PATHWAYS OF ORGANIC CHEMICAL CONTAMINATION IN ECOSYSTEMS

Padma T. Venkatraman
College of William and Mary, USA

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Summary

This chapter examines the fate, transport and degradation pathways of organic anthropogenic chemicals in ecosystems at different spatial scales, ranging from local to global with an emphasis on the use of molecular markers to study such pathways. Sources of pollutants, those that are likely to be of concern in the near future, predominant degradation pathways and how these affect different classes of pollutants is mentioned. The inter-relationships among the physical-chemical properties of compounds and mixtures, the biogeochemical environment into which they are released, and their resulting fate are also briefly discussed. The focus of the chapter, however, is recently developed geochemical tracer tools that allow us to track the pathways of contaminant fate and transport within and between ecosystems.

1. Introduction

Ever since Rachel Carson's book Silent Spring was published, there has been heightening awareness and concern about the persistence and biological effects of anthropogenic contaminants. Although industrialized nations have attempted to ban the use of some persistent and toxic pollutants within their own jurisdictions, many multi-national as well as local companies continue to manufacture them for use in less industrialized nations where such chemicals may still be used due to lack of education or conflicting economic and health interests. For example, in tropical nations, the adverse health conditions that may be caused by outbreaks of malaria or other diseases carried by mosquito vectors necessitate the use of the pesticide dichloro diphenyl trichloroethane (DDT), whose toxic effects and persistence are well known. Complete elimination of DDT will not be feasible until cheap but reliable options are developed for effective control of tropical diseases such as malaria.

Many classes of compounds including organochlorine pesticides such as DDT, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are considered persistent organic pollutants or POPs. These pollutants degrade relatively slowly under typical environmental conditions and hence are persistent in the environment. They generally undergo bioaccumulation and bioconcentration and exert various sublethal effects such as endocrine disruption, immunological and neurological dysfunctions, reduced reproductive success, genotoxicity and teratogenicity. Many are suspected or known carcinogens. POPs have been implicated in serious health effects on human children such as growth retardation.

In the mid nineteen eighties, the World Health Organization (WHO) estimated that the annual death toll due to direct or indirect effects associated with POPs. In the mid nineteen nineties, the United Nations Environmental Program (UNEP) called for international assessment of the "dirty dozen." Recently, an inter-governmental negotiating committee formulated a treaty on POPs, despite opposition from a coalition of certain industrialized nations that tried to label the text of the treaty "unscientific." This international treaty on POPs is now scheduled to be signed in May of the year two thousand and one, in Stockholm.

In light of the fact that POPs that have been used in great quantities all over the globe in the past and that some are still used in parts of the world today, it is important to develop techniques to quantify their fate and transport pathways. It is also necessary to develop tools that can track contaminant pathways of non-POPs, in order to better assess the risks they pose to different parts of the ecosystem under consideration. Such methods when used in conjunction with research on the manner in which physical and chemical properties of chemicals affect their environmental behavior, could help to identify undesirable and desirable characteristics of synthetic chemicals and thus become an invaluable guide to the design and manufacture of "green" chemicals in the future.

2. Sources and Input of Organic Pollutants to the Environment

2.1. Diffusive versus Point Sources

Sources of contaminants to the environment may be classified into two broad categories: diffusive and point sources. A pollutant is said to have a point source when its input into the environment is from a discrete unit. When a pollutant does not emanate from one or a few clearly distinguishable point sources, it may be considered to have a diffusive source.

Point sources are specific locations that may be pin-pointed as the source, for example a particular industrial plant that exclusively produces a certain chemical. If such a plant is the only one located in a certain region such as the bank of an estuary, for instance, and discharges wastes into this estuary, this plant can be located as the source of the chemical. Sewage out falls are another example of a point source.

Diffusive sources are sources that may not be clearly singled out or located on a map. Certain PAHs find their way into the atmosphere as a result of automobile exhaust, in which case they can be said to have a diffusive source because they are not entering into the environment from a discrete entity. Another good example of a diffusive source would be pollutants present in runoff. In general, a pollutant may be considered to have a diffusive source within a particular ecosystem or region when there is no one or small set of discrete locations such industrial out falls that can be pointed out as the primary source(s) for that particular chemical in the environment under study.

2.2. Important Classes of Organic Pollutants

PAHs are predominantly emitted into the atmosphere by the incomplete combustion of fossil fuels. Some PAHs also have natural sources (petroleum formation, seeps, etc.) PCBs are generally stable at high temperatures and thus used in transformers, capacitors and as flame retardants. PCDDs are by products produced during paper bleaching processes and hence they are often found in pulp and paper mill effluents. They were also by-products during the manufacture of Agent Orange. These chemicals are generally emitted into the atmosphere via waste incineration and other industrial activities.

Agrochemicals are another source of contaminants to the environment. Organochlorine pesticides such as lindane, α-hexachlorocyclohexane and DDT are used for mosquito and crop-related pest control in many countries. The high degree of chlorination of these pesticides rendered them relatively resistant to microbial attack and also tended to impart a broad spectrum of toxicity to these pesticides, rendering them dangerous not only to insects but also to higher animals including mammals such as humans. Newer generations of pesticides such as organophosphorus pesticides and acetamide pesticides are usually more specifically targeted in terms of mode of action, and often less persistent.

Organometallic compounds such as tributyl tin (TBT) were usually produced and added to paints in order to prevent bio-fouling of objects placed in or often in contact with water (such as piers, ships etc). TBT is highly toxic, and leaches into seawater, where it is known to bioaccumulate and cause a variety of undesirable effects on aquatic organisms (such as disruption of reproduction by causing imposex in bivalves).

Some of highly volatile pollutants are industrial solvents such as carbon tetrachloride, benzene. Trichloroethane, which is used as a dry cleaning fluid is also soluble and volatile. These pollutants often cause groundwater contamination and also reach aquatic and terrestrial bodies through air-water or air-land exchange processes. Chlorinated fluorocarbons such as freons that were used in refrigeration and as flame retardants are among the most volatile of anthropogenic pollutants.

Another important class of organic pollutants that has a unique set of chemical properties is that of surfactants, which are commonly used in detergents. These chemicals are amphilic i.e. they have a hydrophilic end as well as a hydrophobic functional group. This unique “dual” nature has implications for their fate and transport.

2.3. Degradable versus Persistent Pollutants

The distinction between degradable and persistent pollutants is somewhat arbitrary. In general a pollutant that tends to have residence times on the order of decades may be considered highly persistent, and one that degrades on the order of hours or days may be considered “degradable.” When laboratory studies claiming “degradability” are evaluated, it is extremely important to carefully compare the conditions under which the study was conducted with the conditions that will be faced by the pollutant in the environment, as persistence as well as toxicity may be affected by physico-chemical parameters of the environment as discussed in a following section. The notion of persistence must also take into account the chemical’s inherent properties. A chemical that may be mineralized by a laboratory culture of bacteria within a few days, may persist in the environment if it is highly volatile and thus is not retained for considerable periods of time by aquatic or terrestrial bodies in which such reactions take place.

2.4. Pollutants of Emerging Concern

It has been recognized for the past few decades that POPs are ubiquitous and worthy of study. However, some other pollutant classes have not been studied in as much detail.

Pollutants that may require attention in the future are surfactants and pharmaceuticals.

Recent work on surfactants such as nonylphenols has shown that these chemicals may cause endocrine disruption events. Since surfactants are present in soaps and detergents that are used as household products, they are likely to be present in high quantities in the environment.

Pharmaceuticals and their metabolites are also likely to be associated with high biological activity and may be present in the environment at concentrations high enough to cause action. Very little is known about the occurrence, distribution and pathways of these contaminants in terrestrial and aquatic ecosystems in most parts of the world. Research in this area is beginning to gain some importance on the American continent, and has been receiving attention in Europe. It is an area that requires investigation in the future.

2.5. Compounds and Mixtures

Although some sources of contaminants emit solely or predominantly one type of compound into the environment, contaminants usually find their way into the environment as mixtures. Creosote or coal tar distillate, for example, is a chemical mixture composed primarily of aromatic hydrocarbons.

Industrial formulations of pesticides are often mixtures of closely related chemicals. For instance, commercial formulations of chlordane and technical hexachlorocylcohexane contain mixtures of different isomers of chlordane and closely related compounds, such as cis-chlordane, trans-chlordane etc.) and hexachlorocyclohexanes (HCHs), such as α-, β-, γ-, and δ- HCH, respectively.

Mixtures may be composed of mainly one class of chemicals like the examples given above, or else may contain many different classes of compounds. Sewage wastes may include not only nutrients such as nitrogen and phosphorus that may result in eutrophication of aquatic ecosystems if the sewage is untreated, but also high concentrations of household chemical by-products (such as nonyl-phenols, which are endocrine disrupting pollutants found in detergents) as well as pharmaceutical wastes and toxic metabolites of pharmaceutical chemicals.

3. Transport Pathways within Ecosystems

The pathways available for transport of a pollutant within ecosystem compartments and between ecosystems depend on the mode by which a pollutant is discharged into the environment. For example, particles of soot that are first emitted into the atmosphere during incineration, may then undergo washout, rain out or precipitation out of the atmosphere and onto soils or water bodies. Transport pathways available to effluents include volatilization, sorption to particles in the water body, dissolution etc. The predominant mechanism of transport depends primarily on the chemical properties of the pollutant itself and on the physical, chemical and biological characteristics of the environment into which it is released. For a detailed discussion on the inter-relationships among various chemical properties and environmental processes, the reader is referred to the text by Schwarzenbach and others.

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Bibliography

Bidleman T. F., and Falconer R. L. (1999). Enantiomer ratios for apportioning two sources of chiral compounds. *Environ. Sci. Technol.* **33**, 2299-2301. [A short paper clearly explaining how to use ERs to evaluate environmental sources and processes].

Faller J., Huehnerfuss H., Koenig W. A., and Ludwig P. (1991). Do marine bacteria degrade alpha-hexachlorocyclohexane stereoselectively? *Environ. Sci. Technol.* 25, 676- 678. [A seminal paper on enantioselective separations of environmental compounds].

Hallig-Sørensen B., Nielsen S. N., Lanzky P. F., Ingerslev F., Lütshøft H. C. H., and Jørgensen S. E. (1998). Occurrence, fate and effects of pharmaceutical substances in the environment: a review. *Chemosphere* **36**, 357-393. [A review of pharmaceuticals as emerging environmental pollutants of concern].

Hoefs J. (1997). Stable Isotope Geochemistry. Springer-Verlag, New York. [This provides a thorough grounding in the basic concepts behind stable isotope techniques in environmental geochemistry].

Hühnerfuss H., Faller J., Kallenborn R., König W. A., Ludwig P., Pfaffenberger B., Oehme M., and Rimkus G. (1993). Enantioselective and nonenantioselective degradation of organic pollutants in the marine ecosystem. *Chirality* 5, 393-399. [A short review of enantiomeric ratios of eleven chiral environmental pollutants in different marine ecosystems].

Kurtz D. A., Ed. (1990). *Long-range transport of pesticides and other toxic substances*, Lewis, Chelsea, USA. [This contains many articles on various aspects of the global transport of POPs].

Lajtha K., and Michener R. H. (1994) *Stable isotopes in ecology and environmental science*. 316 pp. Blackwell Scientific Publications, Oxford, UK. [This contains articles on the use of stable isotopes to elucidate processes and distinguish sources in the environment and includes an excellent chapter by S. A. Macko about compound-specific stable isotope use].

Landers D.H., and Christie S. J., Eds.(1995) Special Issue: Ecological Effects of Arctic Airborne Contaminants. **160/161**, 870 pp. *Sci. Tot. Environ.* [This presents many interesting articles by scientists that have worked on various aspects of pollution in polar regions].

Schwarzenbach, R. P., Gschwend, P. M. and Imboden, D.M. (1993). *Environmental organic chemistry*, 681 pp. John Wiley & Sons, Inc., New York. [A clear and comprehensive assessment of the relationship among various environmental factors, chemical properties and the fate and transport pathways of contaminants in different ecosystems and ecosystem components].

Wanda, F.W. and Mackay, D. (1996). Tracking the distribution of persistent organic pollutants. *Environ. Sci. Technol.* **30**, 390A-396A. [A short and thorough analysis of existing data in support of the global distillation hypothesis, along with an explanation of a theoretical model of the process and recommendations to managers and policy makers].

Biographical Sketch

Padma T. Venkatraman completed her master's research on the toxicity and environmental fractionation of polycylic aromatic hydrocarbons present in creosote at the College of William and Mary. She then worked on polychlorinated biphenyls in water, sediments and biota in the Baltic Sea. She has also worked on nonylphenols. She has also conducted some research on the potential use of stable isotopes as tracing tools for contaminant transport. Her currently research focuses on the fate and transport of chiral pollutants in estuarine ecosystems.