes of two PCB congeners in a lactating cow, (a) for the conservative congener 138, and (b) for the semi-persistent congener 74.

In summary then, current knowledge of multimedia foodchain transfers has enabled some reasonably effective predictive models to be developed (Ludwig et al., 1993). These can be used in quantitative pathways analysis of human exposure/milk assessment (Theelen et al., 1993) and will be the subject of further refinements by researchers over the next few years. In some cases, regulatory agencies have set advisory limits on the body tissue concentrations or tolerable daily intakes of specific POPs (e.g. PCDD/Fs and PCBs). An output from foodchain transfer studies and models can therefore be the setting of 'consistent' foodstuff and abiotic media limits which would 'supply' that limit value to the target organism (Ludwig et al., 1993; Loonen et al., 1996).

5.2. Regional and global POPs cycling

As discussed earlier, air–surface exchange of POPs occurs in response to temperature changes. Persistent, semi-volatile compounds can participate in repeated air–surface exchange events and as a consequence, move from one area of the globe to another. Emission to air will tend to occur primarily in 'global source areas' where the POP is used or released. For example, DDT usage has been extensive through the tropics and the high temperatures there will mean greater volatilisation rates of DDT than somewhere cooler. Under cool conditions, gas phase POPs can partition back to the earth's surface, while in rainy areas wet deposition will deposit POPs to the surface. Rates of re-release from the surface will be slower in colder polar or high altitude regions. 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 (Wania and Mackay, 1993, 1995, 1996). Over the last few years there has been an increasing interest in studying and testing this hypothesis of 'global fractionation' or 'cold condensation' for POPs, with evidence steadily accumulating for its occurrence for selected compounds with a certain range of physico-chemical properties (Calamari et al., 1991; Wania and Mackay, 1996; Ockenden et al., 1998). Indeed, concern has been expressed that the polar regions will become 'global sinks' for POPs released/

used elsewhere on Earth. The Canadian Government has been funding research programmes on Arctic pollution, largely arising from concerns that native people living in the far north and dependent on animal fat-rich diets (i.e. marine mammal meat/blubber and fish and vulnerable top predator wildlife species, e.g. wolf, polar bear) are prone to particularly high POPs exposure (Canadian Arctic Contaminants Assessment Report, 1997).

Wania and Mackay (1996) predicted that compounds need to have properties in a certain narrow window to be susceptible to long-range transport and persistence to actually accumulate in the oceans and land surfaces of the poles. However, it should be appreciated that a complex array of processes operate at the global scale to affect the cycling and long-term fate of POPs (de Voogt and Jansson, 1993). Amongst these are:

1. 'atmospheric dilution', taking chemicals from source regions to 'clean' areas where these chemicals have not been widely used;
2. physical removal processes, such as burial in soils, peat bogs and sediments, which take a proportion of the global POPs inventory out of the 'pool' for re-cycling;
3. the physical occlusion and/or formation of bound residues in soils and sediments, as discussed earlier;
4. chemical reaction processes, notably reactions with atmospheric OH radicals (Atkinson, 1996), which will occur at different rates in different parts of the globe;
5. biologically mediated degradation in soils, sediments, the water column and the foodchain; and
6. rate-limitations on the air–surface exchange processes for some POPs.

These factors combine to reduce the threat of accumulation in the polar regions. Indeed the current (very limited) database suggests that whilst global fractionation is occuring, residues of many POPs are *declining* in polar regions, but at slower rates that in tropical and temperate latitudes. Much more research is required on these issues to fully elucidate the processes involved and to monitor trends. A particularly exciting development in this respect is the pioneering work of Bidleman and co-workers, deploying chiral compounds as 'markers' of the environmental re-cycling and selective degradation of POPs (Bidleman et al., 1998). Spatial and temporal trend data for the Arctic are also beginning to reach the literature (Canadian Arctic Contaminants Assessment Report, 1997).

Attention, then, is beginning to focus on constructing regional and global scale budgets, inventories and models for POPs (Cowan et al., 1996; van Pul et al., 1998). These are, of necessity, rather simplistic at present and have substantial gaps in information and data. Foremost amongst the deficiencies of current regional/global cycling models are:

1. poor or non-existent information on past/present regional usage/emission of many POPs;
2. a lack of understanding of how POPs cycle and become transported in the deep oceans;
3. uncertainties over the rates of atmospheric reactions for different POPs, at different heights in the atmosphere and with latitude;
4. uncertainties over the rates of biodegradation in real environmental settings; and
5. a lack of residue data in air, water, soil and sediments for huge areas of the globe, notably in Africa, Asia, the former Soviet Union and China, South America and the oceans.

6. Regional and global equilibration and clearance of POPs

As shown earlier in the paper, a 'pulse' of POPs has entered the global environment in recent decades. As discussed in the last section, this will slowly spread from the areas of use, undergoing reactions and removal from the cyclable pool and endeavouring to achieve equilibrium partitioning between compartments. A fascinating research issue at present are key questions such as:

1. how long will it take to approach 'global multimedia equilibrium' for a POP?;
2. is there evidence that steady state is being achieved for some POPs either regionally or globally?; and
3. if steady state is ever achieved, which global removal mechanisms will 'control' the ultimate global disappearance of the POP?

Unfortunately, there is a real dearth of good quality time trend data for POPs chemicals from different parts of the globe. However, some excellent multimedia datasets are available for biotic and abiotic media in the Great Lakes, and the UK, and a wide array of biota from the Baltic for ~1970–present. These are being compiled and studied together, to compare the rates of disappearance/clearance of POPs from these different environmental systems (Bignert et al., 1998). Fig. 4 illustrates the approach, which allows single, multimedia, regional or global clearance rates or half-lives to be derived. A fascinating observation of this approach are the rather similar trends noted for different media in different places over the same time intervals.

The global scale perspective to POPs research is a relatively new one, but brought into sharper focus by the recent adoption of the United Nations Economic Commission for Europe (UNECE) protocol in long-range transport of POPs air pollutants. Because of concerns over the transport to and potential impact of POPs on regions far from sources an international

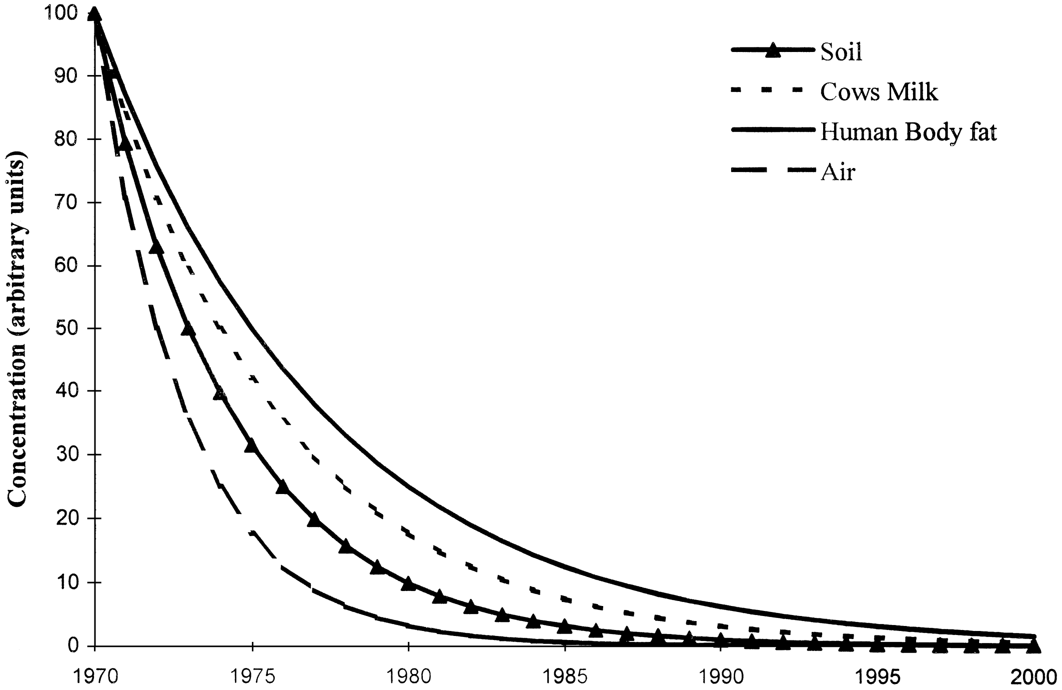

Fig. 4. Time trend/clearance curves for temperate latitude sites.

agreement has been reached to ban the use/emission of several classes of POPs chemicals; details are given in Table 1. This legal instrument also has provision for other substances to be added to the list, when a scientifically based case can be made for their inclusion.

Clearly, if global steady state is approached, ongoing reaction or removal mechanisms, such as atmospheric reactions with OH radicals, would shift the equilibrium partitioning status, resulting in replacement of the atmospheric POP burden from the surface stores. The atmospheric pool would presumably then be 'maintained' by outgassing from the earth's surface until either the rate of supply from the stocks of the POP held in the terrestrial or aquatic compartments became limited or ultimately exhausted. These issues are key to the future levels and trends of POPs in the environment and to understanding how long the globe may take to 'cleanse itself' of POPs. Studies using the fugacity concept or variants of it suggest that—whilst not yet achieved—air–surface equilibrium status may be beginning to be approached for the lighter POPs, such as HCH and HCB, and possibly even for the stock of PCBs which have escaped into the environment from past open uses (Ockenden et al., 1998).

Table 1
United Nations Economic Commission for Europe persistent organic pollutant

Substances scheduled for elimination[a]	
Aldrin	CAS: 309-00-2
Chlordane	CAS: 57-74-9
Chlordecome	CAS: 143-50-0
DDT	CAS: 50-29-3
Dieldrin	CAS: 60-57-1
Endrin	CAS: 72-20-8
Heptachlor	CAS: 76-44-8
Hexabromobiphenyl	CAS: 36355-01-8
Hexachlorobenzene	CAS: 118-74-1
Mirex	CAS: 2385-85-5
PCB	
Toxaphene	CAS: 8001-35-2
Substances scheduled for restriction	
DDT	CAS: 50-29-3
HCH	
PCB	CAS: 608-73-1
Substance scheduled for reduction to 1990 levels	
PAHS[b]	
Dioxins/furans	
Hexachlorobenzene	

[a] Source: Economic Commission for Europe, Executive Body for the Convention on Long-range Transboundary Air Pollution, Special session, Aarhus, Denmark, 24 June 1998, Item 3 of the provisional agenda.

[b] Benzo[a]pyrene; benzo[b]fluoranthene; benzo[k]fluoranthene; indeno[1,2,3-c,d]pyrene.

6.1. Molecular-scale POPs modelling and prediction

While it is evident that the models mentioned above need reliable compound properties and systematic input data, the availability of such data is rather limited. Experimental determination of all relevant compound properties is not feasible. Through an efficient use of available data, properties of unknown compounds may be predicted from known ones or may be derived from more basic, i.e. molecular (structure), properties. This area of research, referred to as quantitative structure–

activity relationships (QSARs), has gained enormous momentum through the improved calculation performances of modern computers. The classic example, originating from pharmacological research and drug design is the extrathermodynamic approach of Hansch et al. (1962), where compound activity (e.g. toxicity) is predicted from a (linear) combination of properties related to a compound's lipophilicity, electronic, and steric structure. Following this early work, a pivotal role has been given to the log K_{ow} in environmental chemistry to express a compound's lipophilicity and to explain or predict its multimedia partitioning, e.g. between sediment/water, biota/water and water/air. QSARs of good statistical quality for the prediction of key properties for the fate of lipophilic POPs have thus been obtained (e.g. bioconcentration factor: Hawker and Connell, 1988; Brunner et al., 1990; Henry's law constant: Dunnivant et al., 1992; Brusseau, 1993).

In recent years, there has been an obvious tendency for QSARs to become more mechanistically based, i.e. the selection of descriptors used in QSARs is derived from the known or assumed mechanism that is involved. Limiting steps in, for example, the partitioning process or the reaction kinetics can be expressed by using an appropriate descriptor pertaining to that particular step. Examples are the specific resistance the toxicant may experience when crossing a particular layer of a multilayered interface exchange model (e.g. seawater/air: Liss and Slater, 1974; or intestinal contents/blood: Dulfer et al., 1995), the membrane–toxicant interactions in narcotic toxicity of PAH (Kraak et al., 1997), and the specific interaction sites in biotransformation enzymes (de Groot et al., 1995). In particular, thermodynamic and quantum mechanic calculations at the electronic/molecular level can be used to predict certain bulk (molar) properties of chemicals (Karelson et al., 1996). Examples are the explanation of the curvature observed in log BCF versus log K_{ow} relationships for POPs from thermodynamic considerations (Govers et al. 1996), or the prediction of biotransformation products from stabilisation energies (de Groot et al., 1995).

As the need for reliable predictions from available compound properties will increase, the demand for data quality will also grow. Hence, criteria need be developed through which the quality of data, whether generated by experiments or by QSARs , can be judged objectively.

6.2. POPs research directions now and in the future

As we have tried to convey in this paper, the environmental chemistry and ecotoxicology of POPs is a fascinating, multi disciplinary, active and energetic area of scientific enquiry. We have tried to highlight key developments and the state of knowledge in this area, but conclude now with our thoughts on active areas of current and future research for the next few years:

1. improvements in the source inventories and refinements in pathways and exposure analyses, so that reliable, quantitative assessments can be undertaken;
2. more detailed, sophisticated and refined studies on the air–surface exchange of POPs, drawing on the considerable expertise of other research communities who have studied trace gas/particulates fluxes for other contaminants; a key aspect of this work will be improvements in understanding and use of chiral compound techniques;
3. global scale inventories, budgets and models, supplemented by a more comprehensive geographical coverage of chemical concentration and flux data;
4. increasing refinement and sophistication in the development of physico-chemical property-based models; this will be paralleled by improvements in the quality and reliability of the physico-chemical property databases for POPs;
5. studies on the form, bioavailability/sequestration and remediation of POPs in soils, sediments and groundwaters;
6. studies to further elucidate and quantify the subtle effects of POPs on humans and wildlife, including molecular modelling of biodegradation, transformation and toxicity mechanisms;
7. a shift from detailed studies on the more 'traditional' POPs (i.e. PCBs, PCDD/Fs) to metabolites and 'newer' classes of POPs (eg. PBDE, chlorinated paraffins, toxaphene) and perhaps more polar persistent compounds; and
8. further improvement of analytical methods to identify and quantify new or hitherto unknown POPs, notably metabolites, stereoisomers and more polar POPs.

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