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Pesticides in rainfall in Europe

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"Capsule": *Lindane was the most commonly detected pesticide.*

Abstract

Papers and published reports investigating the presence of pesticides in rainfall in Europe were reviewed. Approximately half of the compounds that were analysed for were detected. For those detected, most concentrations were below about 100 ng/l, but larger concentrations, up to a few thousand nanograms per litre, were detected occasionally at most monitoring sites. The most frequently detected compounds were lindane (γ-HCH) and its isomer (α-HCH), which were detected on 90–100% of sampling occasions at most of the sites where they were monitored. For compounds developed more recently, detection was usually limited to the spraying season. A classification of pesticides according to their deposition pattern is proposed.

Keywords: Pesticide; Precipitation; Deposition; Rain; Review

1. Introduction

Some organic molecules have the potential to spread world-wide via atmospheric transport and subsequent deposition. Organic contaminants have been found repeatedly on every continent and DDT (1,1-dichloro-2,2-bis[4-chlorophenyl]-ethane) and other organochlorines have even been found in Arctic and Antarctic air, snow, ice, fish and mammals (Chernyak et al., 1996; Harner, 1997; Kallenborn et al., 1998; Li et al., 1998). First evidence of the presence of organochlorines in rainfall was reported in the mid-1960s in England (Abbott et al., 1965; Wheatley and Hardman, 1965; Tarrant and Tatton, 1968). Aerial transport and deposition of pesticides is not limited to organochlorines and a wide range of compounds for which analyses have since been carried out have been found in air or in rainfall. Emission of pesticides into the atmosphere can result from drift and volatilisation during spraying, from post-application volatilisation from treated crops and soil, from wind erosion of soil particles carrying sorbed pesticides and from re-suspension of pesticides previously deposited from the atmosphere. The continuous cycle of transport, dry and wet deposition and re-volatilisation leads to the widespread dispersion of molecules with high vapour pressure and low water solubility such as organochlorines (Oehme, 1991a). Wet and dry deposition of pesticides have been intensively investigated in the north-American Great Lakes area (Hoff et al., 1996). It appears that concentrations of volatile organic chemicals in the Great Lakes are close to a state of long-term equilibrium with the atmosphere, but are in a constant state of short-term seasonal adjustment (Mackay and Bentzen, 1997).

The occurrence of pesticides in the atmosphere and their subsequent deposition have been increasingly investigated in European countries in the last decade. Wet deposition has been particularly monitored as dry deposition contributes to only a minor extent to the total deposition of pesticides (Siebers et al., 1994). This paper reviews recent published studies investigating the deposition of pesticides in rainwater in Europe, and discusses their implications with respect to potential environmental impacts and the possibility of predicting long-range transport and deposition.

2. Materials and methods

A total of 28 European studies from 10 European countries were reviewed. The main characteristics of the studies are summarized in Table 1. Location of the sampling sites within Europe is shown in Fig. 1.

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Table 1
Selected characteristics of the 28 studies reviewed

Reference	Country	Compartment	No. of sites	Study period	No. of pesticides monitored	Type of deposition monitored
Fingler et al. (1994)	Croatia	Rain/snow	4	Dec. 1990–Jun. 1992	8	Total
Cleeman et al. (1995)	Denmark	Rain	4	Jan. 1990–Feb. 1993	2	Total
Kirknel and Felding (1995)	Denmark	Rain	2	May 1992–May 1994	10	Total
Hirvi and Rekolainen (1995)	Finland	Rain/snow	3	May 1991–Nov. 1991 May 1992–Oct. 1992	90	Total
Trautner et al. (1992)	France	Rain/cloud	2	May 1991–Jul. 1991	1	Wet only
Chevreuil et al. (1996)	France	Rain/air	2	Jan. 1992–Sept. 1993	21	Total
Millet et al. (1997)	France	Rain/air/fog	1	Dec. 1991–Feb. 1993	13	Wet only
Oberwalder et al. (1991)	Germany	Rain	2	Apr. 1985–Nov. 1986 Mar. 1988–Aug. 1988	>9[a]	Total + wet only
Siebers et al. (1991)	Germany	Rain	3	Mar. 1990–Mar. 1991	7	Total + wet only
Gath et al. (1992)	Germany	Rain	1	Mar. 1990–Mar. 1991	6	Total + wet only
Scharf et al. (1992)	Germany	Rain	3	May 1990–Aug. 1991	34	Total
Gath et al. (1993)	Germany	Rain	3	Oct. 1990–Oct. 1991	7	Total + wet only
Stähler (1993)	Germany	Rain	7	Apr. 1991–Dec. 1991	8	Total
Scharf and Bächmann (1993)	Germany	Rain	3	Apr. 1991–Nov. 1991	23	Wet only
Siebers et al. (1994)	Germany	Rain	3	Mar. 1990–Mar. 1992	11	Total + wet only
Bester et al. (1995)	Germany	Rain	5	Apr. 1993–Jul. 1993	12	Total
Jaeschke et al. (1995)	Germany	Rain	3	Mar. 1990–Mar. 1992	7	Total + wet only
Hüskes and Levsen (1997)	Germany	Rain	2	Apr. 1992–Nov. 1992	59	Total + wet only
Trevisan et al. (1993)	Italy	Rain/air	4	May 1988–Oct. 1988	12	Total
Lode et al. (1995)	Norway	Rain	3	Jun. 1992–Sept. 1992 May 1993–Sept. 1993	9	Total
Brorström-Lundén et al. (1994)	Sweden	Rain/air	1	Jan./Feb. 1989 Feb. 1990, May 1990	3	Total
Kreuger (1995)	Sweden	Rain	3	1990–1992	31	Total
Buser (1990)	Switzerland	Rain/snow	Various	Feb. 1988–Jun. 1989	10	Total
Clark and Gomme (1991)[b] Fisher et al. (1991)[b] Gomme et al. (1991)[b]	UK	Rain	3	Mar. 1987–Oct. 1988	20	Total
Harris et al. (1992)	UK	Rain/air	1	Jan. 1991–Mar. 1992	6	Total + wet only
Johnson et al. (1996)	UK	Rain	1	Nov. 1993–May 1994	1	Total

[a] Exact number of pesticides monitored not specified in the paper.
[b] The three papers present the same information.

2.1. Choice of sites

In the studies reviewed, the criteria used to select sites for monitoring included land use, pesticide usage in the area, accessibility, altitude, proximity to large water bodies and the direction of prevailing winds. Some studies used a single site because of its comprehensive instrumentation for other purposes (Harris et al., 1992; Brorström-Lundén et al., 1994; Millet et al., 1997), but most studies included two or three sites chosen for their contrasting characteristics such as urban versus rural location (Oberwalder et al., 1991; Chevreuil et al., 1996), urban versus suburban (Fingler et al., 1994), intensive versus extensive agriculture (Siebers et al., 1994), agricultural versus semi-natural (Kreuger, 1995; Lode et al., 1995) or lower versus higher altitudes (Buser, 1990; Trautner et al., 1992). The study of Stähler (1993) is unique in that pesticide deposition was monitored at seven different sampling sites chosen according to the main activity around the site (a nature reserve without any local pesticide usage, an agriculturally intensive region close to a nature reserve, an agriculturally intensive region close to a pesticide storage site, a town suburb, two typical agriculturally intensive regions and a town centre). A number of studies were aimed at determining the atmospheric inputs of organic contaminants to the North Sea and sites were, therefore, chosen along the coast (Wells and Johnstone, 1978) or at increasing distances from the coast (Bester et al., 1995). Trautner et al. (1992) monitored atrazine on the western slope of the Vosges because these mountains induce a rise of air masses that have travelled over intensive agricultural areas of France, leading to condensation and formation of clouds.

2.2. Choice of pesticides monitored

As with the choice of sites, the number and nature of pesticides monitored depended upon the objectives of the study. Some studies concentrated on a limited number of

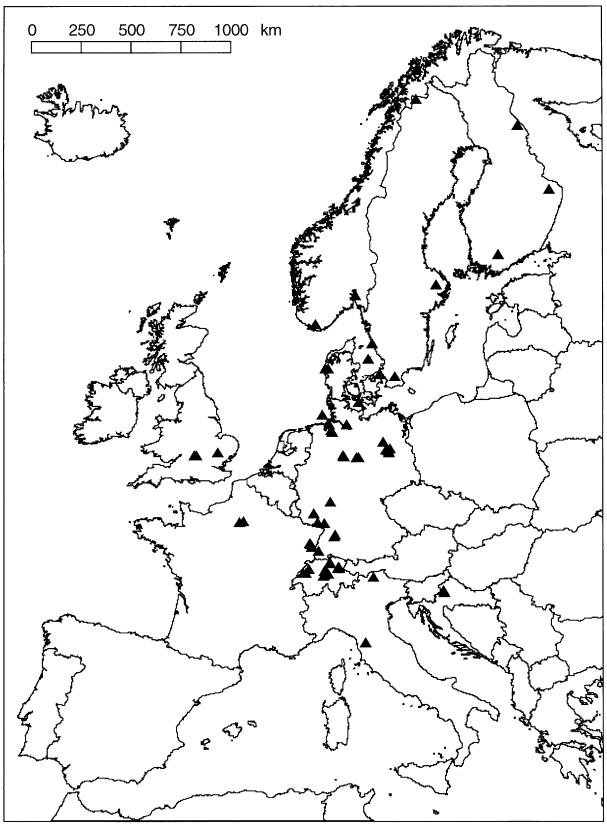


Fig. 1. Map of Europe showing the sampling sites for the 28 studies reviewed.

target pesticides (Trautner et al., 1992; Cleeman et al., 1995) whilst others performed a broad screening of up to 90 different molecules (Hirvi and Rekolainen, 1995). Most studies have concentrated on about six to 12 molecules because of the cost of analysis. Research has usually been focused on the most commonly used pesticides either in the agricultural area around the studied sites (Siebers et al., 1994) or in the country concerned (Buser, 1990; Oberwalder et al., 1991; Harris et al., 1992; Scharf et al., 1992; Chevreuil et al., 1996). A number of pesticides that are not used in the vicinity of the sampling sites but which have been detected elsewhere are often added to the list for analysis. Examples include compounds such as atrazine and organochlorines that have been banned from use in Nordic countries, but have nevertheless been shown to be present in the atmosphere (Cleeman et al., 1995; Hirvi and Rekolainen, 1995; Kirknel and Felding, 1995; Lode et al., 1995). Organochlorines have been detected in air and rain all around the world (Oehme, 1991b) and are thus usually included in the list of monitored pesticides. Trevisan et al. (1993) first listed pesticides used in the areas adjacent to the sampling sites and then used a fugacity model (Mackay and Paterson, 1981) to determine which were most likely to be found in air or rainwater. All but two of the 12 pesticides highlighted by the model were found at least once in rainwater. Some authors based their choice for monitoring on a combination of pesticide properties and national usage (Scharf et al., 1992; Siebers et al., 1994; Jaeschke et al., 1995). This diversity of aims and objectives for the various studies has resulted in a variety of active ingredients and metabolites monitored in the studies reported.

2.3. Sampling strategy and analysis

All the studies reviewed here reported results from samples collected as either total deposition (also referred to as bulk deposition) or wet deposition only. Total deposition includes the total amount of compound deposited by rain in both the dissolved and particulate phases and by dust. Wet deposition excludes the amount of compound deposited by dust. Although many studies only included analyses of total deposition, comparison with results for wet deposition is generally valid because amounts of pesticide deposited via dry deposition are usually very small compared to those from wet deposition (Siebers et al., 1991, 1994; Gath et al., 1993; Jaeschke et al., 1995; Kreuger, 1995).

Frequency of sample collection varied from every week (Millet et al., 1997) to every month (Chevreuil and Garmouma, 1993; Chevreuil et al., 1996) or each rainfall event (Trevisan et al., 1993). Some authors have also investigated the variation of pesticide concentrations within a rainfall event (Oberwalder et al., 1991; Trautner et al., 1992; Fingler et al., 1994; Chevreuil et al., 1996). The length of the monitoring period ranged from 3 months (Trautner et al., 1992) to 3 years (Cleeman et al., 1995; Jaeschke et al., 1995).

Analytical limits of determination and quantification varied between molecules and between studies for the same molecule because of different volumes of rain samples and the use of different analytical techniques (e.g. GC–ECD, GC–NPD, GC–MS, HPLC, Elisa). For instance, the limit of quantification for isoproturon ranged from 2 ng/l (Harris et al., 1992) to 60 ng/l (Fisher et al., 1991). Such discrepancies critically affect both the results reported and their potential impact and limits of detection should, therefore, be clearly given in documents. Confidence in the results presented is also of primary concern and a quality control system covering issues from sample collection and analytical determinations through to data reporting has been proposed (Haugen and Oehme, 1995).

3. Results

3.1. Concentrations and frequency of detection

Table 2 provides a list of pesticides that have been detected in rainwater in Europe. Of the 99 active ingredients, their isomers or metabolites that have been

Table 2
Pesticides which have been found in rainwater in Europe (only papers from 1990 onwards in which there were positive detections are reported)[a]

Alachlor	Trevisan et al. (1993)
Aldicarb	Millet et al. (1997)
Aldrin	Harris et al. (1992), Fingler et al. (1994), Millet et al. (1997)
Atrazine	Buser (1990), Clark and Gomme (1991), Fisher et al. (1991), Gomme et al. (1991), Oberwalder et al. (1991), Siebers et al. (1991, 1994), Gath et al. (1992, 1993), Harris et al. (1992), Scharf et al. (1992), Trautner et al. (1992), Scharf and Bächmann (1993), Stähler (1993), Trevisan et al. (1993), Hirvi and Rekolainen (1995), Kreuger (1995), Lode et al. (1995), Chevreuil et al. (1996), Millet et al. (1997)
Bentazone	Hirvi and Rekolainen (1995), Kreuger (1995)
Bitertanol	Hüskes and Levsen (1997)
Carbaryl	Trevisan et al. (1993)
Chloridazon	Hüskes and Levsen (1997)
Chlorothalonil	Clark and Gomme (1991), Fisher et al. (1991), Gomme et al. (1991), Hüskes and Levsen (1997)
Cyanazine	Kreuger (1995), Chevreuil et al. (1996)
2,4-D	Stähler (1993), Hirvi and Rekolainen (1995), Kreuger (1995)
DDT	Scharf et al. (1992), Scharf and Bächmann (1993), Fingler et al. (1994), Chevreuil et al. (1996), Millet et al. (1997)
Diazinon	Scharf et al. (1992), Scharf and Bächmann (1993), Trevisan et al. (1993)
Dicamba	Kreuger (1995)
Dichlobenil	Trevisan et al. (1993)
Dichlorprop	Oberwalder et al. (1991), Siebers et al. (1991), Stähler (1993), Trevisan et al. (1993), Hirvi and Rekolainen (1995), Lode et al. (1995), Kirknel and Felding (1995), Kreuger (1995)
Dieldrin	Millet et al. (1997)
Dimethoate	Clark and Gomme (1991), Fisher et al. (1991), Gomme et al. (1991), Kreuger (1995)
Etrimfos	Oberwalder et al. (1991)
Fenpropimorph	Scharf et al. (1992), Scharf and Bächmann (1993), Millet et al. (1997)
Flusilazole	Scharf and Bächmann (1993)
HCB	Fingler et al. (1994), Tarrant and Taton (1968), Wells and Johnstone (1978), Chevreuil et al. (1996), Millet et al. (1997)
Isoproturon	Clark and Gomme (1991), Fisher et al. (1991), Gomme et al. (1991), Siebers et al. (1991, 1994), Harris et al. (1992), Gath et al. (1992, 1993), Johnson et al. (1996), Millet et al. (1997)
MCPA	Stähler (1993), Trevisan et al. (1993), Hirvi and Rekolainen (1995), Kirknel and Felding (1995), Kreuger (1995), Lode et al. (1995)
Mecoprop	Clark and Gomme (1991), Fisher et al. (1991), Gomme et al. (1991), Oberwalder et al. (1991), Stähler (1993), Hirvi and Rekolainen (1995), Kirknel and Felding (1995), Kreuger (1995), Millet et al. (1997)
Metalaxyl	Kreuger (1995), Hüskes and Levsen (1997)
Metazachlor	Scharf et al. (1992), Scharf and Bächmann (1993)
Methyl-parathion	Millet et al. (1997)
Metolachlor	Scharf et al. (1992), Scharf and Bächmann (1993), Hüskes and Levsen (1997)
Metribuzin	Scharf et al. (1992), Scharf and Bächmann (1993)
Parathion	Siebers et al. (1991, 1994), Gath et al. (1993), Trevisan et al. (1993),
Pentachlorophenol	Fingler et al. (1994)
Pendimethalin	Scharf et al. (1992), Scharf and Bächmann (1993)
Phorate	Trevisan et al. (1993)
Pirimicarb	Siebers et al. (1991, 1994), Gath et al. (1992, 1993), Kreuger (1995)
Propazine	Scharf et al. (1992), Stähler (1993)
Propiconazole	Scharf et al. (1992), Scharf and Bächmann (1993), Siebers et al. (1994), Hüskes and Levsen (1997)
Propoxur	Siebers et al. (1994)
Simazine	Buser (1990), Oberwalder et al. (1991), Harris et al. (1992), Scharf et al. (1992), Scharf and Bächmann (1993), Stähler (1993), Kreuger (1995), Chevreuil et al. (1996), Hüskes and Levsen (1997)
Tebuconazole	Hüskes and Levsen (1997)
Tebutam	Hüskes and Levsen (1997)
Terbuthylazine	Buser (1990), Oberwalder et al. (1991), Scharf et al. (1992), Scharf and Bächmann (1993), Siebers et al. (1994), Kreuger (1995), Chevreuil et al. (1996), Hüskes and Levsen (1997)
Terbutryn	Buser (1990)
Triadimenol	Gath et al. (1992, 1993), Scharf and Bächmann (1993)

Table 2 (*continued*)

HCH	Clark and Gomme (1991), Fisher et al. (1991), Gomme et al. (1991), Oberwalder et al. (1991), Siebers et al. (1991, 1994), Gath et al. (1992, 1993), Granier et al. (1992), Harris et al. (1992), Scharf et al. (1992), Scharf and Bächmann (1993), Stähler (1993), Fingler et al. (1994), Hirvi and Rekolainen (1995), Kreuger (1995), Lode et al. (1995), Chevreuil et al. (1996), Granier and Chevreuil (1997), Millet et al. (1997)	Triallate	Clark and Gomme (1991), Fisher et al. (1991), Gomme et al. (1991), Scharf et al. (1992), Scharf and Bächmann (1993), Kreuger (1995)
		Trifluralin	Trevisan et al. (1993)
		Vinclozolin	Siebers et al. (1994)

[a] 2,4-D, 2,4-dichlorophenoxyacetic acid; DDT, 1,1-dichloro-2,2-bis[4-chlorophenyl]-ethane; HCB, hexachlorobenzene; HCH, hexachlorocyclohexane; MCPA, 2-methyl-4-chlorophenoxyacetic acid.

monitored in the European studies reviewed here, a total of 48 have been detected (Table 3). The most frequently monitored pesticides, in descending order, are lindane (γ-HCH; HCH: hexachlorocyclohexane) and its main isomer (α-HCH), atrazine, MCPA (2-methyl-4-chlorophenoxyacetic acid), simazine, dichlorprop, isoproturon, mecoprop, DDT, terbuthylazine and aldrin. Possible reasons for local non-detection of a compound detected elsewhere include its lack of use in the region around the site, a long lag between usage and sampling (particularly for compounds with short atmospheric residence time), infrequent sampling (hence compounds with short atmospheric residence time may degrade between sampling intervals) or too high a limit of detection for specific analyses.

The comparison of results from different sites or studies requires careful interpretation because of the variety of reasons for non-detection of a compound and differences in pesticide usage, type of sampling location and timing of sampling between sites and countries. An obvious example is 2-methyl-4-chlorophenoxyacetic acid (MCPA) which has not been detected at five sites in Germany (Scharf et al., 1992; Hüskes and Levsen, 1997) nor at one site in the UK (Gomme et al., 1991), but which has been regularly detected in Nordic countries (Hirvi and Rekolainen, 1995; Kirknel and Felding, 1995; Kreuger, 1995; Lode et al., 1995) where it is one of the most frequently used compounds. The reason for the non-detection of MCPA in Germany may be related to its relatively low regional usage, whereas its non-detection in the UK study may be because the analytical limits of detection were relatively high (40 ng/l). The explanation for the more frequent detection of MCPA in Nordic countries is likely to be the result of larger usage of the compound in these countries, where it is used in place of other compounds that have been banned.

For those compounds detected, most concentrations were below about 100 ng/l, but larger concentrations were occasionally detected at most monitoring sites. The largest maximum concentrations of pesticides in rainwater were found by Millet et al. (1997) on a research site situated in a rural area of Alsace, France, with transient peak concentrations exceeding 2000 ng/l for 10 pesticides. At other sites, maximum reported concentrations in rainwater for the different studies were 10–1110 ng/l for atrazine, 94 to >1000 ng/l for simazine, 26–800 ng/l for terbuthylazine, 140–6200 ng/l for dichlorprop, 20–833 ng/l for lindane, 110–3190 ng/l for MCPA, 32 to >1000 ng/l for mecoprop and 125 to >1000 ng/l for isoproturon. Those studies which compared pesticides in rainfall in urban and in adjacent agricultural areas have reported a similar range of concentrations in both areas (Chevreuil et al., 1996; Hüskes and Levsen, 1997).

The most frequently detected compounds were lindane and its isomer α-HCH, with detections on 90–100% of sampling occasions at most of the sites where they were monitored. Only Tromsø in Norway had no detections of lindane (Lode et al., 1995). No other compounds were detected on all sampling occasions at any of the monitoring sites. For 80% of site–compound combinations, there were detections on less than half the sampling occasions.

3.2. Patterns of detection

Most of the compounds detected (apart from organochlorines) showed a good correlation between their periodic appearance in rainwater or peak in concentrations and their local spraying season(s) (Harris et al., 1992; Siebers et al., 1994; Jaeschke et al., 1995; Kreuger, 1995; Hüskes and Levsen, 1997; Millet et al., 1997). Detections of some of these compounds can extend over a few months after the end of the local spraying season (e.g. terbutylazine or desethylatrazine in Chevreuil et al., 1996), probably as a result of volatilisation from treated soils and plants and long residence time in the atmosphere. Buser (1990) explained the sequence of appearance of pesticides in rainwater by relating it to local usage patterns.

For some compounds, however, discrepancies between local usage and timing of detection have been reported (Kirknel and Felding, 1995). This is exemplified by atrazine, the second most monitored pesticide in Europe after lindane. At two sites in France, Chevreuil et al. (1996) reported a rapid increase in concentrations

Table 3
Pesticide detections and concentrations (ng/l) in a number of European studies[a]

Paper, study site, sample type	Detections
Fingler et al. (1994) Rain samples	13 pesticides monitored, 12 detected >0.1 μg/l: 2,4,5-TCP: 171 (3/10) <0.1 μg/l: aldrin: 3 (8/12) — 2.4-DCP: 48 (8/10) — DDE: 1 (2/12) — DDT: 2 (1/12) — HCB: 1 (9/12) — α-HCH: 7 (12/12) — lindane: 38 (12/12) — PCP: 19 (6/10) — 2,4,6-TCP: 69 (7/10) — 2,3,4,6-TeCP: 63 (4/10) Not detected (0/12): DDD
Fingler et al. (1994) Snow samples	13 pesticides monitored, 10 detected >0.1 μg/l: 2,4,5-TCP: 136 (10/12) — 2.4-DCP: 134 (12/12) — 2,4,6-TCP: 210 (11/12) — 2,3,4,6-TeCP: 527 (11/12) — PCP: 131 (11/12) <0.1 μg/l: aldrin: 4 (12/12) — HCB: 2 (12/12) — α-HCH: 4 (10/12) — lindane: 6 (12/12) Not detected (0/12): DDD — DDE — DDT
Cleeman et al. (1995) Three sites	Two pesticides monitored, two detected <0.1 μg/l: α-HCH: 2 (mean) — lindane: 15.4 (mean)
Kirknel and Felding (1995) Ulborg site	10 pesticides monitored, three detected >0.1 μg/l: Dichlorprop: 389 (2/18) — MCPA: 377 (1/18) — mecoprop: 119 (1/18) Not detected (0/18): atrazine, γ-cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, prochloraz, propiconazole
Kirknel and Felding (1995) Gadevang site	10 pesticides monitored, two detected >0.1 μg/l: dichlorprop: 129 (1/16) <0.1 μg/l: MCPA: 89 (1/16) Not detected (0/16): atrazine, γ-cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, mecoprop, prochloraz, propiconazole
Hirvi and Rekolainen (1995)	90 pesticides monitored, eight detected >0.1 μg/l: dichlorprop: 190 (9/22) — MCPA: 110 (10/22) <0.1 μg/l: 2,4-D: 8 (11/22) — atrazine: 10 (3/22) — bentazone: 5 (5/22) — α-HCH: 6 (22/22) — lindane: 20 (22/22) — mecoprop: 32 (7/22) Not detected (0/22): not specified in the paper
Trautner et al. (1992) First site	One pesticide monitored, one detected >0.1 μg/l: atrazine: 135
Trautner et al. (1992) Second site	One pesticide monitored, one detected <0.1 μg/l: atrazine: 70
Chevreuil et al. (1996) Paris site	21 pesticides monitored, nine detected >0.1 μg/l: atrazine: 400 (18/21) — cyanazine: 120 (14/21) — desethylatrazine: 220 (16/21) — lindane: 130 (14/14) — simazine: 680 (14/21) — terbuthylazine: 120 (14/21) <0.1 μg/l: DDE: 1.9 (8/14) — HCB: 17 (14/14) — α-HCH: 6.9 (14/14) Not detected: ametryn, chlorotoluron, deisopropylatrazine, diuron, isoproturon, linuron, monolinuron, neburon, prometryn, secbumeton, terbumeton, terbutryn
Chevreuil et al. (1996) La Ferté sous Jouarre site	21 pesticides monitored, nine detected >0.1 μg/l: atrazine: 380 (19/21) — desethylatrazine: 150 (12/21) — lindane: 350 (15/15) — simazine: 650 (20/21) <0.1 μg/l: cyanazine: 80 (10/21) — DDE: 11 (9/15) — HCB: 4.5 (15/15) — α-HCH: 6.5 (15/15) — terbuthylazine: 56 (15/21) Not detected: ametryn, chlorotoluron, deisopropylatrazine, diuron, isoproturon, linuron, monolinuron, neburon, prometryn, secbumeton, terbumeton, terbutryn
Millet et al. (1997)	13 pesticides monitored, 13 pesticides detected >0.1 μg/l: aldicarb: 14 000,1700 (20/31) — aldrin: 310,50 (10/31) — atrazine: 5000,220 (7/31) — DDD: 3500,320 (10/31) — DDE: 3400,350 (12/31) — DDT: 6000,500 (5/31) — dieldrin: 2400,500 (20/31) — fenpropimorph: 5000,260 (9/31) — HCB: 350,70 (28/31) — isoproturon: 6000,700 (16/31) — lindane: 800,160 (27/31) — mecoprop: 60 000,16 (21/31) — methyl — parathion 3400,500 (11/31)
Oberwalder et al. (1991) Hailfingen site	Seven pesticides detected >0.1 μg/l: atrazine: 650 (26/42) — dichlorprop: 6200 (15/40) — α-HCH: 230 (22/35) — lindane: 550 (35/40) — mecoprop: 410 (19/40) <0.1 μg/l: desethylatrazine: 90 (14/42) — simazine: 70 (10/42)
Oberwalder et al. (1991) Hohenheim site	Seven pesticides detected >0.1 μg/l: atrazine: 1110 (35/38) — desethylatrazine: 170 (9/38) — dichlorprop: 440 (16/38) — etrimfos: 1130 (6/38) — mecoprop: 150 (13/38) — simazine: 220 (17/38) — terbuthylazine: 800 (28/38)

Table 3 (*continued*)

Paper, study site, sample type	Detections
Gath et al. (1992)	Six pesticides monitored, five detected >0.1 µg/l: atrazine: 430 (6/21) — isoproturon: 136 (6/21) — lindane: 270 (19/21) — triadimenol: 230 (3/21) <0.1 µg/l: pirimicarb: 30 (2/21) Not detected: parathion-ethyl
Scharf et al. (1992) Schauinsland site	34 pesticides monitored, 18 detected >0.1 µg/l: atrazine 135,76 (13/41) — DDD: 102,40 (22/41) — DDT: 87,40 (14/41) — deisopropylatrazine: 174,100 (6/41) — desethylatrazine: 882,258 (9/41) — diazinon: 322,82 (11/41) — fenpropimorph: 300,78 (10/41) — lindane: 833,208 (39/41) — metazachlor: 134,83 (2/41) — metolachlor: 330,215 (5/41) — metribuzin: 130,67 (5/41) — pendimethalin: 260,165 (10/41) — propiconazole: 1388,337 (16/41) — tri-allate: 2137,403 (13/41) <0.1 µg/l: DDE: 95,32 (27/41) — propazine 50,34 (11/41) — simazine: 94,32 (7/41) — terbuthylazine: 34,24 (6/11) Not detected: aldicarb, aldrin, bentazone, carbofuran, chloridazon, chloroxuron, chlorotoluron, endosulfan, isoproturon, MCPA, mecoprop, metamitron, methabenzthiazuron, methoxychlor, metobromuron, metoxuron, monolinuron
Scharf et al. (1992) Deuselbach site	34 pesticides monitored, 17 detected >0.1 µg/l: atrazine 134,36 (7/22) — deisopropylatrazine: 232,103 (3/22) — desethylatrazine: 244,111 (7/22) — diazinon: 188,81 (6/22) — lindane: 760,151 (22/22) — metolachlor: 311,204 (3/22) — propazine 157,78 (15/22) — propiconazole: 295,295 (1/22) — tri-allate: 316,232 (5/22) <0.1 µg/l: simazine: 44,28 (2/22) — DDD: 66,22 (6/22) — DDE: 96,49 (6/22) — DDT: 72,60 (2/22) — fenpropimorph: 69,47 (5/22) — metazachlor: 35,29 (3/22) — metribuzin: 41,31 (4/22) — terbuthylazine: 34,34 (1/11) Not detected: aldicarb, aldrin, bentazone, carbofuran, chloridazon, chloroxuron, chlorotoluron, endosulfan, isoproturon, MCPA, mecoprop, metamitron, methabenzthiazuron, methoxychlor, metobromuron, metoxuron, monolinuron, pendimethalin
Scharf et al. (1992) Bensheim site	34 pesticides monitored, 16 detected >0.1 µg/l: deisopropylatrazine: 133,111 (3/10) — desethylatrazine: 113,113 (1/10) — diazinon: 117,63 (4/10) — lindane: 183,116 (9/10) — metolachlor: 212,212 (1/10) — propazine 126,50 (3/10) — propiconazole: 223,223 (1/10) — tri-allate: 340,176 (2/10) <0.1 µg/l: atrazine 39,25 (5/10) — DDD: 84,44 (4/10) — DDE: 18,18 (1/10) — DDT: 17,17 (1/10) — fenpropimorph: 67,49 (3/10) — metazachlor: 29,29 (1/10) — metribuzin: 60,57 (2/10) — simazine: 63,25 (5/10) Not detected: aldicarb, aldrin, bentazone, carbofuran, chloridazon, chloroxuron, chlorotoluron, endosulfan, isoproturon, MCPA, mecoprop, metamitron, methabenzthiazuron, methoxychlor, metobromuron, metoxuron, monolinuron, pendimethalin, terbuthylazine
Gath et al. (1993) Hortenkopf site	Seven pesticides monitored, six detected >0.1 µg/l: atrazine: 140 (8/21) — isoproturon: 361 (11/21) — lindane: 297 (20/21) — pirimicarb: 1300 (11/21) — triadimenol: 1740 (6/21) <0.1 µg/l: α-HCH: 5 (15/21) Not detected: parathion-ethyl
Gath et al. (1993) Neustadt site	Seven pesticides monitored, seven detected >0.1 µg/l: atrazine: 130 (6/21) — lindane: 200 (21/21) — parathion-ethyl: 210 (6/21) <0.1 µg/l: α-HCH: 5 (12/21) — isoproturon: 62 (7/21) — pirimicarb: <20 (4/21) — triadimenol: 60 (8/21)
Gath et al. (1993) Kleiner Feldberg site	Seven pesticides monitored, six detected >0.1 µg/l: isoproturon: 130 (5/16) — lindane: 120 (16/16) <0.1 µg/l: atrazine: 80 (3/16) — α-HCH: 7 (13/16) — triadimenol: 30 (4/16) — parathion-ethyl: 50 (2/16) Not detected: pirimicarb
Stähler (1993) Seven sites	Eight pesticides monitored, eight detected >0.1 µg/l: atrazine: 100 — 2,4-D: 420 — dichlorprop: 470 — lindane: 360 — MCPA: 650 — mecoprop: 140 — simazine: 8100 <0.1 µg/l: not detailed in the paper
Siebers et al. (1994) Braunschweig site	11 pesticides monitored, eight detected >0.1 µg/l: atrazine: 113,44 (22%) — isoproturon: 168,35 (41%) — lindane: 400,117 (81%) — parathion: 320,122 (15%) <0.1 µg/l: pirimicarb: 12,12 (5%) — propoxur: 27,23 (10%) — terbuthylazine: 22,16 (25%) — vinclozolin: 11,11 (5%) Not detected: chlorpyrifos, α-HCH, propiconazole
Siebers et al. (1994) Rotenkamp site	11 pesticides monitored, eight detected >0.1 µg/l: atrazine: 240,80 (24%) — isoproturon: 376,84 (41%) — lindane: 310,130 (65%) — parathion: 190,117 (14%) — pirimicarb: 150,58 (8%) <0.1 µg/l: terbuthylazine: 20,16 (20%) — propiconazole 33,28 (10%) — vinclozolin: 11,11 (5%) Not detected: α-HCH, propoxur, chlorpyrifos

(continued on next page)

Table 3 (*continued*)

Paper, study site, sample type	Detections
Siebers et al. (1994) Neuenkirchen site	11 pesticides monitored, 10 detected >0.1 μg/l: atrazine: 430,105 (29%) — lindane: 710,171 (77%) — pirimicarb: 490,125 (19%) — parathion: 569,254 (17%) — isoproturon: 230,56 (31%) <0.1 μg/l: α-HCH: 12,12 (6%) — propiconazole 53,37 (11%) — propoxur: 31,31 (5%) — terbuthylazine: 26,19 (21%) — vinclozolin: 16,16 (5%) Not detected: chlorpyrifos
Hüskes and Levsen (1997)	59 pesticides monitored, 11 detected >0.1 μg/l: bitertanol: 140,40 (28/40) — chloridazon: 880,60 (10/40) — chlorothalonil: 1100,160 (34/40) — metalaxyl: 480,100 (19/40) — metolachlor: 510,100 (27/40) — propiconazole: 150,50 (17/40) — simazine: 140,40 (14/40) — tebuconazole: 320,100 (15/40) — terbuthylazine: 520,100 (29/40) <0.1 μg/l: tebutam: 92,30 (10/40) Not detected: alachlor, anilazine, atrazine, bifenox, carbetamide, deltamethrin, desethylatrazine, desethyldeisopropyl-atrazine, desethylterbutylazine, deisopropylatrazine, diazinon, dichlobenil, dichlorfluanid, dichlorprop-2-ethylexyl -ester, diflufenican, ethofumesate, fenpropimorph, fenvalerate, fluazifop-ester, fluorochloridone, fluroxypyr-ester, haloxyfop-ster, iprodione, isoproturon, γ-cyhalothrin, MCPA-butoxyethylester, MCPA-2-thylhexylester, mecoprop-1-octylester, mecoprop-2-octylester, metamitron, metazachlor, methabenzthiazuron, methfuroxam, metribuzin, napropamide, oxadixyl, parathion, pendimethalin, permethrin, phenmedipham, pirimicarb, prochloraz, propazine, prosulfocarb, triadimefon, triadimenol, tri-allate, trifluralin, vinclozolin
Trevisan et al. (1993) Four sites	12 pesticides monitored, 10 detected >0.1 μg/l: alachlor: 810 (5/49) — atrazine: 199 (10/49) — carbaryl: 110 (4/26) — dichlobenil: 3120 (10/49) — dichlorprop: 1810 (1/49) — MCPA: 3190 (4/49) — parathion: 170 (11/49) — trifluralin: 3440 (8/49) <0.1 μg/l: diazinon: 80 (11/49) — phorate: 30 (3/49) Not detected: 2,4-D, fluazifop-butyl
Lode et al. (1995) Lista site	Nine pesticides monitored, four detected <0.1 μg/l: atrazine: 86 (1/28) — dichlorprop: 40 (2/28) — lindane: 84 (11/28) — MCPA: 48 (3/28) Not detected (0/28): cypermethrin, dimethoate, ioxynil, propiconazole, simazine
Lode et al. (1995) Ås site	10 pesticides monitored, four detected >0.1 μg/l: dichlorprop: 250 (10/36) — MCPA: 320 (10/36) <0.1 μg/l: atrazine: 84 (2/36) — lindane: 43 (14/36) Not detected (0/36): cypermethrin, dimethoate, ioxynil, propiconazole, simazine
Lode et al. (1995) Tromsø site	10 pesticides monitored, two detected <0.1 μg/l: dichlorprop: 20 (1/3) — MCPA: 30 (3/3) Not detected (0/3): atrazine, cypermethrin, dichlorprop, dimethoate, ioxynil, lindane, MCPA, propiconazole, simazine
Buser (1990) Many sites	Nine pesticides monitored, three detected >0.1 μg/l: atrazine: 600 (16/24) — simazine: 121 (17/24) — terbuthylazine: 198 (14/24) <0.1 μg/l: terbutryn: 7.4 (1/24) Not detected: atraton, desethylatrazine, prometon, prometryn, propazine
Kreuger (1995) Ekeröd site	31 pesticides monitored, 18 detected >0.1 μg/l: atrazine: 160 (30/54) — MCPA: 170 (28/79) — simazine: 140 (18/54) <0.1 μg/l: bentazone: 32 (21/79) — cyanazine: 23 (3/54) — 2,4-D: 48 (56/79) — desethylatrazine: 70 (22/54) — dicamba: 5 (3/79) — dichlorprop: 92 (44/79) — dimethoate: 20 (1/25) — α-HCH: 4 (27/27) — δ-HCH: 1 (2/27) — lindane: 73 (27/27) — mecoprop: 46 (42/79) — metalaxyl: 20 (6/51) — pirimicarb: 5 (38/54) — terbuthylazine: 50 (19/54) — tri-allate: 9 (2/53) Not detected: cypermethrin, DDD, DDE, DDT, desisopropylatrazine, fenvalerate, β-HCH, malathion, propiconazole, 2,4,5-T, triadimenol, trifluralin
Kreuger (1995) Lurbo site	31 pesticides monitored, 16 detected >0.1 μg/l: dichlorprop: 140 (23/56) — MCPA: 240 (18/56) — tri-allate: 200 (14/41) <0.1 μg/l: atrazine: 60 (8/42) — bentazone: 20 (14/56) — cyanazine: 4 (1/42) — 2,4 — D: 70 (31/56) — desethylatrazine: 17 (4/42) — dicamba: 8 (4/56) — α-HCH: 7 (20/21) — lindane: 29 (20/21) — mecoprop: 32 (16/56) — metalaxyl: 15 (2/41) — pirimicarb: 14 (1/42) — simazine: 40 (3/42) — terbuthylazine: 30 (8/42) Not detected: cypermethrin, DDD, DDE, DDT, desisopropylatrazine, dimethoate, fenvalerate, β-HCH, δ-HCH, malathion, propiconazole, 2,4,5-T, triadimenol, trifluralin
Harris et al. (1992)	Six pesticides monitored, six detected >0.1 μg/l: aldrin: 180 — α-HCH: 280 — isoproturon: 125 — lindane: 560 — simazine: 220 <0.1 μg/l: atrazine: 65

[a] Data are presented in three different formats depending on the information available in papers and reports: [maximum concentration, mean concentration (frequency of detection)] or [maximum concentration (frequency of detection)] or [maximum concentration].

of atrazine in rainwater in March and April with a maximum in late spring and a decrease to a minimum by the end of the summer. This was followed by a second peak in October related to a second period of local application. A similar second usage-related peak for atrazine has been observed by Scharf et al. (1992) at sites in Germany. At a site in the UK, however, Harris et al. (1992) detected off-season peaks of atrazine and attributed them to its use throughout the year for total weed control on roadside verges and railway tracks. In Switzerland, Buser (1990) related the appearance of atrazine in rainwater prior to the spraying season to extensive dust formation resulting from agricultural activities such as ploughing and harrowing. This conclusion is supported by the results of Scharf and Bächmann (1993) for fenpropimorph and atrazine showing a clear correlation between increased concentrations in rainwater and harvesting operations. There may be other explanations for the appearance of some compounds in rainwater prior to the main agricultural spraying seasons and Hirvi and Rekolainen (1995) proposed long-distance transport from regions where the spraying season started earlier.

With respect to organochlorines, lindane and its main isomer have frequently been detected in rainwater throughout the year (Oberwalder et al., 1991; Scharf et al., 1992; Gath et al., 1993; Fingler et al., 1994), even in countries such as Finland and Sweden where the compound is no longer used (Hirvi and Rekolainen, 1995; Kreuger, 1995). In general, lindane concentrations show less variation than those of other pesticides, although distinct seasonal peaks have been noted in some studies (Granier et al., 1992; Harris et al., 1992; Stähler, 1993; Cleeman et al., 1995) and have sometimes been attributed to relatively recent local usage. Other organochlorine compounds that are no longer used in Europe have a more transient pattern of detection possibly related to a specific combination of atmospheric conditions. It has been noted in some studies that concentrations of pesticides in the first rainfall event following a prolonged dry period are likely to be very high (Buser, 1990; Oberwalder et al., 1992), especially if the rainfall volume is small (Gath et al., 1993; Jaeschke et al., 1995). By monitoring the prevailing wind direction or calculating back trajectories of air masses during the sampling period, correlations between increased concentrations of specific pesticides and a particular wind direction have been identified (Harris et al., 1992; Trautner et al., 1992; Brorström-Lundén et al., 1994; Cleeman et al., 1995; Lode et al., 1995).

Finally, some authors have monitored the evolution of pesticide concentrations in rainwater throughout a single rainfall event. Although a decrease in the concentrations with time was noted by some authors (Oberwalder et al., 1991; Trautner et al., 1992; Fingler et al., 1994), no such relationship was found by Chevreuil et al. (1996).

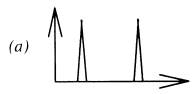
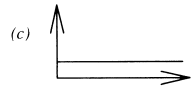
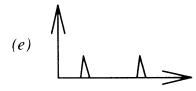
4. Discussion

4.1. Long-range atmospheric transport and patterns of deposition

The detection of pesticides in rainwater samples at times that cannot be related to the local spraying seasons and the detection of pesticides that are believed not to be used in the vicinity of a sampling site suggests that there has been some form of long-range transport via the atmosphere. Long-range atmospheric transport contributes to the dispersion of pollutants over 'large' distances, along with other forms of long-range transport via sea currents, biota and ice transport in the polar regions.

The expression 'long-range transport' has been widely used to describe atmospheric transport over a few to many thousands of kilometres. Wells and Johnstone (1978) defined a short (0–50 km), medium (50–500 km) and long (> 500 km) distance transport whereas Levy (1990) defined long-range transport as movement from continental source regions to the oceans and to other continents as well as transport between the hemispheres. Glotfelty et al. (1990) used the expression 'regional-scale' transport to cover distances in the order of 10^3 km and Bossan et al. (1995) have used the term 'meso-scale' transport to distinguish movements over shorter distances than those covered in 'long-range' transport. A classification of atmospheric transport according to deposition pattern and duration was presented by Torstensson (1995) who distinguished between short-distance (< 1 km), long-distance (1–1000 km) and global transport. In the authors' view, debate about the exact definitions of terms used to classify atmospheric transport is not useful in this context. However, a classification of the different patterns of atmospheric deposition related to types of transport as suggested by Torstensson (1995) does appear useful as a first step in categorising the potential for different pesticides to be dispersed in the atmosphere. The suggested classification of patterns of deposition and associated transport mechanisms which is proposed in Fig. 2 is based on the results of the various studies reviewed here and is discussed below.

Most organochlorines have high volatility, low solubility in water and low photo-oxidation and thus have considerable potential to persist in the atmosphere and be transported over long distances. Compounds such as lindane appear to be ubiquitous in the atmosphere, albeit mostly at concentrations of just a few nanograms per litre. In remote regions, or in areas where the compounds are not used and there is little seasonal air movement from other usage areas, their pattern of deposition will correspond to that in Fig. 2c with relatively uniform concentrations of up to a few nanograms per litre. In areas where the compound is used, or where

Deposition pattern[a]	Time scale	Concentrations	Transport range	Examples
 (a)	Spraying operation	Intermediate/High (few 10 ng l^{-1} to few 1,000 ng l^{-1})	Short range (< 1 km)	Siebers et al. (1994) with vinclozolin Siebers et al. (1991) with pirimicarb
 (b)	Spraying season	Intermediate/High (few 10 ng l^{-1} to few 1,000 ng l^{-1})	Medium to long distance (1 to a few 1,000 km)	Chevreuil et al. (1996) with terbutylazine and desethylatrazine
 (c)	Throughout the year	Low (few ng l^{-1} to a few 10 ng l^{-1})	Global (several 1,000 km)	Cleeman et al. (1995) with α-HCH
 (d)	Throughout the year	Low to Intermediate/High (few ng l^{-1} to a few 1,000 ng l^{-1})	Global background with regional use superimposed	Stähler et al. (1993), Scharf and Bächmann (1993) with lindane
 (e)	Occasionally	Low (few ng l^{-1} to a few 10 ng l^{-1})	Global	Fingler et al. (1994) with DDT

[a] Concentration *vs.* time of year

Fig. 2. A classification of pesticide transport according to deposition pattern in Europe.

the compound is not used but there is significant seasonal air movement from other usage areas, the pattern of deposition is likely to correspond to that in Fig. 2d with seasonal peaks of up to a few hundred nanograms per litre. Other organochlorine compounds whose use has long been discontinued in Europe appear to have a pattern of deposition corresponding to that in Fig. 2e. They must be present in the atmosphere, but in such small amounts that they normally give rainwater concentrations below the limit of detection. Occasionally, however, a series of atmospheric conditions combine to give a major 'wash-out' event that produces detectable concentrations in the order of a few nanograms per litre.

For most other pesticides which do not have the combination of physico-chemical properties exhibited by organochlorine compounds, the pattern of deposition is likely to be that shown in Fig. 2a. This pattern is clearly related to short-range transport from local spraying operations. Such transport is unlikely to extend beyond one or two kilometres and can give peak concentrations ranging from a few nanograms per litre (e.g. vinclozolin in Siebers et al., 1994) to a few micrograms per litre (e.g. propiconazole and tri-allate in Scharf et al., 1992) depending on a combination of factors including pesticide volatility, solubility in water and octanol–water partition coefficient, the local application rates and amount used within the transport range, and the local atmospheric conditions. However, some pesticides that do not exhibit high vapour pressures appear to be susceptible to transport over longer distances and show a deposition pattern as shown in Fig. 2b. Atrazine has a relatively low vapour pressure (4×10^{-5} Pa at 20°C), but has been seasonally detected in regions where it is no longer used (Hirvi and Rekolainen, 1995; Kreuger, 1995) or at times when there is no local usage (Buser, 1990; Scharf and Bächmann, 1993). It has been suggested that this is because photo-degradation is considerably reduced when atrazine binds to solid particles (Scharf and Bächmann, 1993; Bossan et al., 1995), thus rendering the compound susceptible to transport over considerable distances via atmospheric dust. Unexpected detection has also been attributed to local re-release to the atmosphere in dust particles generated by agricultural cultivation or harvesting. This type of atmospheric transport or local 're-activation' produces a seasonal deposition pattern that may extend over a few months during the main harvesting, cultivation and spraying operations within a region. The extent of the transport would vary from a few tens to a few thousands of kilometres, depending on the prevailing direction of atmospheric mass-movements.

The extended seasonal deposition pattern observed for some other compounds with low vapour pressures and relatively rapid photodegradation (such as isoproturon — Harris et al., 1992; Siebers et al., 1994; Jaeschke et al., 1995; Millet et al., 1997) is more difficult to explain, especially as no phenylureas were detected in rainfall in other studies despite their local usage (Chevreuil et al., 1996; Hüskes and Levsen, 1997). This illustrates the complexity of factors affecting atmospheric transport and deposition of specific pesticides and the difficulty of predicting their patterns of deposition.

4.2. Modelling and prediction of deposition

Predicting the deposition of pesticides in the atmosphere is particularly difficult because of the limited knowledge relating to the complex interactions of chemical and physical phenomena that take place between the emission of a pesticide droplet from a nozzle and its final deposition in a specific remote location. Although volatilisation of pesticides is related to their vapour pressure, compounds with high vapour pressure and a tendency to vaporise often also have high Henry's constants and thus tend to remain in the vapour phase rather than the aqueous phase of a cloud or rain droplet (Hüskes and Levsen, 1997). Furthermore, both vapour pressure and Henry's law constant are very temperature dependent and thus vary with the time of day, season and latitude (Atkinson et al., 1992). In addition, many other factors such as the amount and frequency of usage, the potential for binding to dust particles or aerosols and the prevailing patterns of atmospheric movement can influence atmospheric transport. As a result, most studies that have attempted to link pesticide deposition solely to their physico-chemical properties have failed (Siebers et al., 1994). Any attempt to quantitatively describe the deposition of pesticides in a given place must take into account weather information, pesticide properties and usage and integrate both the spatial and temporal variations in these factors. This is a particularly challenging task, especially where information on detailed pesticide usage at a high spatial and temporal resolution is not available.

Some models have been developed that use high quality meteorological data to simulate the transport within Europe of hazardous airborne pollutants accidentally released to the atmosphere from point-sources. However, it will be difficult to adapt them for diffuse-source emissions using high-resolution pesticide usage data and state-of-the-art knowledge about degradation reactions in the atmosphere. Van Jaarsveld et al. (1997) used a model initially developed to simulate the transport and deposition of acidifying compounds (Asman and van Jaarsveld, 1992) to describe the European scale transport and deposition of lindane and benzopyrene for which emission data were available. Simulations of lindane concentrations in precipitation were correlated with observed data for a number of stations around the North Sea, but under-estimated absolute values by a factor of three. The authors concluded that further information on emission mechanisms and atmospheric degradation were needed if improved predictions were to be made.

As an alternative to the use of meteorologically based models, a generic procedure for determining the potential for long-range atmospheric transport of substances using a relatively simple calculation of atmospheric residence time has recently been proposed by van Pul et al. (1998). The atmospheric residence time is calculated using first-order and time-averaged reaction rates for the atmospheric removal processes of dry and wet deposition and degradation in air. Although this method is relatively simple compared to mechanistic meteorologically based models, it still requires a number of atmospheric and soil input parameters for which global estimates have to be made. A preliminary sensitivity analysis suggested that, apart from the Henry's constant and the degradation rate in air, expected uncertainties of input parameters (which ranged between factors of 2 and 10) resulted in predicted residence times varying by less than a factor of 2. It was also suggested that if all input parameters are known to within a factor of 2, then calculated residence times will generally be within a factor of 4. The model shows some promise as a screening tool, but will require further and more precise testing and calibration against regional or national datasets before it can be used with any confidence.

4.3. Potential impacts from atmospheric transport and deposition

Within Europe, the concentrations of pesticides in rainfall are mostly below around 100 ng/l. Maximum values of a few micrograms per litre have been recorded for 14 compounds, but such concentrations are usually very transient and relate to short-distance transport from very local usage. Their impact on the local agricultural environment, including any small water bodies present, is likely to be small compared to that from normal agricultural applications (Dubus et al., 1998). For those compounds with evidence of transport over longer distances (patterns b–e in Fig. 2), seasonal peak concentrations of a few to a few hundred nanograms per litre appear to be possible in areas far away from where those compounds were used. However, the largest concentrations probably only apply to atrazine and lindane or its isomers and maximum concentrations of other seasonally transported compounds are likely to be in the order of a few tens of nanograms per litre. Nevertheless, such concentrations in rainfall clearly have the potential to form a significant input to natural or semi-natural ecosystems (Dörfler and Scheunert, 1997). The actual impact of such inputs will be dependent on the location of the ecosystem in relation to agricultural areas. For fresh-water, estuarine and coastal ecosystems subject to riverine or other surface drainage inputs from agricultural areas, the contribution of pesticides via atmospheric deposition is likely to be negligible (Harris et al., 1992; Bester et al., 1995). For other fresh-water, marine or terrestrial ecosystems, however, contamination originates mainly from aerial inputs (Bester et al., 1995), but potential impacts are as yet uncertain because there is little available

information on the long-term ecotoxicological effects of pesticides at low concentrations. Although the impact of atrazine on terrestrial and freshwater ecosystems is documented, corresponding information for the marine ecosystem is scarce (Hühnerfuss et al., 1997). A number of papers have suggested effects on non-target organisms from aerial deposition in Europe. Lindane uptake by zooplankton in a Swedish pond was related to atmospheric deposition (Larsson, 1989) and compounds such as lindane have the potential for bio-accumulation along the food chain resulting in contamination of some organisms (Larsson et al., 1992). De Jong et al. (1995) estimated the emission, dispersal and deposition rates of four pesticides in the Netherlands at the local and national scale using a modelling approach. They estimated that fungi and vascular plants from over 25% of the country would be subject to non-target side effects from atrazine, although these were primarily resulting from a wide distribution of use of atrazine and short range (<2 km) transport from treated plots rather than longer range transport. For other compounds, Trevisan et al. (1993) showed that pesticides are probably one factor contributing to the mixture of many air pollutants that affect forest health. Chevreuil et al. (1996) suggest that the combined effect of a mixture of pesticide compounds could possibly produce adverse impacts at concentrations below their individual toxic threshold values.

5. Conclusions

The published studies reviewed here show that a large number of pesticides have been monitored in atmospheric deposition throughout Europe. Approximately half of the monitored compounds have been detected in atmospheric deposition. Five broad patterns of atmospheric deposition can be identified, depending on the complex interactions between pesticide physico-chemical properties, local and regional usage patterns, prevailing atmospheric conditions and, in some cases, timing of agricultural operations. Although some models have been developed to predict the atmospheric transport of pesticides, they are mostly complex, meteorologically based and not suitable for regulatory assessments. One simpler screening model has recently been developed but requires further testing, evaluation and regional calibration.

The range of concentrations detected in the European studies suggests that atmospheric impacts are likely to be minimal in areas where pesticides are directly applied or where there are significant inputs from surface waters derived from agricultural areas. In other areas, there is the potential for some specific compounds to accumulate as a result of aerial deposition, albeit at small concentrations, and the ecotoxicological consequences of this have yet to be fully explored.

Identification of the origin of air pollution by pesticides has concentrated on agricultural use, but there is evidence that non-agricultural use of pesticides could make a significant contribution to atmospheric inputs, transport and subsequent deposition.

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