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# SIGNIFICANCE OF THE LONG RANGE TRANSPORT OF PESTICIDES IN THE ATMOSPHERE

(Technical Report)

*Prepared for publication by*

J. B. UNSWORTH<sup>1</sup>, R. D. WAUCHOPE<sup>2</sup>, A. W. KLEIN<sup>3</sup>, E. DORN<sup>4</sup>, B. ZEEH<sup>5</sup>, S. M. YEH<sup>6</sup>,  
M. AKERBLOM<sup>7</sup>, K. D. RACKE<sup>8</sup> AND B. RUBIN<sup>9</sup>

<sup>1</sup> Rhone-Poulenc Agriculture, Ongar, Essex, UK

<sup>2</sup> US Dept. of Agriculture, Tifton, GA, USA

<sup>3</sup> Umweltbundesamt, Berlin, Germany

<sup>4</sup> AgrEvo, Frankfurt, Germany

<sup>5</sup> BASF Corp., Research Triangle Park, NC, USA

<sup>6</sup> Zeneca Ag. Products, Richmond, CA, USA

<sup>7</sup> Swedish University of Ag. Sciences, Uppsala, Sweden

<sup>8</sup> Dow AgroSciences, Indianaolis, IN, USA

<sup>9</sup> Hebrew Univ. of Jerusalem, Rehevot, Israel

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## **Pesticides report 41. Significance of the long range transport of pesticides in the atmosphere (Technical Report)**

*Abstract:* Since the 1960s there has been a growing body of data regarding the presence of pesticides in the atmosphere. The monitoring results obtained show that traces of pesticides may undergo long range transport and be deposited considerable distances away from the treatment areas, including remote areas such as the Arctic and Antarctic regions. Pesticides have been found in air, rain, cloud water, fog and snow. The appearance and subsequent behaviour of pesticides in the atmosphere are complex processes and the concentrations found depend on several variables such as their volatility, photostability, method of application and extent of use. Whilst volatility of pesticides can be linked to their Henry's Law constant this is very much a simplification since it is also influenced by the surfaces treated, e.g. soil or leaves, and by the extent to which aerosols are formed during the application. The disappearance of pesticides from the atmosphere is due to hydrolysis, indirect photolysis via OH radicals and to deposition in rain. Pesticides which are resistant to hydrolysis and photolysis can be transported over great distances, for example, organochlorine insecticides have been detected in the Arctic regions. In general, concentrations in rainwater are, when detected, in the low or sub  $\mu\text{g/L}$  range and highest concentrations are found during the time of application. The use of fugacity models has been shown to be a useful approach to predict concentrations in air. Under most conditions the presence of pesticides in air, or rainwater, has no significant effects on non-target systems, including direct and indirect effects. Exceptions to this are damage by auxin-type herbicides to sensitive plants which has resulted on restrictions in their use in certain areas and transient chlorotic spotting thought to be caused by drift of aerosols from application of low rate sulfonyl urea herbicides. For animal species one possible exception has been postulated. This is for persistent organochlorine pesticides in Arctic regions where, due to the very oligotrophic nature of the Arctic ocean, they are more liable to bioaccumulate and be transported in the food web giving enhanced levels in mothers' milk.

### **THE IUPAC COMMISSION ON AGROCHEMICALS AND THE ENVIRONMENT MAKES THE FOLLOWING RECOMMENDATIONS**

Based on the conclusions from this review, several recommendations for further areas of research are suggested. Since the factors governing the fate and behaviour of pesticides in the atmosphere are the same for any organic contaminant, whether from natural or anthropogenic sources, research studies on pesticides in air should be considered in the same way as any organic contaminant in the atmosphere.

- 1** Investigations should be encouraged into obtaining a better understanding of cloud chemistry and its role in the long and intermediate transport of organic contaminants, including pesticides.
- 2** Investigations should be encouraged into the application of fugacity models in the prediction of atmospheric concentrations of organic contaminants, including pesticides, in defined areas due to long range transport.
- 3** In order to refine and validate current models specifically for pesticides additional investigations are required into:
  - the chemical reactivity of pesticides, particularly their photodegradation under environmental conditions.
  - the transfer of pesticides between environmental compartments to give the key factors leading to their occurrence in the atmosphere.
  - the parameters required to define the 'unit world', i.e. an identified and limited geographic area, for use in fugacity models.

- 4 Since pesticides, as with all anthropogenic organic contaminants, will have an impact on sensitive ecosystems it is essential that steps are taken to ensure that they will not be distributed by long range transport in concentrations likely to pose a risk to non-target systems. It is recommended therefore that:
- an assessment scheme is developed and validated to determine which pesticides show volatilisation behaviour and hydrolytic and photolytic stability which would indicate an extended residence time in the atmosphere.
  - for pesticides likely to have an extended residence time in the atmosphere assessments are carried out using fugacity models to predict their likely distribution in defined geographic areas.

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## 1 INTRODUCTION

Over the past few decades techniques for collecting and analysing atmospheric samples for organic contaminants, from both natural and anthropogenic (man made) sources, have been developed and improved. The resulting body of data shows that the atmosphere can be an important transport system and sink for many organic compounds [1–3]. The presence of pesticides in the atmosphere was first reported 30–40 years ago when there was significant usage of chlorinated products on a global scale; in particular DDT, lindane and dieldrin, which were found not only near their site of application but also in the polar regions. Since the 1960s there has been a growing body of literature demonstrating the presence of low levels of many different types of pesticides [4] in air, rain, fog and snow. In general, the highest levels of pesticides are found close to the site of application and for a period which corresponds to the maximum application time. However, pesticides can be detected at other times of the year, e.g. atrazine has been detected in rainfall throughout the year in Maryland [5], and they can also be found in areas far removed from the sites of application. Thus pesticides have been found in locations such as the Swiss Alps [6], the West Indies [7], Enewetak Atoll in the Pacific Ocean [8], the Arctic [9] and the Antarctic [10]. Their appearance in such areas can only have been from the result of atmospheric transport and subsequent wet or dry deposition.

Thus since some pesticides can travel long distances under certain conditions, and their deposition may have an impact on sensitive ecosystems, it is necessary to have a good understanding of the mechanisms of their atmospheric transport and subsequent deposition. Mathematical models would play a key role if they could predict the likely magnitude of atmospheric loading and transport of pesticides. These models, coupled with the known toxicological and ecotoxicological effects of the pesticides, could then be used to assess the likely impact of new pesticide uses.

Certain extremely volatile pesticides used as soil fumigants have been linked with ozone depletion [11]. However, since ozone depletion is not a general concern for pesticides it is not considered further in this paper.

This paper is not intended to be a comprehensive review of the occurrence of pesticides in the atmosphere. Its objective is to examine the current knowledge of the processes whereby pesticides come to be present in the atmosphere, their subsequent long range transport and transformation, their actual concentration in air and precipitation and the significance of the levels found in toxicological and ecotoxicological terms. Finally, based on the information available today, recommendations are made on the assessment of risk from pesticides in air and possible impact on international regulatory guidelines (e.g. [12]).

## 2 ENTRY OF PESTICIDES INTO THE ATMOSPHERE AND THEIR SUBSEQUENT DEPOSITION

### 2.1 Entry of pesticides into the atmosphere

Entry of pesticides into the atmosphere can occur by several routes (see below, based on Dietz [13]).

The major transport and distribution of pesticides occurs close to the site of use although there is also ample evidence that atmospheric transport can occur on a global scale, particularly for the more stable products such as the hydrolytically stable organochlorines [2,3,14,15]. The appearance of pesticides in air or in precipitation (rain, snow and fog) results from drift during application, from volatility after application and from suspended particulate matter originating from wind erosion of treated soil [16]. Thus dry and wet deposition on non-target areas after horizontal and vertical translocation has been reported after pesticide treatments [17]. In extreme cases soil particles containing adsorbed material can be transported over significant distances, e.g. Cohen & Pinkerton [18] found various pesticides in dust brought to Ohio by a massive dust storm originating in the Texas/Oklahoma/New Mexico region. Additionally, there is evidence that organic compounds, including pesticides, are preferentially deposited at higher latitudes according to the cold condensation hypothesis of Wania & Mackay [19] (Table 1).

Spray drift, in its widest sense, is an important contributor to the presence of pesticides in the atmosphere and even those pesticides classed as nonvolatile will be found, as aerosols in the atmosphere, near the spray area and in down wind air. For any pesticide, if the spray droplets are less than 100–150  $\mu\text{m}$  diameter they can be transported over long distances by air currents before they precipitate.

**Table 1** Entry of pesticides into the atmosphere [13]

Activity	Sources
Agriculture, Forestry	Application losses, drift, post-application volatilisation, wind erosion
Public Health	Spraying for control of insect vectors of disease
Industrial	Pesticide manufacture/formulation, effluents, fumes, vapours, dust
Commercial	Moth proofing, protection of stored food, industrial hygiene, sanitation, insect control in buildings
Home and Garden	Local application
Accidents	Spills, improper disposal

Reports in the published literature indicate that a significant proportion of some pesticides, on a percentage basis, disappear from the target area (soil or plants) and are present in the atmosphere immediately after application [20]. Volatilisation can also continue to occur a few days after application. Thus in a study with trifluralin in soybean it was shown that 79% volatilised over the first 18 days after application [21]. Similarly, evaporative loss of parathion was shown to be in excess of 90% within a few days following treatment [22]. However, losses due to volatilisation depend on the nature of the pesticide. In a recent study [23] it has been shown that losses of fenpropimorph were less than 1% of the applied material, losses of chlorothalonil were 1–2% and losses of parathion-ethyl 16.5%. It has also been demonstrated, with terbutylazine and pendimethalin applied to nearly bare soil, that losses are influenced by microclimatic events [24]. It has also been demonstrated [25,26] that increased volatilisation of hydrophobic pesticides from moist soil is not due to codistillation but by transfer to the soil surface by water movement with wicking of pesticides to the soil surface [27].

The process of volatilisation can be a significant contributing factor to the presence of pesticides in the atmosphere away from the use area. At first sight the most obvious factor in the volatilisation of pesticides should be the vapour pressure ( $P_v$ ) of the active substance and this has been used to classify pesticides into three categories [28]:

- (i) volatile ( $P_v > 10^{-3}$  hPa) e.g. some organophosphates or carbamates
- (ii) medium volatile ( $10^{-3}$  hPa  $< P_v < 10^{-7}$  hPa) most active substances
- (iii) low or nonvolatile ( $P_v < 10^{-7}$  hPa) e.g. triazines, DDT, aldrin, pyrethroids

Vapour pressure gives, however, a measurement of the volatilisation tendency of the pure pesticide in its condensed state from inert surfaces [29], and is probably only useful as an indicator of volatilisation from highly concentrated spray deposits. A more appropriate indicator for many situations may be the Henry's Law Constant [30], which is a measure of the volatilisation tendency of a pesticide from dilute aqueous solution, and has been used to group pesticides into various classes [31]. Since water is ubiquitous in soils and on plant surfaces, this gives a better prediction of volatility since those pesticides with a low vapour pressure and low solubility will have an appreciable Henry's Law Constant and will be subject to evaporative loss.

It is also interesting to note that Henry's Law Constants are usually very temperature sensitive and the values change diurnally and seasonally. Thus, diurnal variations in atmospheric concentrations have been demonstrated for endosulfan [32] and trifluralin [33]. Similarly, dieldrin and heptachlor showed a diurnal pattern in volatilisation from grass [34].

The use of this type of ranking is, however, limited since under real conditions the cultivation practices and the formulation type can influence the extent of evaporation [35]. In addition substances can be adsorbed on to soil surfaces which will tend to reduce evaporation, e.g. it has been shown that as soil surfaces dry volatilisation slows due to increased adsorption [36], whilst on plant surfaces, especially from relatively rough leaves such as bean and wheat plants, evaporation can be significantly more important when compared to evaporation from soil [37–39], Leaf wax can also have an effect on volatilisation as the more lipophilic pesticides will tend to be dissolved in it [40,41], Pesticides will also occur bound to small particles or in aerosols in the atmosphere as a result of spray drift or wind erosion of

treated soil. Thus, the use of vapour pressure or even of the Henry's Law Constant cannot be used alone to predict the occurrence of pesticides in the atmosphere.

Studies have been carried out under laboratory and simulated field conditions [39,42–44] to simulate volatilization of pesticides under true field conditions. Similarly, studies have also been carried out under controlled conditions in the field [24,45], Laboratory and field procedures for assessment of the inherent tendency of pesticides to volatilise into the air have also been proposed [46] and compared [47,48], Whilst these types of studies can provide a means of evaluating the effects of various microclimatic parameters they are not easy to carry out, particularly for pesticides with low volatility, and results must be interpreted with care.

## 2.2 Deposition of pesticides from the atmosphere

Deposition of pesticides from the atmosphere is a complex process occurring through wet and dry deposition. It is recognised that dry deposition, i.e. as particulate matter, generally accounts for a relatively small part of the total deposition of pesticides from the atmosphere [49–53].

Volatilisation of pesticides creates gaseous concentration gradients, spreading vertically and laterally from application sites, which may be reflected in the concentrations in the local rainfall. Scavenging, in relation to such gradients, would explain the spatial and temporal variations observed [49].

It has been proposed [51] that removal of pesticides from the atmosphere by wet deposition is a combination of in-cloud scavenging and below cloud scavenging. However, the effectiveness of in-cloud scavenging should be many times higher and thus one would expect no dilution with precipitation. This has been borne out by Chevreuril *et al.* [54] but not in other studies where the highest concentrations were found at the beginning of the rainfall event [49] or where higher concentrations were found when precipitation was low and vice versa [55].

A monitoring study for atrazine, cyanazine and alachlor showed that their concentrations rapidly decreased during the first three hours of a rainfall event but the atrazine and alachlor concentrations then returned to high values in the samples collected 7 and 9 h after the beginning of the rainfall period [56]. According to Richards *et al.* [57] these types of results might be related to the variability in fallout quality that depends on the cloud heterogeneity of the atmosphere rather than on a reduction in the atmospheric stock during the rainfall period.

Very simply, differences in the concentrations of pesticides found in rainfall depend on whether their presence arises from in-cloud scavenging, below cloud wash out or a mixture of both mechanisms. These in turn will depend on whether the pesticides are present in the gas phase, as aerosols or absorbed to solid particles. In-cloud scavenging will tend to give a more constant concentration during a rainfall event, and can lead to an enrichment process due to the formation of an organic layer around the droplets facilitating transfer of the pesticide into the droplet [58], whilst below cloud washout will tend to give a peak concentration at the start of a rainfall event. Under normal environmental conditions a mixture of the two processes can be used to explain results which differ from these two simple scenarios.

## 3 DEGRADATION OF PESTICIDES IN THE TROPOSPHERE

### 3.1 General considerations

Most pesticides are not inert compounds and they are able to undergo chemical degradation and transformation in the atmosphere that will decrease their concentration. For pesticides that do not readily hydrolyse photodegradation is the most important process for degradation in the atmosphere. Hydrolysis is relatively easy to measure under laboratory conditions and is not considered in detail in this paper. On the other hand photodegradation can be a complex process that is difficult to measure under experimental conditions.

The photodegradation and transformation of pesticides in the atmosphere can occur by direct and indirect photochemical reactions [59]. The degree of degradation depends on both the influence of environmental variables and the mode of transport, whilst meteorological conditions such as light intensity, duration of sunshine and spectral distribution of the incident light (especially the short wavelength cut-off edge) govern the degradation processes. Rate and mechanism may also be influenced

by the physical state of the chemical which might be mono-molecularly dispersed in the troposphere, adsorbed or absorbed on aerosols or exist as a homogeneous aerosol. These variables are further superimposed on the rate of removal from the troposphere to other environmental compartments by dry deposition, absorption and solution in water, and washout by rain.

A comprehensive OECD Monograph [60] gives the criteria to estimate if an organic molecule has the potential to be degraded photochemically, either indirectly or directly, in the air.

In indirect photolysis degradation of the pesticide occurs by reaction with photolytically generated radicals. In most cases this occurs through reaction with OH<sup>•</sup> radicals which generally react rapidly with the majority of organic chemicals [61,62], Reactions with other photolytically produced radicals, e.g. HO<sub>2</sub><sup>•</sup>, NO<sub>3</sub><sup>•</sup> are of lesser importance as a degradation pathway. Reaction with ozone is generally of secondary importance and only for low molecular weight unsaturated aliphatics may reaction with ozone in the troposphere be more rapid than reaction with OH<sup>•</sup> radicals. Indirect photolysis is predominant in air, especially for compounds which do not absorb solar UV-visible light under tropospheric conditions and cannot therefore undergo direct photolysis [63,64], The main transformation processes involving OH<sup>•</sup> radicals are the abstraction of reactive hydrogen atoms, addition to nonaromatic multiple bonds, addition to aromatic rings and reactions with nitrogen, sulfur and phosphorus moieties. The sequence of reactions for the abstraction of reactive hydrogen atoms starts with formation of water and an alkyl radical, this radical then reacts with oxygen to give an alkylperoxy radical which can yield the corresponding aldehyde or ketone. Further reactions with OH<sup>•</sup> radicals will give CO<sub>2</sub>, nitrogen dioxide as well as mono- and di-carboxylic compounds. The addition of OH<sup>•</sup> radicals to aromatic rings results in the formation of hydroxyaromatic compounds, hydroperoxy radicals or cleavage of the aromatic ring. Radicals formed can also react with nitrogen oxides and sulfur oxides present in the atmosphere.

The products formed upon photodegradation are more polar and of higher water solubility compared to the parent pesticide and, consequently, may be sorbed to aerosols, subjected to further degradation processes and/or washed out in rain. Since most pesticides contain one or more of the above moieties indirect photolysis is an effective way of removal, via degradation, from the atmosphere.

### 3.2 Direct photolysis

The estimation method for primary (direct) photolysis calculates the rate of light absorption as a maximum rate constant assuming a quantum yield of unity for all wavelengths where absorption occurs. Thus the absorption spectrum in the solar region, either calculated or experimentally determined, as well as the sunlight intensities at a given latitude have to be known. This estimation method gives the upper limit of direct photodegradation.

In the troposphere direct phototransformation may be rapid but only for a limited number of organic chemicals since the rate depends on the overlap between the solar light emission spectrum under tropospheric conditions, the light absorption spectrum of the compound and the quantum yield. The quantum yield, i.e. the fraction of molecules of an organic chemical that is transformed after absorption of a photon, is generally in the range of 0.1–0.001. However, it should be noted that whereas in the troposphere secondary photoreactions will predominate, primary photoreactions will occur more easily in the stratosphere due to the shorter wavelengths of light present < 290 nm. It has been suggested that for some chemicals, e.g. halocarbons, secondary reactions may be preceded by primary degradation processes in the stratosphere [65].

### 3.3 Indirect photolysis

As far as secondary (indirect) photolysis is concerned the different reactive species have to be considered individually. However, as previously stated the most important species is the OH<sup>•</sup> radical and several estimation methods have been proposed for this moiety [61,66–72]. In the most recent method, Atkinson [72] critically analysed the hydroxide radical data ( $k_{OH}$ ) for a large number of organic molecules and developed a number of SAR (structure activity relationship) methods based solely on the chemical structure of these chemicals. In developing these SAR methods he assumed that a number of OH<sup>•</sup> reaction pathways exist and that these can be separated and treated individually. Thus, rate constants can be calculated for each of these reaction pathways. The reaction pathways and rate constants for each of these

pathways are:

$$k_{\text{abstr}} = k \text{ (H-atom abstraction from C-H and O-H bonds)}$$

$$k_{\text{add}} = k \text{ (OH}^\cdot \text{ addition to C=C and C}\equiv\text{C bonds)}$$

$$k_{\text{arom}} = k \text{ (OH}^\cdot \text{ addition to aromatic rings)}$$

$$k_{\text{inter}} = k \text{ (OH}^\cdot \text{ interaction with N-, S- and P-containing groups)}$$

Atkinson postulated that the overall OH<sup>·</sup> rate constant  $k_{\text{OH}}$  is equal to the sum of the rate constants for each of these reaction pathways. Therefore, the OH<sup>·</sup> rate constant is given by the equation:

$$k_{\text{OH}} = k_{\text{abstr}} + k_{\text{add}} + k_{\text{arom}} + k_{\text{inter}}$$

where  $k_{\text{abstr}}$ ,  $k_{\text{add}}$ ,  $k_{\text{arom}}$  and  $k_{\text{inter}}$  are expressed in cm<sup>3</sup>/molecule/s

If the mean concentration of OH<sup>·</sup> radicals is known then, using the calculation model AOP (Atmospheric Oxidation Program), values can be calculated for the half-life of pesticides in air [71], see Table 2 [73].

**Table 2** Half-life of selected substances in the atmosphere\*

Substance	Half-life (days)
Atrazine	0.11
<i>N</i> -de-isopropylatrazine	0.18
<i>N</i> -de-ethylatrazine	0.16
Terbutylazine	0.12
Fenpropimorph	0.12
Pendimethalin	0.17
Propiconazole†	0.27
Lindane	12
DDT	4.4
DDE	2.3
DDD	3.3

\* Calculated with AOP Version 1.4 [W. Meylan & P. Howard. Syracuse Res. Corp., NY 13210, USA].

† 5-membered ring could not be calculated; it was simulated by a slightly reactive methyl group.

It should be noted that rate constants are generally calculated at 25 °C, whilst in the troposphere temperatures are much lower and the impact on the calculated half-lives must be assessed. However, these calculations do allow a comparison between different pesticides.

When considering ozone reactivity the reactions of ozone with multiple bonds and aromatic rings are taken into account. For these reactions an SAR method comparable to the estimation method for OH<sup>·</sup> has been developed [70].

The above mechanisms have been shown to be of relevance for monomolecularly dispersed molecules in the atmosphere. However, in the troposphere organic compounds with a relatively low vapour pressure are strongly attracted towards the very large surface areas of aerosols and water droplets. Adsorption on to, or solution into, these particles/droplets results in heterogeneous or condensed phase conditions [59]. In addition pesticides entering the troposphere via spray drift, wind erosion or being aggregated in the course of their transport or transformation processes can also occur as aerosols. Macroscopically they also exist as dusts, smokes or fogs. These conditions may be responsible for either lowering, via enclosure, scavengers, quenching effects, or increasing via catalytic effects, photosensitizers, the rate of the phototransformation processes. As an example, adsorption by water droplets can affect the rate of secondary photolysis by formation of H<sub>2</sub>O<sub>2</sub> which will increase degradation and transformation [74], e.g. it has been found that MCPA has a half-life of 3.9 h in droplets suspended in sunlight [75]. Because of the exceptional physico-chemical state of chemicals in aerosols, mechanisms of photodegradation in the



gaseous, aqueous or solid/adsorbed phase give only limited information on the specific photodegradation mechanisms of aerosols. Investigations should therefore be carried out either using isolated droplets or in aerosol smog chambers under environmentally relevant conditions, neither of which are easy to perform experimentally. Where measurements of the reaction kinetics of pesticides in model chambers have been carried out longer half-lives may be obtained compared to those calculated, e.g. lindane. This will explain why certain pesticides have been shown to undergo long to medium range transport even though their calculated half-lives in the troposphere are relatively short. It has been suggested [76] that if a calculated half-life is greater than 2 days the pesticide should be considered persistent.

### 3.4 Experimental techniques

In general, investigations into the photolytic behaviour of pesticides in air are carried out in a stepwise manner:

- firstly on experimental estimation methods, i.e. calculations using spectral data and structure activity relationship (SAR) constants to determine dominant reaction paths;
- secondly on further laboratory tests to measure values for the respective reaction constants;
- thirdly on tests in outdoor chambers and/or field studies.

Various test methods have been used to measure experimentally rate constants for direct photolysis and OH<sup>-</sup> rate constants, however, these do not cover all variables influencing the rate and mechanisms of photodegradation [60]. This is particularly true for the behaviour of compounds sorbed on aerosols and substances with low volatility, although relatively simple methods for studying photodegradation on aerosols have been developed [77]. Only for exceptional cases have detailed studies using highly sophisticated equipment such as aerosol smog chambers or chambers simulating special environmental conditions been used so far. Such experiments, which mimic, for example reactions in the condensed phase, may in some cases be helpful for the description of the photolytic behaviour of a pesticide in air and its removal from the atmosphere. Thus in one study [78], which investigated the fate of different pesticides under simulated atmospheric conditions and field conditions, the substances were vaporised in a special chamber and irradiated with UV-light, in some cases in the presence of ozone. During the field study downwind air was sampled at defined distances from a treated field. The results indicated that conversions in air are predominantly oxidative and that rates of conversion are rapid with, in some cases, half lives of a few minutes.

## 4 PREDICTIVE MODELLING OF PESTICIDE CONCENTRATIONS IN THE ATMOSPHERE

Organic pollutants, including pesticides, are either released into or, by volatilisation, diffuse into the lowest part of the atmosphere in direct contact with the surface, the planetary boundary layer (PBL). This plays a critical role in the vertical movement and horizontal distribution of airborne pesticides and is subject to diurnal fluctuations in height and stability. Movement from this layer into the upper atmosphere, leading to potential widespread regional and world-wide distribution, can occur through instabilities in the PBL [20]. Once in the upper atmosphere the global wind circulation patterns, including the westerlies, NE and SE trade winds and the polar fronts promote regional transport of pesticides. Local transport will take place in a matter of minutes, regional transport in hours or days, intrahemisphere transport in months and interhemisphere transport may take a year [79].

In general terms the factors which govern entry of pesticides into the atmosphere have been elucidated [20]. However, the number and interdependencies of these parameters, together with the inherent variability in, for example, application techniques, formulation type, environmental surfaces, agricultural practices, meteorological conditions, etc. lead to an extremely complex system which cannot be described in simple terms.

In order to try to understand and predict the appearance of pesticides in the atmosphere it is necessary either to measure each parameter separately, for a given active substance and its application, over a range of scenarios and farming practices with subsequent integration, or to carry out large scale field experiments in which several of the processes could be considered as already being integrated. In either of these extreme cases a large amount of data would be required in order to give meaningful extrapolation to

other conditions [80]. Ideally therefore a mathematical model is required that will accurately predict volatilisation, transport, degradation and deposition using realistic scenarios.

#### 4.1 Modelling pesticide spray drift

Predictive modelling of spray drift has been extensively described by Hashem & Parkin [81] and Thompson & Ley [82]. However, no one model yet exists which allows the complete understanding of atmospheric drift. As a result there are many published drift models and databases from various countries such as Germany [83–85], Netherlands [86–88] and the UK [89–92].

In the US, the Environmental Protection Agency and a group of 32 manufacturers have collaborated on a joint project, the 'Spray Drift Task Force', in which resources were pooled to develop a single proprietary database which is used to estimate drift [93–95]. Assuming that drift is more a function of equipment, formulation and environmental conditions than of active ingredient, the result is a 'generic' database which may be used by all of the co-operating manufacturers to develop drift data required for registration. A significant finding with aerial application [93] is that under normal application conditions (where winds are suitable for application), droplet size distribution is more important than wind speed in controlling drift. The Task Force is also evaluating the US Department of Agriculture Forest Service's FSCBG/AGDISP (Forest Service Cramer-Barry-Grim and Agricultural DISpersion Prediction) models [96] and the Dow AgroSciences model DESDM (DowElanco Spray Deposition Model) [97].

Work is continuing in the area of spray drift using a combination of interpolative modelling and relevant experimental data to predict the deposition rate ( $\mu\text{g}/\text{m}^2$ ) relative to the target rate on fields. Several generic models have been developed on the basis of this work which can be used to predict spray drift (on a surrogate basis) in the proximity of the target area.

#### 4.2 Modelling pesticide volatilisation

##### 4.2.1 Specific models

Various examples of mathematical models exist in the literature for predicting volatilisation of pesticides on a local or national basis. A complex model, GEMS/PCGEMS (Graphical Exposure Modelling System), with many subprograms, set up by the US Environmental Protection Agency [98], can simulate entry of chemicals into air, soil and groundwater and is used to estimate pollutant exposures. To support the model, databases such as weather and wind statistics and different soil types are included. The subprograms allow the determination of different parameters required for the program such as hydrolysis, Pow, degradation, etc. and include EXAMS II (Exposure Analysis Modelling System), SESOIL 4 (SEasonal SOIL compartment), etc. Despite its complexity this program could play an important role in assessing the entry of pesticides into air. The model EXAMS has been used to describe and predict the volatilisation rate from water as measured in a laboratory chamber and in flooded rice fields [99].

Similarly a modification of the model LEACHM, LEACHV (LEACHing Estimation and Chemistry Model) has been developed to simulate vapour phase advection of pesticides such as the relatively volatile soil fumigant 1,3-dichloropropene [100]. A model developed by Burkhard & Guth [101] has also been used to determine volatilisation from soil. This model uses soil parameters, including water content, to calculate volatilisation from a wet field by consideration of the soil adsorption and water evaporation. A correlation with laboratory investigations gave correlation coefficients of  $>0.99$ . An excellent approach to modelling the rapid then slow dissipation of pesticides from soil that occurs during volatilisation has been described by Hill & Schaalje [102]. A more general model, such as AMSIVOL. (AgrarMeteorological Simulation of VOLatilisation) [103], which takes into account meteorological parameters can be used to calculate the daily flux density of the emission of pesticides.

Several models have been developed in an attempt to predict the degree of transport under various conditions.

The model SAMS (Screening Assessment of Model Systems) [104] includes the atmospheric transportation from surface and point sources under constant atmospheric and meteorological conditions. For emissions from areas with several treated agricultural areas the 'box-model' can be used. The model considers dilution through wind and reduction through deposition and photochemical degradation and

calculates a steady state concentration in air. A model entitled DRANC (Dutch Risk Assessment of New Chemicals) [105] has been set up with the specific environmental conditions of the Netherlands. In this model estimates of exposure are carried out for a local sector with a standard environment based on a point source with continuous emission. The drawback of using a point source scenario can be overcome if the distance between the grid points of the sources is small enough. This model is a good starting point for estimating concentrations in air, especially for an assessment of the effect of airflow, however, since the parameters are based on specific Dutch conditions it is difficult to transfer the model to other countries. Another local model is ADMS (Atmospheric Dispersion Modelling System) [106] which has been developed in the UK and serves to forecast the distribution of local emissions and relies therefore on the corresponding local data. This model will give information on air concentrations and deposition based on a steady state scenario. The meteorological data can only be varied with difficulty and it is not suitable for dealing with fogs.

A generic model based on atmospheric residence times, calculated from rates for wet and dry deposition and degradation in air, has also been used to determine the long range transport potential of various pesticides [107]. In this model a high atmospheric residence time is interpreted as indicating a high potential for long range transport, however, compounds with a high adsorption affinity are considered to be efficiently removed by rain and therefore their atmospheric residence time should be significantly reduced.

#### 4.2.2 Fugacity models

Several general models exist which are based on the volatilisation and subsequent equilibrium distribution of chemicals and which can be used to assess the likely concentrations of pesticides in various environmental compartments. These fugacity models are based on the 'unit world', i.e. a defined and limited geographic area, starting point with the entry of chemicals into the compartments water, soil, air and, in the more refined models, biomass. The Mackay model [108] in its simplest form (Level I) calculates the equilibrium concentrations in air, water, soil, sediment, suspended sediment and fish in order to give an indication of any medium in which accumulation is possible. The Mackay Level I model can be extended by adding a compartment for the terrestrial biomass [109]. The Level II version [110,111] simulates the situation whereby the chemical is delivered continuously into the multi-environmental medium and the rate of entry and exit are equal, whilst the Level III and IV versions are more complex and include transport from one compartment to another. A similar model is Chemfrance [112,113], based on the Mackay Level III model, which uses a set of base parameters pertinent to conditions in France. Similarly the model MNSEM (Multi-phase Non-steady State Equilibrium Model) [114] based on Japanese conditions, assumes a continuous entry of chemical into one or several environmental media which are linked so that in this model the phase air/water (raindrops) can also be included. This model does not take into account any degradation of the chemical and although it can be used to calculate transport of a chemical from one phase to another it does not calculate its removal.

Fugacity models have been used to predict environmental concentrations of pesticides and have given useful results. Thus the Mackay Level II model has been used to determine the environmental equilibrium distribution and levels of persistency of 20 organophosphorus insecticides [115]. The results from the model predictions indicated the correct order for air concentrations of these compounds. Similarly the model Chemfrance has been used to determine the environmental fate of atrazine [116] and lindane [117]. From these studies it was concluded that Chemfrance is a useful tool for estimating the environmental fate of organic chemicals in France [117].

A comparison has been made of the use of fugacity models and worst case calculations for estimating the atmospheric deposition of a number of organic pollutants, including organochlorine pesticides [118]. As might be expected it was found that the fugacity model, which took account of attenuation processes during atmospheric transport, predicted much lower levels of deposition compared to the worst case calculations.

### 4.3 Utility of models

In considering the utility of the various models it is clear that the various spray drift models can give an indication of local and generally short-term pesticide concentrations close to the site of application. The

results obtained can be used to determine likely effects on local ecosystems from applications and therefore be used to decide if preventative measures against contamination, e.g. buffer strips, are necessary.

The volatilisation and transport models can be useful on a local basis, either in predicting the degree of volatilisation, e.g. LEACHV, or in the transport away from treated areas, e.g. ADMS. However, of more general use are the fugacity models based on the unit world concept and the local variants devised for specific national conditions, e.g. Chemfrance. These models can be useful tools in predicting environmental concentrations of pesticides over defined regions [115–118]. However, it must be noted that for these models to give accurate predictions a significant amount of high quality data is required for the input parameters.

## 5 MONITORING OF PESTICIDES IN THE ATMOSPHERE

### 5.1 Pesticides in the atmosphere

There are many factors that influence the entry, transport and subsequent concentrations of pesticides in the atmosphere, including the extent and manner of application. Thus, the usage of a pesticide can have a significant effect on amounts present in the atmosphere, e.g. isoproturon is widely used in Europe and can be found in low concentrations in the atmosphere, despite its extremely low vapour pressure and Henry's Law Constant [50] and field and volatilisation chamber studies which showed only negligible amounts of volatile isoproturon [119]. In the USA pesticide concentrations in rainfall in midwestern and north-eastern states showed seasonal and geographic patterns related to use intensity [120]. There is now an increasing body of information available on the monitoring of pesticides in the atmosphere, particularly in rainwater. However, since the levels found are generally low (ng/L) this work presents a great challenge to the analytical chemist and in assessing the results it should be noted that the collection of samples, their subsequent handling and the method validation are not carried out to the same degree of quality control in all cases. The necessary precautions that are required when carrying out monitoring studies are given by Haugen & Oehme [121]. Studies have been carried out for fog [122–126], snow [50,127,128] and cloud water [129–131] but the largest amount of data has been collected for pesticides in rainwater, in which a large variety have been detected (Table 3).

**Table 3** Pesticides and some of their metabolites found in precipitation\*

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#### Organochlorine compounds

Aldrin, DDT (DDD and DDE), lindane (and other HCHs)

#### Phenoxy acids

2,4-D, dichlorprop, MCPA, mecoprop

#### Triazines

Atrazine (*N*-de-ethylatrazine, *N*-de-isopropylatrazine = *N*-de-ethylsimazine), cyanazine, propazine, simazine, terbutryne, terbutylazine

#### Others

Alachlor, azinphos-methyl, bentazone, butylate, carbaryl, chlorpropham, chlortoluron, cypermethrin, diazinon, dicamba, diclobenil, dimethoate, diuron, endosulfan, EPTC, fenvalerate (esfenvalerate), fluazifop-butyl, fonofos, isoproturon, malathion, metalaxyl, metolachlor, metoxuron, metribuzin, parathion, pendimethalin, phorate, pirimicarb, propachlor, prometryn, propiconazole, trichloroacetic acid (TCA), toxaphene, triadimenol, triallate, trifluralin, vinclozolin

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\* Taken from L. Torstensson [*Pesticides in Precipitation and Surface Water*, Vol. 558, p. 86, TemaNord (1995)].

The monitoring results indicate that pesticides in rainwater can be divided into three separate categories:

- (i) Pesticides that are relatively stable in the atmosphere and can undergo long range transport
- (ii) Pesticides that are less stable in the atmosphere but can undergo medium range transport
- (iii) Pesticides that are relatively unstable in the atmosphere and are rarely detected even close to areas of application.

As an indication of the pesticide levels found in rainwater, and the complexity involved in their transport, degradation and deposition, monitoring results obtained under different climatic and geographic conditions are given below for two pesticides (lindane and atrazine) that have been extensively studied.

## 5.2 Monitoring of lindane in rainwater

Lindane, which contains approximately 99% of the  $\gamma$ -isomer of hexachlorocyclohexane ( $\gamma$ -HCH), has a significantly longer half-life compared to other pesticides under photochemical conditions, see Table 2, and has been detected in remote areas such as the Arctic [132–133]. Lindane has been widely used as an insecticide in most parts of the world, although its use is now declining and in many countries it is either banned or severely restricted. In some countries, e.g. India, a less pure HCH is used which contains a large amount of the  $\alpha$ -isomer (70–80%) with smaller amounts of the  $\gamma$ -isomer (15–25%) and other isomers (5%). The use of this material could give rise to the  $\alpha$ -HCH found in rainwater and it is also reported that photochemical reactions in the atmosphere can convert  $\gamma$ -HCH to  $\alpha$ -HCH [2,3], with a concomitant decrease in the concentration of lindane in the atmosphere. In general, however, the monitoring results, particularly for Europe where technical HCH has been prohibited for many years, e.g. since 1979 in Germany, indicate that the amount of the  $\gamma$ -isomer is significantly greater than that of the  $\alpha$ -isomer in the same samples. An exception to this can be found from results obtained from the Atlantic region of Canada where ratio of  $\alpha$ -HCH to lindane ( $\gamma$ -HCH) are between 2.9 and 6.0. In this case long range sources (continental and global) are responsible for the appearance of the HCH isomers at this site [133]. Indeed it has been suggested that the ratio of  $\alpha/\gamma$  isomers can be a measure of the age of an air mass, with ratios from remote areas being greater than 1 [134].

Monitoring results for lindane indicate that it can be found at all periods of the year, nevertheless, there is evidence that peak concentrations often occur in spring/early summer which can be correlated with its usage. This is particularly true in areas of high usage, e.g. in mosquito control during the monsoon season [135]. Clearly lindane is relatively stable in the atmosphere and can be transported over considerable distances. Lindane has been reported as being widely distributed via the atmosphere [1] and is found in Arctic air and snow [136–138], where it is among the most abundant organochlorine compounds; in Finland results obtained in 1991/2 indicated that it was the most common pesticide in precipitation [127]. Table 4 gives some typical monitoring results reported as lindane ( $\gamma$ -HCH) in rainwater.

## 5.3 Monitoring of atrazine in rainwater

A typical example of pesticides that can be placed in the second category (pesticides that can undergo medium range transport) is the triazine family. These are herbicides that have been widely used since 1957, particularly in Europe and North America. They are used in agriculture with the most significant use being in maize, as well as for industrial use such as roads and railway tracks. Monitoring results have shown that several members of this family, including atrazine, cyanazine, simazine and terbutylazine, may occur in rainwater and undergo medium range transport [6,50,54,141,142]. However, the largest number of monitoring results are available for atrazine.

Atrazine is a widely used herbicide in both Europe and North America where it is applied during the spring and early summer, and globally is one of the most used pesticides although its use is now being restricted in several countries, notably in Northern Europe. It should have a relatively short half-life in the atmosphere, see Table 2, but as with other triazine herbicides, it appears that photolytic degradation may be slower in the environment [143,144] than under laboratory conditions [145], possibly due to its absorption on particles [129]. The occurrence of atrazine in rainwater has been extensively studied at sites both close and remote, i.e. at several hundred kilometers, to its use and many results, particularly from Northern Europe, have been reported (Table 5).

## 6 ASSESSMENT OF THE TOXICOLOGICAL AND ECOTOXICOLOGICAL SIGNIFICANCE OF PESTICIDES IN THE ATMOSPHERE

In assessing the toxicological and ecotoxicological significance of pesticides in air it is important to distinguish between those pesticides that have high use rates and those which are more active and have much lower use rates. The assessment of the toxicological and ecotoxicological significance must finally be done on a case by case basis since a highly active pesticide will have a bigger impact at a given

**Table 4** Monitoring results for lindane in rainwater

Country	Site	Av. conc. ( $\mu\text{g/L}$ )	Max. conc. ( $\mu\text{g/L}$ )	Ref.
France	Ferte <sup>s</sup> /Jouarre	–	0.35	54
	Paris	–	0.13	54
UK	Medmenham	0.0116	0.061	118
Finland	3 sites	–	0.02	127
Croatia	Zagreb	–	0.036	128
Canada	Ellerslie (1981)	0.0072	–	133
	Ellerslie (1985)	0.002	–	133
	Kejimkujik (1981)	0.0053	–	133
	Kejimkujik (1985)	0.0009	–	133
	Kejimkujik (1988)	0.0017	–	133
	Jackson (1985)	0.0009	–	133
	Jackson (1988)	0.0015	–	133
India	Delhi <sup>(1)</sup>	1.29	8.6	135
Germany	Kleinmachnow	–	0.25	139
	Hohenfinow	–	0.26	139
	Krielow	–	0.25	139
	Niedergörsdorf	–	0.36	139
	Ruhlsdorf	–	0.22	139
	Berlin-Dahlem	–	0.12	139
	Neuglobsow	–	0.12	139
USA	Hawaii	0.003	0.009	140

–: Not given.

\* Accounting for 24% of total HCH found, the high levels are probably due to its extensive use in mosquito control.

**Table 5** Monitoring results for atrazine in rainwater

Country	Site	Av. conc. ( $\mu\text{g/L}$ )	Max. conc. ( $\mu\text{g/L}$ )	Ref.
Germany	Dürnast (1990–92)	0.06–0.16	0.28–3.29	146
	Berg (1990–92)	0.20–0.43	1.14–4.18	146
	Waldhof (1991–92)	0.06–0.10	0.40–0.49	146
	Barenlochriegel (1991–92)	0.05–0.06	0.21–0.31	146
	Barenlochriegel (1991–92) forest	0.08–0.13	0.41–0.56	146
	Watzmann (1991–92)	0.03–0.04	0.04–0.05	146
	Watzmann (1991–92) forest	0.05–0.06	0.09–0.23	146
Sweden	Ekeröd	0.016	0.16	142
Norway	Lurbo	0.01	0.06	147
	Lista	–	0.086	147
	Ås	–	0.084	147
France	Ferte <sup>s</sup> /Jouarre (1991)	–	0.35	143
	Ferte <sup>s</sup> /Jouarre (1992–93)	–	0.11–0.38	54
	Paris (1991)	–	0.14	143
	Paris (1992–93)	–	0.25–0.40	54
Italy	Vallombrosa	–	1.99	148
	Renon	–	0.33	148
Switzerland	Lagen	–	0.60	6
	Zurich	–	0.25	149
USA	Iowa	0.91	40	49
	Iowa	–	1.5	49
	Maryland	–	2.2	5

–: Not given.

concentration compared to a less active pesticide at the same concentration. It is important therefore to bear in mind not only the concentrations of pesticides found in the atmosphere (and rainwater) but also their activity.

A distinction must be made between local transport, caused mainly by spray drift, and long distance transport away from the vicinity of the treated area. In the case of spray drift the local concentrations close to the area treated can be relatively high and precautions must be taken to avoid adverse effects on local ecosystems and non-target organisms. There are many documented cases of damage to neighbouring vegetation by spray drift, although damage is often superficial and the plants recover (for example [150–152]), The effects of pesticide drift have been studied in extensive glasshouse experiments monitoring the response of wild plant species to defined levels of pesticides in spray drift [153]. A study with chlorsulfuron (a low rate herbicide active at 10 g/ha) indicated that in unstable air non-target plants would have to be close (< 10 m) to the release of spray before significant biological effects would occur, even if aerosols were enriched in sizes < 100  $\mu\text{m}$  in diameter [154].

Long distance transport of pesticides through air and subsequent deposition away from treated areas decreases as distance from the treated area increases, but it can be an important source of contamination, albeit at low levels, in non-agricultural areas where there is little or no use of pesticides. However, in this case contamination is very diffuse and the effects are difficult to assess. One approach to assess the possible effects of pesticides in air on various organisms is based on likely maximum exposure from various scenarios. These scenarios can be divided into five classes:

- Direct effects on non-target plants;
- Direct effects on terrestrial invertebrates;
- Direct effects on aquatic organisms;
- Direct effects on animals;
- Indirect effects on organisms via the food chain.

### 6.1 Direct effects on non-target plants

The effect of a pesticide on a non-target plant will depend on species susceptibility, thus the uptake and development of phytotoxicity following exposure to 2,4-D butyl vapour by tomato and lettuce plants has been investigated under controlled conditions [155–156], The results obtained showed that these species are extremely sensitive to this material since, although visible symptoms of phytotoxicity only developed several days after the period of exposure, they were caused by a dose of the order of  $10^{-5}$  times the amount used in field application.

Grapes are also particularly sensitive to 2,4-D and this herbicide has been implicated in damage to vines in eastern Washington State [157] due to long range transport. Similarly, in Australia 2,4-D has damaged tomato plants [158] and in South Africa symptoms typical of those caused by auxin-type herbicides have been observed on vegetables [159]. In order to prevent the reoccurrence of this type of damage restrictions have been introduced on the use of these types of herbicides and/or their formulations and lower volatility esters, such as ethylhexyl, have also been developed for use in place of more highly volatile ones.

The uptake of pesticide vapour by plants has been examined in several studies. In a recent study [23] the uptake of fenpropimorph, chlorthalonil and parathion-ethyl was examined close to the borders of a treated field. The results showed that local concentrations in air differed in front of and behind a hedge due to the aerodynamic conditions around the hedge. Uptake of fenpropimorph and chlorothalonil by the leaves of the hedge was demonstrated and it was concluded that ecotoxicologically relevant concentrations on the leaves of the hedge cannot be excluded.

Studies have also shown that organic chemicals can be found on the surface and in leaves of non-target forest plants [152,160–162]. An extensive study using ponderosa pines [163] showed that the organophosphorus pesticides diazinon and chlorpyrifos accumulated significantly in pine needles, at the  $\mu\text{g/g}$  level, when exposed to their vapour in air, with average bioconcentration factors of approximately 10 000. Exposure both in chamber experiments and in the field indicated that the cuticular wax and the

remainder needle compartments are most likely to be the sites of residue accumulation. In a chamber experiment using spruce pines Figge, using the model compound tetrachlorethene, also showed concentrations in the needles in the  $\mu\text{g/g}$  level [164], however, the bioconcentration factors were much lower. This can be attributed to the greater concentrations of vapour present in the air in this study, as well as to differences in properties between tetrachlorethene, diazinon and chlorpyrifos. Whilst these studies show that forests could be potential sinks for certain pesticides they do not indicate what effects, if any, there could be on the trees themselves.

A study [165] with two deciduous woody species, *Carpinus betulus* L. and *Fagus sylvatica* L., was designed to measure any changes in physiological parameters, indicating plant stress, when the trees were treated with pesticides. In this study treatments were carried out twice monthly in the growing season for either three years (*Fagus*) or one year (*Carpinus*). A mixture of herbicides and insecticides were applied by overhead irrigation in concentrations such that the lowest dose was equivalent to the average concentrations registered after each rain episode sampled in two Italian forests. The results showed that, whilst there were effects at higher concentrations ( $10\times$  and  $100\times$ ), the changes in stomatal conductance, transpiration, photosynthesis and chlorophyll levels were not significant for *Carpinus* after treatment with doses similar to those found in rainfall. Similar results were obtained with *Fagus* where treatment at the low dose showed no changes in stomatal conductance, transpiration or photosynthesis, although a decrease in chlorophyll was measured. Thus, regular exposure to levels of pesticides found in rain did not cause significant damage. Although herbicides have been implicated in damage to forests [148,166] via long range transport there is no clear evidence conclusively demonstrating this. It should be noted that one herbicide, TCA (trichloroacetic acid), found in forest foliage and implicated in damage also arises from the atmospheric oxidation of airborne C-2 chlorocarbons [166,167].

In a comprehensive study the levels of atrazine and metolachlor were measured in rain samples, predominantly from the US corn belt [168]. The typical concentrations found (of the order of  $1\ \mu\text{g/L}$  or less) and the biological effects of precipitation into lakes, on to soil and on to plants were considered. The general conclusion was that the concentrations and deposition rates are a small fraction of LOEL (Lowest Observable Effect Level) and NOEL's (No Observable Effect Level).

The absence of any significant damage due to pesticides in rain is borne out by a comprehensive study [169] carried out in Germany which showed, using bioassay techniques with duckweed, mustard, and oats, that the threshold levels for effects in these species from alachlor, atrazine, dichlorprop, MCPA, mecoprop, metamitron, pendimethalin, simazine, terbutylazine and triallate were about 100 times the rainwater concentrations. These results are not surprising since typical monitoring values for wet deposition, the major route for deposition from the atmosphere, indicate deposition values for individual pesticides of  $<1\ \text{g/ha}$  per year [79,142,169,170], although an annual deposition of  $8\ \text{g/ha}$  has been recorded in the Netherlands for atrazine [170]. The amounts available to affect plants will be reduced by bioavailability and metabolism within the plant and soil, as well as by renewed evaporation. The total maximum exposure of plants to pesticides in the atmosphere away from the treated areas is therefore likely to be from zero to a few  $\text{g/ha/year}$  under most conditions. With this low exposure, effects on non-target plants would not be expected to be significant.

With low use rate herbicides significant damage of non-target species might be expected if they were to be deposited from the atmosphere at rates of a few  $\text{g/ha}$ , since many are used at rates of  $10\text{--}50\ \text{g/ha}$  for weed control. In one study [157] it has been postulated that chlorotic spotting on sensitive species (biomonitoring with sentinel plants) is due to the deposition of sulfonyl urea herbicides several kilometres from the site of application. Since sulfonyl urea herbicides have extremely low vapour pressures, combined with relatively high solubilities, the resulting low Henry's Law Constants indicate that significant volatilisation is unlikely, thus the distribution is thought to be due to the drift of aerosols.

In general, with the exception of the auxin-type herbicides, adverse impacts on plants due to pesticides in the atmosphere have not been observed, and are not expected given the extremely low concentrations present.

## 6.2 Direct effects on terrestrial invertebrates

Direct effects on invertebrates could occur through direct exposure to wet and dry deposition or, for soil dwelling organisms, by contamination of the soil by wet and dry deposition. For direct exposure wet



deposition is the most important route. Concentrations in rainfall of most pesticides are generally in the low  $\mu\text{g/L}$  range and would not be expected to have a significant impact on terrestrial invertebrates. As an example, snails, crustaceans, mayflies and caddis flies had over 90% survival rates when treated with MCPA and dichlorprop at 10 mg/L, some thousand-fold higher than concentrations found in rain [171]. With maximum levels of insecticides found in rainfall in the low or sub  $\mu\text{g/L}$  range [4], giving a rate of 0.2 g/ha for a rainfall event of 2 cm containing 1  $\mu\text{g/L}$  insecticide, it is also unlikely that these will have a direct effect on invertebrates.

For contamination of the soil the maximum possible exposure (mg/kg) can be calculated by taking the total deposition in a given period and assuming this is evenly distributed in the top 2.5 cm of soil which has a soil density of 1.2 g/cm<sup>3</sup>. Taking, as an example, a value of 1 g/ha/year, see above, this would indicate a maximum concentration of 0.003  $\mu\text{g/g}$  in soil. This concentration would be attenuated by chemical and biological breakdown, renewed evaporation, dissipation by air and water transport and possible incorporation below 2.5 cm. These values are substantially below those expected to have an effect on, for example, earthworms.

### 6.3 Direct effects on aquatic organisms

For water bodies, one approach is to consider that if the concentration of a pesticide in rainwater exceeds its NOEC (No Observable Effect Concentration) for the most sensitive organism there is a potential ecological risk [4]. A similar approach is to use the proposed European surface water criteria of ( $0.1 \times \text{NOEC}$ ) or ( $0.01 \times LC_{50}$ ) which builds in a significant safety factor. However, this is not a realistic approach as it assumes that there is no dilution of the pesticide concentration in the rainwater by the water body itself. Dilution factors may range from one (primary streams receiving large volumes of run-off from a watershed) to several orders of magnitude (large bodies of water receiving an insignificant fraction of their volume from a remote precipitation event). For example, taking into account the dilution effect of the water body the reduction in concentration compared to that present in the rainwater will be in the order of 50 times, assuming a 2-cm rainfall event on a 100-cm deep water body. Expected maximum concentrations due to deposition of pesticides from the atmosphere would therefore be less (and usually very much less) than 50 ng/L (see Table 5). Even taking this value the concentration is less, and usually significantly less, than the NOEC for sensitive species and various pesticides, e.g. daphnia (cypermethrin [172], diuron [173], permethrin [174], pirimicarb [172]), algae (dichlobenil [173], terbutylazine [173]), phytoplankton (atrazine [174]) and aquatic plants (dichlorprop [175], MCPA [175]). Similarly the value is also significantly below the  $LC_{50}$  of various insecticides and herbicides for fish species [176].

### 6.4 Direct effects on animals

For pesticides in air the predominant route of exposure is by inhalation. Pesticides may also be absorbed through the skin but this route of entry is limited largely to substantial direct contact between a liquid form of the pesticide and the skin.

Levels of pesticides found in air, when detected, are generally in the low or sub  $\mu\text{g/m}^3$  (ng/L) range (e.g. [23,159,177]), these concentrations are well below those measured as  $LC_{50}$  values in acute toxicity inhalation studies [176], e.g. parathion (50  $\mu\text{g/L}$ ), diazinon (3500  $\mu\text{g/L}$ ),  $\alpha$ -cypermethrin (320  $\mu\text{g/L}$ ), atrazine (> 5800  $\mu\text{g/L}$ ), acetochlor (> 3990  $\mu\text{g/L}$ ), MCPA (> 6360  $\mu\text{g/L}$ ). It has been demonstrated that in fog water there can be an enrichment of pesticides compared to levels in air [125] and enrichment factors of between approximately 2 and 60 were demonstrated for organophosphorus insecticides in two areas of California [52,178], Enrichment factors of around 3000 were demonstrated for a few products, e.g. pendimethalin [125], however, even in these cases the concentrations in the fog water were less than the  $LC_{50}$  values for inhalation toxicity. In this study a high level of paraoxon, an oxidation product of parathion, was found in fog water in one location and it is suggested that this concentration is of concern because of cholinesterase inhibition. In general, there appears to be little need to be concerned about toxic effects, acute at least, from even the highest recorded concentrations in fog [126]. The main reason for this arises from the fact that there is little actual water even in a dense fog (maximum 0.3 mL/m<sup>3</sup>) and therefore the amount of fog water consumed by a human or bird would be very low relative to their body weight. However, data are needed to verify this since, for example, bird respiration may be much higher

than humans, exposure through bird lung tissues may be direct and the exposure duration would normally be longer [126]. In one study [179] red-tailed hawks captured during the dormant spraying period in California were found to show effects from organophosphorus exposures with reduced blood cholinesterase activity, however, the mechanism of uptake was determined to be through the feet of the birds as they landed on branches treated with dormant oil sprays and there appears to be little evidence that inhalation was the major route of exposure.

A comprehensive study has been carried out in a cotton growing area of Queensland, Australia, in order to determine the exposure of the local population to pesticides used during the growing season [177]. Cotton is one of the most intensively sprayed crops and it is common for a single cotton crop to be sprayed up to 9–14 times per season. In this study 17 separate insecticides were used and almost all were applied to the cotton crop by fixed-wing aircraft. Air samples were taken in urban areas close to the cotton fields. Analysis of these samples showed that endosulfan and methyl-parathion were the major insecticides detected, accounting for 92.6% of the positive results. In this study heptachlor, used for termite (white ant) control in the subsurface treatment of concrete slabs on building sites, was also detected. The results obtained were compared with the WHO recommended ADI which, although based on ingestion, was considered appropriate to interpret intake by other routes, in particular inhalation, where the substance does not have any additional respiratory health effect [177]. The conclusions drawn from this study were that the background average seasonal exposure of the local community to aerially applied insecticides was estimated, on a worst case scenario basis to comprise no more than 0.2% of the WHO recommended ADI for each insecticide detected during the study, and that the background maximum daily exposure, on a worst case scenario basis, comprised less than 1.0% of the WHO recommended ADI for insecticides except endosulfan, where the value was about 5%. Thus, the background exposure of the local community was very low and was not considered to pose a risk to public health.

## 6.5 Indirect effects on organisms via the food chain

For land animals exposure could occur via the ingestion of plants contaminated by deposition of a pesticide from the atmosphere. According to Bates [180] residue studies on grass, which gave the highest residue for treated plants, showed that treatment with a pesticide at 1000 g/ha gave an initial residue of 100 mg/kg. Thus, on this basis, assuming an annual deposition of 1 g/ha, the maximum residue would be 0.1 mg/kg. In the worst case the diet of an animal would consist of 100% of the contaminated plants and would therefore ingest this residue level. Clearly, the actual intake would be attenuated by a varied diet, degradation and growth dilution in the contaminated plants and lower contamination in the rain. Even with this artificial 'worst case' scenario, it is unlikely that these levels would pose a problem to land animals.

For animals that ingest aquatic species exposure could occur through ingestion, for example, fish that had concentrated the pesticide. Thus if the concentration in water due to contaminated rain is 50 ng/L (see Section 6.3) and there is a bioaccumulation factor of 1000 this would approximate to a residue level in the fish of 50 ng/g (i.e. 50 p.p.b.). If it is assumed that the animal eats fish equivalent to 1/10 of its body weight the residue is 'diluted' by a factor of 10 and the daily exposure is therefore 1/10 of the residue level in the fish. Again this maximum level of residue is unlikely to pose a problem to animals eating aquatic species as long as the pesticide is not further bioaccumulated. Clearly, the actual intake would be attenuated by degradation in the water, binding to the sediment and lower levels of contamination in the rain.

However, under certain conditions there is a potential for the bioaccumulation of pesticides, which are long lived and lipophilic in nature, in the food chain. The major source of organic pollutants, including long lived organochlorine insecticides, in the Arctic is long range transport via air currents, followed by cold condensation [19,181,182]. In this region levels of organochlorine insecticides are found at higher levels in human milk compared to populations living outside this area [181] which have given rise to concern for breast fed babies [181]. The results can be explained by the deposition of the insecticides into the Arctic ocean which is very oligotrophic (low nutrient system). Thus the lipophilic molecules are taken up by the available plankton, biomagnification then occurs as the plankton are consumed by fish, the fish by seals and fish and seals by the indigenous population. This effect appears to be as a result of the particular nature of the Arctic environment and there is evidence that as organochlorine uses reduce there is a decrease in the exposure of the local population.

## 7 CONCLUSIONS AND RECOMMENDATIONS

### 7.1 Conclusions

- 1 Available information on pesticides in the atmosphere.** The fate and behaviour of pesticides in the atmosphere have been extensively studied and there exists a large body of published information on their distribution and possible effects on ecosystems.
- 2 Occurrence of pesticides in the atmosphere.** The occurrence of pesticides in the atmosphere depends on many factors including their Henry's Law Constant, their stability to hydrolysis, direct and indirect photolysis, the application method and timing and the total amount used in a given region.
- 3 Removal of pesticides from the atmosphere.** Hydrolysis and indirect photolysis can play a major role in the degradation of pesticides in the atmosphere. The rate at which indirect photolysis occurs can be estimated using published methods. The major route for the deposition of pesticides from the atmosphere is by wet deposition via rainwater, with dry deposition being of only minor importance.
- 4 Estimation of concentrations of pesticides in the atmosphere.** The relative distribution of pesticides in air, soil, water and biota can be calculated for a defined region using fugacity models, as long as sufficient data of a high quality are available.
- 5 Typical levels of pesticides found in the atmosphere.** Levels of pesticides found in air, when detected, are of the order of  $\text{ng/m}^3$ . In rainwater maximum levels may reach several  $\mu\text{g/L}$  but, when detected, average levels are generally in the sub  $\mu\text{g/L}$  level.
- 6 Potential impact of pesticides in the atmosphere on environmental compartments.** The impact of pesticides from the atmosphere on environmental compartments is not significant under most conditions. Cases have occurred in the past of damage to non-target plants due to the volatilisation and subsequent transport of auxin type herbicides. This phenomenon is well known and the risk has been alleviated by restrictions on their use and use of nonvolatile formulations. For animal species one possible exception has been postulated. This is for persistent organochlorine pesticides in Arctic regions where, due to the very oligotrophic nature of the Arctic ocean, they are more liable to bioaccumulate and be transported in the food web giving enhanced levels in mothers' milk.

### 7.2 Recommendations

Based on the conclusions from this review, several recommendations for further areas of research are suggested. Since the factors governing the fate and behaviour of pesticides in the atmosphere are the same for any organic contaminant, whether from natural or anthropogenic sources, research studies on pesticides in air should be considered in the same way as any organic contaminant in the atmosphere.

- 1 Investigations should be encouraged into obtaining a better understanding of cloud chemistry and its role in the long and intermediate transport of organic contaminants, including pesticides.
- 2 Investigations should be encouraged into the application of fugacity models in the prediction of atmospheric concentrations of organic contaminants, including pesticides, in defined areas due to long range transport.
- 3 In order to refine and validate current models specifically for pesticides additional investigations are required into:
  - the chemical reactivity of pesticides, particularly their photodegradation, under environmental conditions.
  - the transfer of pesticides between environmental compartments to give the key factors leading to their occurrence in the atmosphere.
  - the parameters required to define the 'unit world', i.e. an identified and limited geographic area, for use in fugacity models.
- 4 Since pesticides, as with all anthropogenic organic contaminants, will have an impact on sensitive ecosystems it is essential that steps are taken to ensure that they will not be distributed by long range

transport in concentrations likely to pose a risk to non-target systems. It is recommended therefore that:

- an assessment scheme is developed and validated to determine which pesticides show volatilisation behaviour and hydrolytic and photolytic stability which would indicate an extended residence time in the atmosphere.
- for pesticides likely to have an extended residence time in the atmosphere assessments are carried out using fugacity models to predict their likely distribution in defined geographic areas.

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