Chapter 1
Significance of Photo-degradation in Environmental Risk Assessment

1
Introduction

Photo-degradation (or transformation) occurs under the influence of solar radiation mainly in the atmosphere, and to a lesser extent in the hydrosphere and on soil surfaces. New developments in environmental risk assessment have given photo-degradation new significance, which will be described in this introduction. The data collected in this book refer to gas-phase photo-degradation in the atmosphere, and so does this introduction. Photo degradability is an intrinsic property of a chemical substance and must be measured. Quantitative structure activity relationships (QSARs) for estimating gas-phase rate constants of the indirect photo-degradation of organic chemicals are available and will be discussed in Section 5. Reactive species, which degrade a chemical substance in the atmosphere, are the hydroxyl radical, ozone and the nitrate radical. As these species are produced via solar radiation, this mechanism of degradation is known as “indirect”, in order to distinguish it from the direct photolysis by solar radiation.

Photochemistry is a discipline within physical chemistry, and more specifically, atmospheric chemistry that is dealt with in the text books by Finlayson-Pitts and Pitts [1, 2]. Photo-degradation of organic substances is the subject of Chapter 2. The subject of interest to environmental chemists and administrators is the capacity of solar radiation to degrade, destroy and finally eliminate man-made chemical substances from the atmosphere. Atmospheric distribution of a chemical substance is critical because it can potentially lead to world-wide dissemination, if it is long-lived (persistent) and not destroyed. If this elimination mechanism did not occur, mankind would have suffered from severe air pollution and respiratory health problems, which are still the case in urban agglomerations as a result of air pollution, where the atmospheric elimination processes are not sufficiently efficient.

In the early 1980s Atkinson [3] and Becker et al. [4] began the systematic testing of volatile organic substances on gas-phase photo-degradation with the hydroxyl radical. At the time that the regulation of chemicals was drawn up,

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"photo-degradation" under the term of "abiotic degradation" was not considered important. Photo-degradation was not part of the OECD pre-minimum set of data in the assessment of chemicals [5], which was the example for the European legislation in the 6th Amendment of the 67/548/EEC Directive (1979).

This book, with the data collected in it, underlines the role of photo degradability as one of the important intrinsic properties that steers the atmospheric fate of chemicals and thereby contributes to "persistence" and "long-range transport potential". With the acceptance of multimedia environmental fate models in legal exposure assessment, photo degradability underwent a renaissance of importance as shown below.

2

Persistence and Long-range Transport Potential in Chemicals Regulation

Environmental persistence of organic substances was heralded by two publications that shook the scientific community as well as the politicians: Rachel Carson's *Silent Spring* [6] in 1962, and the discovery by Rowland and Molina [7] in 1975 that fluorochlorocarbons are stable (persistent) molecules in the troposphere (the lower 10 to 15 km of the atmosphere) and may deplete the ozone in the next layer of the atmosphere, the stratosphere. Persistence implies the absence of chemical, biological and physical degradation processes in the environment so that organic molecules, once emitted from the technosphere by anthropogenic activity, remain, distribute and accumulate in the worldwide environment. Persistence is an environmental (negative) term and should be distinguished from the (positive) term "durability" of a chemical product during use. In the following we will draw attention to the interaction between the scientific and the administrative communities with respect to the slow change in perception of the term "persistence".

"Persistence" first surfaced in the OECD in 1966, when the OECD Committee for Scientific Research held a conference on "Research on the Unintended Occurrence of Pesticides in the Environment". At that time the OECD established a study group on this problem, and its report led, in 1971, to the creation of the OECD Environment Committee with the following recommendations:

> *"The Group wishes to stress the need internationally for means to make comprehensive investigations of the consequences of use, and limitations in use, of those chemicals which could be regarded as having unacceptable effects on man and his environment resulting from, either*
> *a) their undue persistence in natural conditions in biologically active form, or*
> *b) their wide distribution through water and air, or*
> *c) their accumulation which may lead to biological effective levels in organisms exposed to even low concentrations."* [8, p. 11]

At the same time the United Nations Conference on the Human Environment (1972) recognised persistence as a negative environmental property in Recommendation 71:

> *"It is recommended that Governments use the best practical means available to minimize the release to the environment of toxic or dangerous substances, especially if they are persistent substances such as heavy metals and organochlorine compounds, until it has been demonstrated that their release will not give rise to unacceptable risks or unless their use is essential to human health or food production, in which case appropriate control measures should be applied."* [9]

These two recommendations have not changed with the years and read like a contemporary political mandate. However, the environmental regulatory discussion treated "persistence" only as a sub-element of environmental effects assessment, and it took several years and arguments before "persistence" was accepted as an environmental criterion in its own right and designated as an "endpoint" in environmental exposure assessment equivalent to "ecotoxicity". In 1977 Stephenson foresaw the future problem of persistent chemicals, when he wrote:

> *"Persistent materials, because of this property, will accumulate in the environment for as long as they are released. Since the environment is not effective at cleansing itself of these materials, they will remain for indefinite periods, which were not recognized at the time of their original release. The problem could become entirely out of control and it would be extremely difficult if not impossible to do anything about it. Materials which are strongly persistent can accumulate to rather high levels in the environment and effects which would not otherwise be important could become so."* [10, p. 48]

Frische et al. (1982) [11] and Klöpffer (1994) [12, 13] advocated that "*persistence*" *is the* "*central and most important environmental criterion*" often replacing ecotoxicity, which can never be determined with acceptable certainty.

At the beginning of the 1990s, semi-volatile organic chemicals (SOCs) came into focus for analytical chemists because of the worldwide distribution, ubiquitous occurrence and geo accumulation in remote areas (Ballschmiter and Wittlinger [14], Ballschmiter [15], Ockenden et al. [16], and AMAP [17]). This was a disturbing signal for sustainable chemical production and use, and alarmed the regulatory community, after "sustainable development" had been established as the key policy environmental term at the Earth Summit in Rio de Janeiro in 1992. In fact, Agenda 21 formulated the future chemicals risk assessment policy, by including:

> *"Governments, through the cooperation of relevant international organisations and industry, where appropriate, should adopt policies and regulatory and non-regulatory measures to identify, and minimize exposure to toxic chemicals by replacing them with less toxic substitutes and ultimately phasing out the chemicals that pose unreasonable and otherwise unmanageable risk to humans and the environment and those that are*

> *toxic, persistent and bio-accumulative and whose use cannot be adequately controlled."* [18, Chap. 19.49 (c)]

Another milestone in this policy discussion was the Esbjerg Declaration, which nine European countries neighbouring the North Sea and the European Commission adopted in Esbjerg, Denmark, 8th–9th June 1995, at the Fourth International Conference on the Protection of the North Sea. The statement of zero concentrations for man-made synthetic substances in the North Sea was revolutionary and was received with scepticism, but did not miss its policy objective.

> *17. The Ministers AGREE that the objective is to ensure a sustainable, sound and healthy North Sea ecosystem. The guiding principle for achieving this objective is the precautionary principle.*
> *This implies the prevention of the pollution of the North Sea by continuously reducing discharges, emissions and losses of hazardous substances thereby moving towards the target of their cessation within one generation (25 years) with the ultimate aim of concentrations in the environment near background values for naturally occurring substances and close to zero concentrations for man-made synthetic substances. Esbjerg Declaration 1995.* [19]

In 1997 the Chemicals Policy Committee of the Swedish Ministry of the Environment outlined specific sustainability goals: "Substances that are persistent and liable to bioaccumulation should be banned, even if they are not known to have toxic effects." The Committee argued:

> *"Experience tells us, that new unexpected forms of toxicity may be uncovered in the future. For substances that are persistent and liable to bioaccumulate that knowledge will come too late. To act only when the knowledge of the hazard becomes available is not prevention. We therefore conclude that known or suspected toxicity is not a necessary criterion for measures against organic man-made substances that are persistent and liable to bioaccumulate. Such substances should in the future not be used at all."* [20]

One year later Martin Scheringer et al. [21], [22, Chap. 1–3], [23, Chap. 1–3] advocated a change in the paradigm of environmental risk assessment, in short a shift from the effects-based to the exposure-based assessment. Scheringer and Berg [24, 25] had prepared this change by introducing the following three indicators for measuring environmental threat:

- spatial range (potential for long-range transport)
- temporal range (persistence)
- bioaccumulation potential

Scheringer and Hungerbühler [26, p. 176] concluded:

> *"An exposure-based assessment requires different (and usually less) data than effect-based assessments and is (usually) performed faster than the various toxicity tests required for an effect-based assessment.*

It should be noted that the combination of persistence and bioaccumulation, although relevant for many semi-volatile organic substances, is "narrower" than the concepts of Klöpffer and Scheringer and would not include, for example, new types of freons contributing to global warming or other, hitherto not recognized effects. The same is true for persistent water-soluble substances and thus not bioaccumulating substances.

Subsequently, in 2001, the German Umweltbundesamt [27] and Steinhäuser [28] argued similarly, when they published five policy principles on sustainability, two of which are concerned with persistence:

- *"The irreversible release of persistent and bioaccumulative or persistent and highly mobile pollutants (xenobiota) in the environment must totally be avoided regardless of their toxicity. This also holds for metabolites with the same properties.*
- *The increase of releases must be avoided independently of known adverse effects and other intrinsic properties, if it is practically impossible to recollect the substance from the environment because of its high mobility and/or its significant partitioning."* [27, pp. 7–8]

In Canada, indigenous people, such as the Inuit, complained that they were not users of persistent chemicals, but suffered from the air-borne fallout and the contamination of their grounds living in the Arctic.

Important milestones in this policy discussion on persistence were the 1985 Vienna Convention for the Protection of the Ozone Layer [29] and the Montreal Protocol on Substances that deplete the Ozone Layer [30]. This Convention and its Protocol triggered off an intensive research on the gas-phase photo-degradation and the global warming potential of hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs) [31] and polyfluoroethers [32], because such fluorated chemicals have valuable uses and are of high economic interest.

"Persistence," "bioaccumulation" and "long-range transport" of industrial chemicals and pesticides came into focus when Persistent Organic Pollutants (POPs) were detected in the remote and assumedly pristine areas of the Arctic. Analytical chemists were interested in measuring concentrations (Ballschmiter and Wittlinger [14], Ballschmiter [15], AMAP [17]), and environmental modellers tried to simulate the environmental movement of chemicals in multimedia fate models (Wania and Mackay [33, 34], Cowen et al. [35], Scheringer [22, 23, 36, 37], Wania [38]). Persistence and long-range transport potential were identified as the *intrinsic chemical properties* responsible for environmental migration. Transportation over the atmosphere is most probably the fastest route to worldwide distribution, and photo-degradation is the most likely elimination process of air-borne chemicals. Rivers and ocean currents transport chemicals much more slowly, particularly hydrophilic substances that are less volatile. Wash-out, especially of aerosol-bound chemicals, temporarily removes persistent chemicals from the atmosphere, but not from the environment. They may re-enter the troposphere by re-volatilisation from soil and surface waters (grasshopper-effect). Physical environmental sinks such as river or ocean sediments do not reduce the persistence because they do not eliminate the chemical from the environment.

How did the administrations react to this new environmental threat?

The administrative community had already reacted in November 1979, when the United Nations Economic Commission for Europe convened a High-level Meeting in Geneva in response to acute problems of transboundary air pollution through acidification. It resulted in the signature of the Convention on Long-range Transboundary Air Pollution by 34 Governments and the European Community [39]. The Convention was the first international legally binding instrument to deal with problems of air pollution on a regional basis. The Convention set up an institutional framework bringing together research and policy. Under this Convention, on 24th June 1998 in Aarhus, Denmark, the UN ECE adopted the Protocol on Persistent Organic Pollutants (POPs) [40]. It focuses on a list of 16 substances that have been singled out according to agreed risk criteria. The substances comprise 11 pesticides, two industrial chemicals and three by-products/contaminants. The ultimate objective is to eliminate any discharges, emissions and losses of POPs. The Protocol bans the production and use of some products outright (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene). Others are scheduled for elimination at a later stage (DDT, heptachlor, hexachlorobenzene, PCBs). Finally, the Protocol severely restricts the use of DDT, HCH (including lindane) and PCBs. The Protocol includes provisions for dealing with the wastes of products that are banned. It also obliges Parties to reduce their emissions of dioxins, furans, PAHs and HCB below their 1990 levels (or an alternative year between 1985 and 1995). For the incineration of municipal, hazardous and medical waste, it lays down specific limit values. Since it was enforced in October 2003 several "new" POP candidates have been added to the Protocol (http://www.unece.org/env/popsxg, May 2006).

In May 1995 the UNEP Governing Council was "aware that persistent organic pollutants pose major and increasing threats to human health and the environment" and adopted Decision 18/32 on Persistent Organic Pollutants and

> *"**Invited**, ... the Intergovernmental Forum on Chemical Safety to develop recommendations and information on international action, including such information as would be needed for a possible decision regarding an appropriate international legal mechanism on persistent organic pollutants, to be considered by the Governing Council and the World Health Assembly no later than in 1997."* [41]

Regulatory action on hazardous properties such as toxicity, carcinogenicity, mutagenicity or reproductive toxicity was straightforward; however, the fact that a chemical substance is recalcitrant to breakdown processes in the environment was not linked to these effects. This attitude changed when POPs were detected, and the voice of the Inuit populations in Canada and Greenland requested fairness and equity in regions where the benefits of POPs were not achieved, because these chemicals had not been used there. The international scientific and administrative community recognised these arguments and gave "persistence" and "long-range transport potential" the status of exposure assessment "criteria" in the Stockholm Convention [42, Annex D] in addition to "bioaccumulation" and "adverse effects." In 2004 the European Community transferred the Stockholm Convention and the UN ECE POP Protocol into European legislation by Regulation (EC) 850/2004 [43]. Industry's contribution to persistence is summarised in an ECETOC Monograph [44].

Persistence and long-range transport are not considered in isolation, but assessed in combination in two assessment schemes that reflected the policy discussions of the previous years:

- vPvB assessment = very persistent and very bioaccumulative
- PBT assessment = persistent, bioaccumulative and toxic

The Stockholm Convention set the stage in Annex D [42] for national or regional legislations by specifying values to these criteria[1]:

- *Persistence*
  - half-life in water > 2 months or
  - half-life in soil > 6 months or
  - half-life in sediment > 6 months or
  - evidence that the chemical is otherwise sufficiently persistent

- *Potential for long-range environmental transport*
  - measured levels in locations distant from the source of release
  - monitoring data showing long-range environmental transport
  - environmental fate properties and/or model results
  - half-life in air > 2 days

The Commission of the European Union and other Governments had already begun programmes to identify persistent and bioaccumulative chemicals:

- European Commission (2003): Technical Guidance Document, Part II: vPvB and PBT [45]
- US EPA: POP-Profiler [46]; Rodan et al. 1999 [47]
- Environment Canada (1995): Persistence and Bioaccumulation Criteria [48]
- Japan: Ikeda et al. 2001 [49]

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[1] Only these two criteria relevant for photo degradation are presented.

It is the intention of these programmes to screen new and existing commercial chemicals and pesticides against the Stockholm criteria. In fact, the Stockholm Convention stipulates in Article 3:

> *(3) that "each party (to the Convention) that has one or more regulatory and assessment schemes for new pesticides or new industrial chemicals shall take measures to regulate with the aim of preventing the production and use of new pesticides or new industrial chemicals which, taking into consideration the criteria in paragraph 1 of Annex D, exhibit the characteristics of persistent organic pollutants."*

and

> *(4) that "each party that has one or more regulatory and assessment schemes for pesticides and industrial chemicals shall, where appropriate, take into consideration within these schemes the criteria in paragraph 1 of Annex D when conducting assessments of pesticides or industrial chemicals currently in use."* [42]

The draft REACH regulation of 29th October 2003 [50] incorporates this task into Articles 54 and 55 with the criteria of Annex XII.[2] It is estimated that in the European Union about 30 000 existing chemicals will be screened within the next 15 years against the Stockholm Convention criteria. This legislation, in combination with the Precautionary Principle, should prevent POP-like chemical substances being produced and put on the market.

3

Multimedia Models as Tools to Estimate Persistence and Long-range Transport Potential

The above mentioned regulatory approaches in the PBT and vPvB assessment to measure persistence via the single media transformation (degradation) rate constants in the environmental compartments water and soil may have shortcomings because they do not consider the environmental partitioning of the chemical. Evidently, the persistence of a chemical partitioning, mostly to air, will not be adequately described by only measuring biodegradability in water. Environmental modellers took up this critique and created an integrated approach to persistence by introducing environmental fate models that were based on both environmental partitioning and transformation rate constants (Cowan et al. [35], Scheringer [22, 23], Webster et al. [51], Bennett et al. [52], Beyer et al. [53]).

This controversy became evident, when administrators and environmental modellers met in October 2001 in Ottawa in the OECD workshop on the use of

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[2] The REACH draft [50] presents the PBT and vPvB assessment criteria in Annex XII. They are not in full conformity with the concept of the Stockholm Convention [42, Annex D], because the criterion "potential for long-range environmental transport" is missing, which includes the half-life in air. The EU Council adopted the Common Position of the REACH draft in the 27th June 2006 version. Annex XII became Annex XIII and was not changed.

multimedia models for estimating overall persistence and long-range transport in the context of PBT/POPs assessment. This workshop's objective was to explore common ground for the use of multimedia models in screening chemicals against the two Stockholm criteria, "persistence" and "long-range transport potential" [54]. Upon recommendation of this workshop OECD established an expert group of modellers, who elaborated a Technical Guidance Document (OECD [55]) and two scientific articles (Fenner et al. [56], Klasmeier et al. [57]) and a consensus multimedia model for screening chemicals for high persistence and long-rang transport potential (Wegmann et al. [58]). OECD performed three workshops for the application of this screening software in Zürich, Switzerland (August 2005), Ottawa, Canada (May 2006) and Tsukuba, Japan (June 2006). This multimedia approach and its underlying philosophy slowly found its way into regulatory science. It can support industry and administrators in the task of screening industrial chemicals and currently used pesticides for the two criteria "overall persistence (Pov)" and "long-range transport potential (LRTP)". Overall persistence differs from the above mentioned single media persistences in water, soil, sediment and air. It constitutes a weighted persistence in the four environmental compartments: water, sediment, soil and air, in which a chemical partitions as a consequence of its physicochemical properties. Green and Bergman [59] reflected this multimedia understanding by proposing the following definition of "persistence":

> *"The persistence of a chemical is its longevity in the integrated background environment as estimated from its chemical and physicochemical properties within a defined model of the environment."* [59]

A chemical that partitions to air is liable to atmospheric transport. This new concept of overall persistence, expressed in half-life [days], is the output of the multimedia fate model and is considered an adequate representation of the Stockholm persistence criterion. The long-range transport potential is the other output expressed in the "half-distance" [km], that the chemical may migrate with a certain wind speed. The plot of Pov versus LRTP (Fig. 1) is divided into four sectors [37, 57] and provides an indication for the chemical in question with respect to both criteria relative to a set of benchmark chemicals, amongst which are some of the agreed POPs. With this multimedia model the chemical industry and administrators will have a tool to hand that allows these two criteria to be determined in advance, so that persistent new chemicals will no longer be placed on the market and existing chemicals can be screened, as Schmidt-Bleek and Hamann [60] had called for in 1985 in their appeal to systematically screen chemicals for early warnings:

> *"Early recognition is understood to mean the timely observation of deleterious effects and changing exposure situations before significant damage manifest themselves. From an environmental protection point of view it would seem reasonable to approach a systematic solution from the exposure potential side for reasons of logic as well as saving time and resources:*

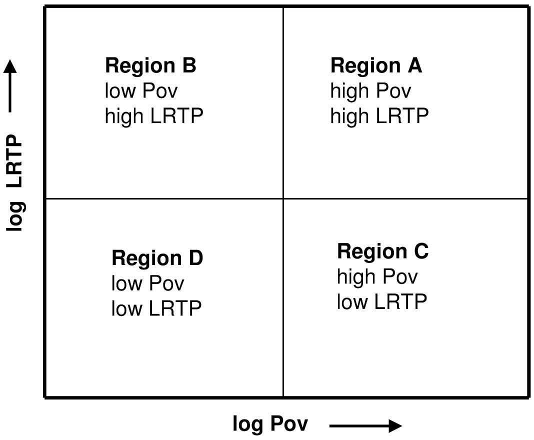

Fig. 1 Classification of chemicals in the Pov/LRTP space (adapted from Klasmeier et al. 2006 [57], copyright of American Chemical Society).

> – *if significant quantities can reach the environment*
> – *if the environmental persistence of a chemical is long-term, and*
> – *if its environmental mobility is high, such a chemical can be regarded as a threat to the environment, even in the absence of knowledge on its effect potentials."*
> [60, p. 462–463]

4
Data Requirements for Multimedia Models

Klöpffer [61] identified the following data required in the application of multimedia models in screening chemicals for Pov and LRTP:

- *Physicochemical properties (partitioning)*
  - chemical identity
  - molecular weight
  - water solubility
  - vapour pressure
  - *n*-octanol/water partition coefficient
- *Transformation (degradation) half-lives*
  - biodegradation in water
  - biodegradation in soil
  - biodegradation in sediment
  - abiotic degradation
    - hydrolysis
    - indirect photo-degradation by hydroxyl radicals, ozone, nitrate radical
    - direct photolysis in air

Hydrolysis and direct photolysis in air are believed to be of subordinate importance for the persistence of most substances, as special structures are needed (hydrolysable groups, chromophores) to be effective. The reaction with hydroxyl radicals is by far the most important and predominant atmospheric elimination process (Bidleman [62]), so that the abiotic degradation in the *screening phase* may be expressed, by the rule of thumb, through the indirect photo-degradation with the hydroxyl radical. A more detailed discussion of the photo transformation processes, as required for a deeper understanding and refined assessment, is presented in Chapter 2.

The indirect photo-degradation is a decisive transformation rate constant that accounts for persistence and long-range transport potential of volatile and semi-volatile substances in multimedia fate models. The availability of literature data on reactions of organic substances with hydroxyl radicals has been the subject of several international workshops:

- Driebergen, The Netherlands 22–24 April 1998 (Bidlemann [62], Atkinson et al. [63])
- SETAC Pellston Workshop in Fairmont Hot Springs, British Columbia, Canada 12th–19th July 1998 (Franklin et al. [64], Chap. 2)
- OECD/UNEP Workshop in Ottawa, Canada 30th October – 1st November 2001 [54, Annex 7]

All three workshops concluded that the availability of photo-degradation data for semi-volatile substances is not sufficient. This book presents the rate constants for indirect photo-degradation of 1081 chemicals. The majority of these data result from volatile substances (vapour pressure $> 10^{-3}$ Pa).

There is, however, a lack of rate constants for semi-volatile substances (vapour pressure $< 10^{-3}$ to 10^{-6} Pa) because of experimental difficulties. Palm demonstrated (as quoted by Franklin et al. [64], Fig. 2-2) that the majority of currently used pesticides exhibit a vapour pressure of $< 10^{-3}$ Pa and therefore constitute semi-volatile and non-volatile substances. A similar survey of the vapour pressure of existing industrial chemicals can probably not be made because of missing data.

5
Estimation of the Rate Constant of Organic Substances with Hydroxyl Radicals

The experimental rate constants collected from the literature, as given in this book, represent only a minority of chemicals *vis-à-vis* the 30 000 industrial chemical substances to be evaluated in Europe under the new legislation [50]. In the 1990s Meylan and Howard [65, 66] developed the empirical Atmospheric Oxidation Programme (AOP) based upon Atkinson's experimental data [cf. 67]. This QSAR software programme allows estimation of the gas-phase hydroxyl rate constant at 298 K from increments of the chemical structure. Its use is well established in industry and accepted in the administrative communities (Sabljic and Peijnenburg [68], Meylan and Howard [69], and Schüürmann [70]), but is often used in regulatory applications beyond its limitations. The SETAC Pellston Workshop expressed these limitations (Franklin et al. [64]):

> *"The empirical estimation method of Atkinson allows the OH rate constants at 298 K of 90% of approximately 500 to 600 organic compounds used in its development to be predicted within a factor of 2 of the experimental values.*
> *The limitations of present OH rate constant estimation methods must be recognised. In particular, most estimation methods cannot be used with any degree of liability for organic compounds outside of those compounds actually used in the development of the estimation method. Compound classes for which experimental data are not available for at least one member of the homologous series could have uncertainties in the estimated rate constants for reactions with the OH radical of a factor of 5 or greater. In such cases expert judgment should be sought. Atkinson's estimation technique has not been tested sufficiently to warrant its use for most N-, S- and P-containing compounds.*
> *Further studies need to be carried out to extend Atkinson's estimation method to additional compound classes represented by POP-type compounds and to develop more direct methods for the calculation of OH radical reaction rate constants."* [64, pp. 52–53]

These qualifying conclusions are particularly true for semi-volatile, persistent, particle-bound substances, which represent many existing organic substances and for which experimental hydroxyl rate constants are missing. The major obstacle to measuring the hydroxyl rate constant for semi-volatile substances lies in the low vapour pressure at room temperature so that traditional methods can not be used. In addition, semi-volatile substances ad- or absorb to atmospheric aerosols, thereby shielding the access of the hydroxyl radical.

Junge [71], and later Bidleman and Harner [72], Goss [73] and Goss and Schwarzenbach [74] created approximation models to predict the adsorption of semi-volatile organic substances to solid (aerosol) particles. The SETAC Pellston Workshop described (Franklin et al. [64]):

> *"Absorption of a gaseous species into an outer organic layer deposited on an inorganic particle may isolate the substance from gas-phase OH and hence impede its degradation. In a similar manner, adsorption onto the surface of pores whose particular shape hinders access by gaseous OH may lead to a reduced rate of degradation."* [64, p. 53]

These conclusions still hold. Scheringer [23, pp. 174–176] and [37, 75] discussed this dilemma and advocated introducing an effective atmospheric degradation rate constant in multimedia model calculations that is smaller than the gas-phase rate constant and accounts for a particle-bound fraction.

$$k_{\mathrm{eff}} = (1 - \Phi)\, k_{\mathrm{OH}} + \Phi\, k_{\mathrm{part}} \tag{1}$$

where k_{eff} = effective atmospheric degradation rate constant; Φ = fraction of the particle-bound substance; k_{OH} = atmospheric rate constant for the gas-phase reaction with the hydroxyl radical; k_{part} = atmospheric rate constant of the particle-bound fraction. This latter rate constant is set to zero in most multimedia fate models.

He also pointed out that the multimedia model long-range transport results using AOP predicted hydroxyl rate constants for POPs are much too short and disagree with the findings of POPs in remote areas. The argument given was that either the hydroxyl rate constant is predicted to be too high or the model that assumes the sheltering of particle-bound substances from the hydroxyl radical reaction is incorrect. Wania and Daly [76] explained these inconsistencies with calculations of their Globo-POP multimedia model in a plausible manner. They adapted the hydroxyl radical concentration to tropospheric vertical and temporal conditions and the temperature dependent gas/aerosol partitioning to the tropospheric average temperature of –18 °C. By varying these two environmental parameters they showed that the atmospheric half-lives of PCBs, derived from laboratory hydroxyl rate constants increased substantially. They concluded:

> *"Reaction rate constants of the PCBs with OH radicals derived in the laboratory do not disagree with the observed global fate of these contaminants. However, the real atmospheric lifetimes of POPs are longer than may be expected from a cursory inspection of laboratory-derived reaction rate constants, as a result of low temperatures, variable OH radical concentrations and partitioning of semi-volatile chemicals onto atmospheric particles. ... Even a chemical with a seemingly fast atmospheric degradation rate constant can be subject to long-range atmospheric transport, especially if the chemical is semi-volatile and the atmosphere is cold and/or dark."* [76]

6
Research Requirements for Photo-degradation of Semi-volatile Substances

Wania and Daly advocated further research for improving the quantitative knowledge on the reactions that PCBs may undergo when adsorbed to atmospheric particles, especially the kinetics of such reactions [76]. Researchers, therefore, are encouraged to engage in new approaches to kinetic photo-degradation studies of semi-volatile substances particularly when adsorbed on aerosols (cf. Wagner [77, 78], Scheringer [75, 79]).

Indeed, this issue has been the subject of research ever since and various approaches have been tried. The low vapour pressure of semi-volatile substances caused experimental difficulties, which have not yet been solved satisfactorily. Since the late 1980s Zetzsch and his group (Behnke et al. [80, 81]) have devoted research to heterogeneous photo-degradation of semi-volatile substances adsorbed on particles in smog chambers of different sizes. Palm et al. obtained rate constants for two semi-volatile pesticides (terbutylazine and pyrifenox) adsorbed on particles [82–84]. The group of Hites (Anderson and Hites [85, 86] and Brubaker and Hites [87, 88]) used a heated system (75–159 °C) to measure gas-phase hydroxyl reaction

Table 1 Reaction rate constants and half-lives for lindane coated on Aerosil®.

Substance CAS No.	$k_{OH} \times 10^{-12}$ [cm^3 $molecule^{-1}$ s^{-1}]	Half-life [d][a]	Experimental conditions	Reference
Lindane 58-89-9	0.60 ± 0.3	26.7	Smog chamber 27 °C 50% humidity	Behnke and Zetzsch 1989 [94], Zetzsch 1991 [95]
Lindane	0.345 ± 0.3	46.5	Eletrodynamic trap room temperature	Rühl 2004 [89]
Lindane	3.0 ± 0.3	5.3	Smog chamber 6.5 °C	Krüger et al. 2005 [90]
Lindane	0.19 ± 0.06	84.4	Measured at 73–113 °C and extrapolated to room temperature: 25 °C	Brubaker and Hites 1998 [88]

a) Calculated with 5×10^5 OH radicals per cm^3.

rate constants of polychlorinated dibenzo-*p*-dioxins and furans in addition to PCBs and α- and γ-hexachlorocyclohexanes and hexachlorobenzene and extrapolated them to room temperature through the Arrhenius equation. More recently two research groups provided particle-bound rate constants for lindane (Table 1). Rühl [89] used an electrodynamic trap to expose lindane coated particles and analysed its decay by infrared spectroscopy. Krüger et al. [90] used a smog chamber at 6.5 °C with conventional gas chromatographic analysis. Both experiments were performed with artificial inorganic aerosols (Aerosil®, silica flocks from Degussa) mimicking desert sand aerosols, i.e., particles containing no organic matter. The situation with an organic matter surface that covers the inorganic nucleus of an aerosol may be different [cf. 76]. The other extreme is particles covered by a water layer [cf. 74]. All variations may occur in nature, depending on the origin and chemical composition of the aerosol particle and the atmospheric conditions (humidity, temperature). Recently, Sun et al. [91] measured the gas-phase hydroxyl reaction rate constant of four semi-volatile pesticides at 296 K (dichlorvos, carbaryl, chlordimeform and 2,4-D-butyl ester) with a Fourier transform infrared spectrometer (FTIR). Feigenbrugel et al. [92] also measured dichlorvos with an FTIR technique at room temperature.[3] Mandalakis et al. [93] determined the hydroxyl reaction rate constant of PCBs in a field experiment in Crete (Greece) by monitoring the gas concentrations over one day. The known rate constant for PCB 28 served as the reference. The field rate constants were notably coherent with the laboratory measured values. The research aim may still be the conclusion of the Pellston Workshop (Franklin et al. [64]), which recommended that

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[3] The rate constants of the quoted papers are summarised in Chapter 3.

“consistent data from at least two independent studies (preferably using different techniques) are needed before a rate constant can be considered to be well established.” [64, p. 14]

7
Conclusions

The international scientific and administrative communities now agree that persistence has a central role in environmental exposure and risk assessment. Screening multimedia fate models have now been developed and tested to such an extent that regulatory science can rely on their results for persistence and long-range transport potential. This multimedia approach realises the change in paradigm from effects to exposure based environmental risk assessment, as postulated above by several workers and institutions.

Multimedia models require two classes of intrinsic substance properties: partitioning and degradation (transformation) data. Environmental partitioning data are reliably calculated on the basis of measured physicochemical properties. The weak and salient point is still the experimental determination of transformation half-lives in water, soil, sediment and air. In particular, the last half-life in air is responsible for assessing the world-wide distribution of a chemical. This book presents the state-of-the-art methodology for measuring indirect and direct gas-phase photo-degradation (transformation) and includes quality checked photo-degradation rate constants for 1081 chemicals published in the literature up to July 2006. Research is needed to develop new methods for measuring the photo-degradation of semi-volatile chemical substances, which, at environmental temperatures, adsorb partially or totally to aerosols [72]. Such data could extend the database of the Atmospheric Oxidation Programme (AOP) and then make this QSAR programme more valuable.

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