



Levels and Sources of Organophosphorus Flame Retardants and Plasticizers in Indoor and Outdoor Environments

av

Anneli Marklund

Akademisk avhandling

som med vederbörligt tillstånd av rektorsämbetet vid Umeå universitet för avläggande av Filosofie Doktorsexamen vid Teknisk-Naturvetenskapliga fakulteten i Umeå, framlägges till offentlig granskning vid Kemiska institutionen, hörsal KB3B1 i KBC-huset, fredagen den 9/12, 2005, klockan 13.00.

Fakultetsopponent: Associate Professor Roland Kallenborn, University Centre in Svalbard (UNIS), Norway.

Levels and Sources of Organophosphorus Flame Retardants and Plasticizers in Indoor and Outdoor Environments

Anneli Marklund, Environmental Chemistry, Department of Chemistry, Umeå University, Umeå, Sweden

Abstract

Global consumption of organophosphate esters (OPs), which are used as flame retardants and plasticizers, is rapidly increasing. Their use as additives in diverse applications poses a risk as they may be emitted from the products they are added to and be further transported in the environment. Therefore, the levels, distribution, and possible sources of 15 OPs, some of which are reported to be toxic, were investigated in indoor and outdoor environments. An exposure assessment was performed, and the exposure to OPs via inhalation was examined for five occupational groups. In addition, based on the findings of the studies, the total flow of OPs in Sweden was estimated.

In indoor environments, the OPs detected in air and dust varied between the sites, but generally reflected the building materials, furniture etc. used in the premises. A majority of the analysed OPs were detected in all samples, and public buildings tended to have higher levels than domestic buildings. The chlorinated OPs dominated in indoor air and wipe samples from vehicles. They were also abundant in the dust samples. Some occupational groups were significantly more exposed to OPs than others. Aircraft technicians, for example, were exposed to about 500 times more tributyl phosphate than day care centre personnel.

Upon domestic and industrial cleaning, OPs are discharged with the wastewater via the sewage system to sewage treatment plants (STPs). Irrespective of the size of the STPs investigated, they had similar levels of OPs in their influents, indicating that products containing OPs are widely used by the communities they serve. In some cases, it was possible to trace elevated levels of individual OPs to specific sources. The OPs were poorly removed from the wastewater, and the chlorinated OPs especially tended to pass through the STPs without being removed or degraded. Thus, levels of OPs in their effluents were also similar, as were the levels in their sludge. Of the total amounts of OPs entering the STPs, 50% was emitted to the recipients via the effluent. Hence, there is room for significant improvement in the treatment processes. Carps living in a pond, receiving STP effluent were found to contain relatively high levels of OPs compared to perch collected in lakes from background locations.

Air and road traffic were also identified as sources of OPs: the concentration of total OPs decreased with increasing distance from a major road intersection, and OPs were detected in lubricants, hydraulic fluids and waste oil. OPs are emitted from both diffuse and direct sources to the environment and may then be spread by long-range air transport, rivers and streams. This probably explains why OPs were also detected in air and fish from background locations.

Finally, OPs are ubiquitous substances in both indoor and outdoor environments. The possibility that prolonged exposure to OPs at the levels found may cause adverse effects, for instance in aqueous organisms, cannot be excluded. For example, the OP levels in snow were of the same magnitude as reported effect concentrations. Similarly, in some premises, indoor exposure to OPs was close to the suggested guideline value. However, since these studies include only a limited number of samples, and data regarding the health and environmental effects of OPs are sparse, no definitive conclusions regarding their possible environmental effects can be drawn.

Key words: organophosphate esters, OPs, flame retardants, plasticizers, analysis, TCEP, TPP, TCPP, TBP, TBEP, human exposure, air, dust, sewage treatment plants, sludge, oil, snow, deposition

ISBN 91-7305-930-7

Levels and Sources of Organophosphorus Flame Retardants and Plasticizers in Indoor and Outdoor Environments

Anneli Marklund



UMEÅ UNIVERSITY
Department of Chemistry, Environmental Chemistry
Umeå 2005

© 2005 Anneli Marklund

UMEÅ UNIVERSITY
Department of Chemistry
Environmental Chemistry
SE-901 87 Umeå
SWEDEN

ISBN 91-7305-930-7

Printed in Sweden by VMC, KBC, Umeå University, Umeå 2005

ABSTRACT

Global consumption of organophosphate esters (OPs), which are used as flame retardants and plasticizers, is rapidly increasing. Their use as additives in diverse applications poses a risk as they may be emitted from the products they are added to and be further transported in the environment. Therefore, the levels, distribution, and possible sources of 15 OPs, some of which are reported to be toxic, were investigated in indoor and outdoor environments. An exposure assessment was performed, and the exposure to OPs via inhalation was examined for five occupational groups. In addition, based on the findings of the studies, the total flow of OPs in Sweden was estimated.

In indoor environments, the OPs detected in air and dust varied between the sites, but generally reflected the building materials, furniture etc. used in the premises. A majority of the analysed OPs were detected in all samples, and public buildings tended to have higher levels than domestic buildings. The chlorinated OPs dominated in indoor air and wipe samples from vehicles. They were also abundant in the dust samples. Some occupational groups were significantly more exposed to OPs than others. Aircraft technicians, for example, were exposed to about 500 times more tributyl phosphate than day care centre personnel.

Upon domestic and industrial cleaning, OPs are discharged with the wastewater via the sewage system to sewage treatment plants (STPs). Irrespective of the size of the STPs investigated, they had similar levels of OPs in their influents, indicating that products containing OPs are widely used by the communities they serve. In some cases, it was possible to trace elevated levels of individual OPs to specific sources. The OPs were poorly removed from the wastewater, and the chlorinated OPs especially tended to pass through the STPs without being removed or degraded. Thus, levels of OPs in their effluents were also similar, as were the levels in their sludge. Of the total amounts of OPs entering the STPs, 50% was emitted to the recipients via the effluent. Hence, there is room for significant improvement in the treatment processes. Carps living in a pond, receiving STP effluent were found to contain relatively high levels of OPs compared to perch collected in lakes from background locations.

Air and road traffic were also identified as sources of OPs: the concentration of total OPs in snow samples decreased with increasing distance from a major road intersection, and OPs were detected in aircraft lubricants and hydraulic fluids and in waste oil from cars and lorries. OPs are emitted from both diffuse and direct sources to the environment and may then be spread by long-range air transport, rivers and streams. This probably explains why OPs were also detected in air and fish from background locations.

Finally, OPs are ubiquitous substances in both indoor and outdoor environments. The possibility that prolonged exposure to OPs at the levels found may cause adverse effects, for instance in aqueous organisms, cannot be excluded. For example, the OP levels in snow were of the same magnitude as reported effect concentrations. Similarly, in some premises, indoor exposure to OPs was close to the suggested guideline value. However, since these studies include only a limited number of samples, and data regarding the health and environmental effects of OPs are sparse, no definitive conclusions regarding their possible environmental effects can be drawn.

Key words: organophosphate esters, OPs, flame retardants, plasticizers, analysis, TCEP, TPP, TCPP, TBP, TBEP, human exposure, air, dust, sewage treatment plants, sludge, oil, snow, deposition

SAMMANFATTNING

Den globala konsumtionen av organiska fosfatestrar (OP) för användning som flamskyddsmedel och mjukgörare har ökat kraftigt på senare tid. Det breda användningsområdet för dessa additiv medför en risk att de kan avges från de produkter de är satta till och transporteras vidare ut i miljön. Följaktligen undersöktes källor till, halter av, och fördelning i inom- och utomhusmiljöer av 15 OP, varav en del har toxiska effekter. Vidare har exponering för OP i bl.a bostäder och offentliga byggnader beräknats. Utöver detta undersöktes exponeringen för OP via inandning hos 5 yrkesgrupper. Slutligen användes resultaten för att uppskatta det totala flödet av OP i Sverige.

I de olika inomhusmiljöerna uppmättes ett flertal OP i varierande halter i damm och luft, men generellt speglade halterna byggnadsmaterial, möbler etc. som fanns i lokalerna. De offentliga lokalerna tenderade att uppvisa högre halter än privata hus, förmodligen beroende på högre brandskyddskrav. Klorerade OP dominerade i inomhusluft samt i avstrykningsprov från fordon och förekom även i höga halter i damm. Vissa yrkesgrupper var exponerade för betydligt högre halter OP än andra, t.ex. exponerades flygtekniker för upp till 500 ggr högre lufthalter av tributylfosfat jämfört med förskollärare.

I samband med våtskurning i inomhusmiljöer (hushåll, industrilokaler, osv.) släpps avsevärda mängder OP ut i avloppet och når till sist reningsverk. Oberoende av storlek på reningsverken var halterna av OP relativt lika, i vardera ingående vatten och slam, vilket indikerar en bred användning av OP i samhället. I vissa fall kunde specifika källor till OP i avloppsvattnet spåras. Exempelvis hade två av reningsverken högre halter av en klorerad OP jämfört med övriga reningsverk. Dessa behandlade vatten från en skumplastfabrik, respektive en fabrik som tillverkar flamskyddad färg. Avskilningsgraden av OP från avloppsvatten visade sig generellt vara dålig, i synnerhet klorerade OP tenderade att passera genom reningsverken utan att degraderas eller avskiljas från vattnet. Av den mängd OP som nådde reningsverken släpptes 50 % ut till miljön via utflödet. Som ett resultat av detta uppvisade karp från en damm påverkad av utflödet från ett reningsverk höga halter OP jämfört med abborrar från referenssjöar. Det finns därför anledning att förbättra tekniken på reningsverken.

Flyg- och vägtrafik kunde också identifieras som källor till OP i miljön. OP uppmättes i hydrauloljor och smörjmedel för flygplan samt i spillolja från bilar och lastbilar. Vidare minskade totalhalten OP i snöprov med ökat avstånd från en större vägkorsning. OP släpps således ut från både diffusa och direkta källor och kan sedan spridas vidare via luft och vattendrag. Därmed var det inte förvånande att OP även påträffades i luft och fisk från bakgrundslokaler.

Avslutningsvis förekommer OP i varierande halter i såväl inom- som utomhusmiljöer. Det kan inte uteslutas att långvarig exponering för de halter av OP som uppmätts skulle kunna orsaka negativa effekter hos t.ex vatten- eller jordlevande organismer. I smälta snöprov från en flygplats uppmättes exempelvis halter av OP i samma storleksordning som rapporterade effektkoncentrationer. Dessutom visade sig den beräknade exponeringen av OP, i några av de provtagna inomhuslokalerna, uppgå till halter nära det föreslagna riktvärdet för OP i Tyskland. Dessa studier inkluderar dock ett begränsat antal prov och provtyper och kunskapen om dessa föreningars miljö- och hälsoeffekter är bristfällig. Därför bedöms underlaget som för litet för att några definitiva slutsatser ska kunna dras angående OPs eventuella effekter på miljön.

LIST OF PAPERS

This thesis is based on the following papers, which will be referred to by their respective Roman numerals.

- I. **Screening of organophosphorus compounds and their distribution in various indoor environments**
Marklund A, Andersson B and Haglund P.
Chemosphere 2003, 53: 1137–1146.
- II. **Organophosphorus flame retardants and plasticizers in air from various indoor environments**
Marklund A, Andersson B and Haglund P.
Journal of Environmental Monitoring 2005, 7: 814–819.
- III. **Traffic as a source of organophosphorus flame retardants and plasticizers in snow**
Marklund A, Andersson B and Haglund P.
Environmental Science & Technology 2005, 39: 3555–3562.
- IV. **Organophosphorus flame retardants and plasticizers in Swedish sewage treatment plants**
Marklund A, Andersson B and Haglund P.
Environmental Science & Technology 2005, 39: 7423–7429.

Published papers are reproduced with kind permission from Elsevier Science (Paper I), the Royal Society of Chemistry (Paper II) and the American Chemical Society (Papers III and IV).

Contribution of the author of this thesis

Papers I-IV

I planned the studies in close cooperation with my supervisors, Haglund and Andersson. I also coordinated the samplings and was responsible for the collection of samples, except for the samples from sewage treatment plants, fish and background air. In addition, I was responsible for all experimental work, the data evaluation and for writing the papers.

ABBREVIATIONS

AChE	acetylcholinesterase	PE	polyethylene
ABS	acrylonitrile-butadiene-styrene	PUF	polyurethane foam
CLP1	tris(2-chloroethyl) phosphite	PVC	polyvinyl chloride
DCE	dichloroethane	RS	recovery standard
DCM	dichloromethane	RSD	relative standard deviation
DOPP	di-n-octylphenyl phosphate	SPE	solid-phase extraction
dw	dry weight	TBEP	tris(2-butoxyethyl) phosphate
EHDPP	2-ethylhexyl diphenyl phosphate	TBP	tributyl phosphate
GC-NPD	gas chromatography with a nitrogen phosphorus detector	TiBP	tri- <i>iso</i> -butyl phosphate
GC-MS	gas chromatography - mass spectrometry	TCEP	tris(2-chloroethyl) phosphate
GPC	gel permeation chromatography	TCP	triclesyl phosphate
IS	internal standard	T CPP	tris(2-chloroisopropyl) phosphate
KemI	National Chemical Inspectorate of Sweden	TDCPP	tris(1,3-dichloro-2-propyl) phosphate
LC ₅₀	lethal concentration; aqueous concentration at which 50% of test organisms dies	TEEdP	tetraethyl ethylenedi-phosphonate
LD ₅₀	lethal dose, e.g. by injection or oral administration, causing 50% of test organisms to die	TEHP	tris(2-ethylhexyl) phosphate
NOEC	no observed effect concentration	TMP	trimethyl phosphate
OPIDN	organo-phosphate-induced delayed neuropathy	TOCP	tri- <i>ortho</i> -cresyl phosphate
OPs	organophosphate esters	TPeP	tripentyl phosphate
		TPP	triphenyl phosphate
		TPrP	tripropyl phosphate
		v/v	volume to volume
		w/w	weight to weight
		ww	wet weight

LIST OF CONTENTS

ABSTRACT	I
SAMMANFATTNING.....	III
LIST OF PAPERS.....	V
ABBREVIATIONS	VI
1. INTRODUCTION.....	1
2. ORGANOPHOSPHATE ESTERS.....	5
CHEMICAL STRUCTURES AND APPLICATIONS	5
FLAME RETARDANT MECHANISMS	7
OCCURRENCE IN THE ENVIRONMENT	8
UPTAKE AND ELIMINATION	8
DEGRADATION.....	10
BIOLOGICAL EFFECTS.....	10
HUMAN EXPOSURE.....	12
REGULATORY LIMITS.....	13
3. EXPERIMENTAL SECTION	15
SAMPLING, EXTRACTION AND CLEAN-UP.....	16
Indoor Environments.....	16
<i>Dust and Windscreens</i>	16
<i>Air</i>	16
<i>Human Exposure</i>	17
Outdoor Environments	18
<i>Snow</i>	18
<i>Product Samples</i>	19
<i>Background Air and Deposition</i>	19
<i>Sewage Treatment Plants</i>	20
Biological Samples	21
<i>Fish</i>	21
ANALYSIS	22

Instrumental Analysis.....	22
Calibration and Quantification	23
QUALITY ASSURANCE AND QUALITY CONTROL.....	23
4. LEVELS AND SOURCES.....	25
INDOOR ENVIRONMENTS.....	25
Dust and Air.....	25
Windscreens	28
Human Exposure.....	30
OUTDOOR ENVIRONMENTS	33
Product Samples	33
Snow.....	34
Background Air and Deposition.....	35
Sewage Treatment Plants.....	35
BIOLOGICAL SAMPLES	38
Fish	38
5. ESTIMATION OF MASS FLOW	41
6. CONCLUSIONS AND FURTHER PERSPECTIVES	45
7. ACKNOWLEDGEMENTS	49
8. REFERENCES	51

INTRODUCTION

From time to time, alarming reports with titles like "New environmental pollutants with toxic and hazardous effects" are published. A few examples of groups of chemicals posing potential risks that have been investigated recently include the perfluorinated compounds, such as FTOH (fluorotelomer alcohols) and PFOS (perfluorooctane sulfonates) which are used *inter alia* as impregnating agents to protect textiles, paper and cardboard; acrylamides, which have been shown to be present in fried food; phthalates, used as softeners in plastic materials, including toys for children; and brominated flame retardants (e.g. polybrominated diphenylethers), which have been shown to be persistent, toxic and bioaccumulating. When such a substance is confirmed to cause adverse effects, it may be replaced by another, hopefully less harmful, substance. However, prohibiting or replacing a specific chemical is not always straightforward. Factors that may be evaluated before any ban is introduced include economic costs and benefits, the potential risks and even political considerations. To help promote a sustainable environment, the Swedish parliament adopted 15 environmental quality objectives such as "clean air" and "a non toxic environment" in 1999. On the other hand, the toxicity and environmental fates of most of the thousands of chemicals we use on a daily basis in modern society are poorly documented. One group of chemicals for which such data are lacking is the organophosphate esters (OPs), which are mainly used as flame retardants and plasticizers.

The worldwide consumption of flame retardants is closely linked to regulations concerning fire precautions^[1]. Organophosphorus flame retardants account for approximately 15% of the total amount of flame retardants used, comparable to the brominated retardants, which account for 20%^[2]. The use of OPs is rapidly increasing. For example, between the years 1995 and 2001 their global consumption increased from 108 000 tonnes to 186 000 tonnes^[2,3]. In Western Europe the consumption, evenly distributed between chlorinated and non-chlorinated OPs, increased from 58 000 tonnes to 83 000 tonnes from 1998 to 2001^[2,4]. OPs are mainly used as additives, i.e. they are not chemically bound to the products they are added to. Thus, they may diffuse out of the products and reach the environment by leaching, volatilization and abrasion throughout the products' entire lifetime (Fig. 1).

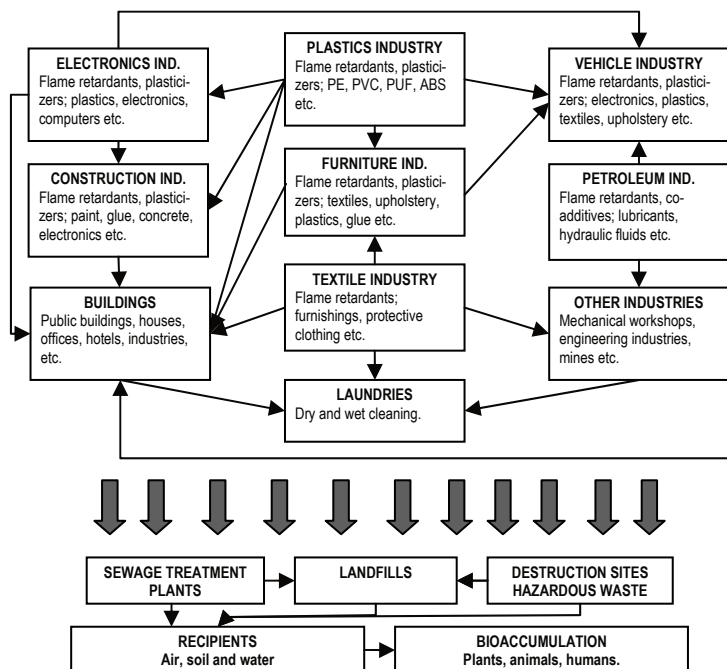


Figure 1. Chart illustrating the flow of organophosphorus flame retardants and plasticizers. The diversity of applications of OPs increases the risk that they may end up in different environmental compartments via volatilization, leaching or abrasion (Paper I).

The principal aims of the studies underlying this thesis were to investigate levels, distribution patterns and sources of up to 15 OPs in different environmental compartments, and to estimate their total flow in Sweden. Indoor and outdoor environments, product samples, biological samples and human exposure to OPs were investigated in order to generate data which may be used for risk assessments. An additional aim was to develop analytical methods which could be utilized to analyse OPs in different matrixes.

The OPs selected for study were primarily those imported in the largest quantities into Sweden. TCEP, TCPP, TDCPP, TBP, T_iBP, TEHP, TPP, TBEP, EHDPP and TCP (see Table 1 for abbreviations) dominated the Swedish imports of OPs as bulk chemicals in 1999 and 2003^[5]. Furthermore, the chlorinated OPs; TCEP, TCPP and TDCPP, are included in the European Commission priority lists EC 2268/95^[6] and EC 2364/2000^[7] and are currently undergoing risk assessments in the European Union. The other five substances are not known to be imported as pure chemicals into Sweden, but are (or have been) used internationally and may be present in imported goods.

1. Introduction

Table 1. Acronyms, CAS numbers and applications of the studied organophosphorus compounds

Name	CAS number	Acronyms	Flame retardant	Plasticizer	Stabilizer	Hydraulic fluid	Floor finishes, wax	Laquer, paint, glue	Anti-foaming agent	Cosmetic products	Industrial processes	Fungus resistance	Reference
tris(2-chloroisopropyl) phosphate	13674-84-5 ^a	TCP	X	X									[8]
tris(1,3-dichloro-2-propyl)phosphate	13674-87-8	TDCPP	X	X				X					[8]
tris(2-chloroethyl) phosphate	115-96-8	TCEP	X	X				X			X		[8]
tributyl phosphate	126-73-8	TBP		X		X	X	X	X		X		[9]
tri-iso-butyl phosphate	126-71-6	TIBP						X	X		X		[10]
tris(2-butoxyethyl) phosphate	78-51-3	TBEP	X	X			X	X	X				[11]
triphenyl phosphate	115-86-6	TPP	X	X		X		X					[12]
tris(2-ethylhexyl) phosphate	78-42-2	TEHP	X	X								X	[11]
2-ethylhexyl diphenyl phosphate	1241-94-7	EHDPP	X	X				X					[13]
tricresyl phosphate	1330-78-5	TCP	X			X		X			X		[14]
tris(2-chloroethyl) phosphite	140-08-9	CLP1	X		X	X							[13]
trimethyl phosphate	512-56-1	TMP									X		[13]
tripropyl phosphate ^b	513-08-6	TPrP											
di-n-octylphenyl phosphate	6161-81-5	DOPP		X							X		[15,16]
tetraethyl ethylene diphosphonate	995-32-4	TEEdP								X	X		[17]

^a The commercial mixture of TCP contains four isomers, of which tris(2-chloroisopropyl) phosphate is the most abundant.

^b For tripropyl phosphate, no application was listed in the literature or databases consulted.

ORGANOPHOSPHATE ESTERS

Chemical Structures and Applications

The organophosphate esters (OPs) comprise the most commonly used group among the organophosphorus flame retardants, which also include phosphonates, phosphites and phosphines^[18]. OPs are industrially produced by reacting phosphorus oxychloride (POCl_3) with various reactants. Structurally, they are derivatives of phosphoric acid that can be divided into three groups; trialkyl-, alkyl diaryl-, and triaryl phosphates. Further, the alkyl phosphates can be halogenated or non-halogenated. In general, OPs are semi-volatile compounds with low to moderate solubility in water and a relatively high affinity to particles. However, because of the variations in their substituent characteristics, they have strongly differing chemical and physical properties (Fig. 2). These variations in properties make them useful in diverse applications (Table 1).

Different OPs are used as additives for different materials, depending on the desired properties. Triaryl phosphates are more thermally stable than trialkyl phosphates and are thus more effective as flame retardants. On the other hand, trialkyl phosphates have better plasticizing properties and improve the low-temperature flexibility of plastics and synthetic rubber^[3]. Consequently, OPs are utilized as flame retardants and/or plasticizers in a wide range of materials, *e.g.* polyvinyl chloride (PVC), polyurethane foams (PUF), thermoset resins, thermoplastic materials, textile finishes, cellulosics and polyesters. Triaryl phosphates are used to improve the flame retardance of plastic materials such as PVC and cellulose acetate^[19]. Computer housings made of a blend of acrylonitrile-butadiene-styrene (ABS) and polycarbonate (PC) are generally flame retarded with TPP. The chlorinated OPs are used to flame retard both flexible and rigid PUF, rubber and textile coatings^[8]. Rigid PUF are primarily used for thermal insulation while flexible PUF can be found in products such as upholstered furniture and mattresses. Mattresses for hospitals and prisons are commonly treated with TDCPP^[20]. Other products in which halogenated alkyl phosphates (TCPP, TCEP and TDCPP) have been found include sound- and shock-absorbing materials, foam fillers and wood preservation coatings^[21,22]. TEHP and TBEP are used as flame retardants and low temperature plasticizers in PVC and synthetic rubber *e.g.* in seals, hoses and soles of shoes^[11,23]. TBEP is also used as a levelling agent in waxes, floor polishes and paper coatings^[23].

2. Organophosphate Esters

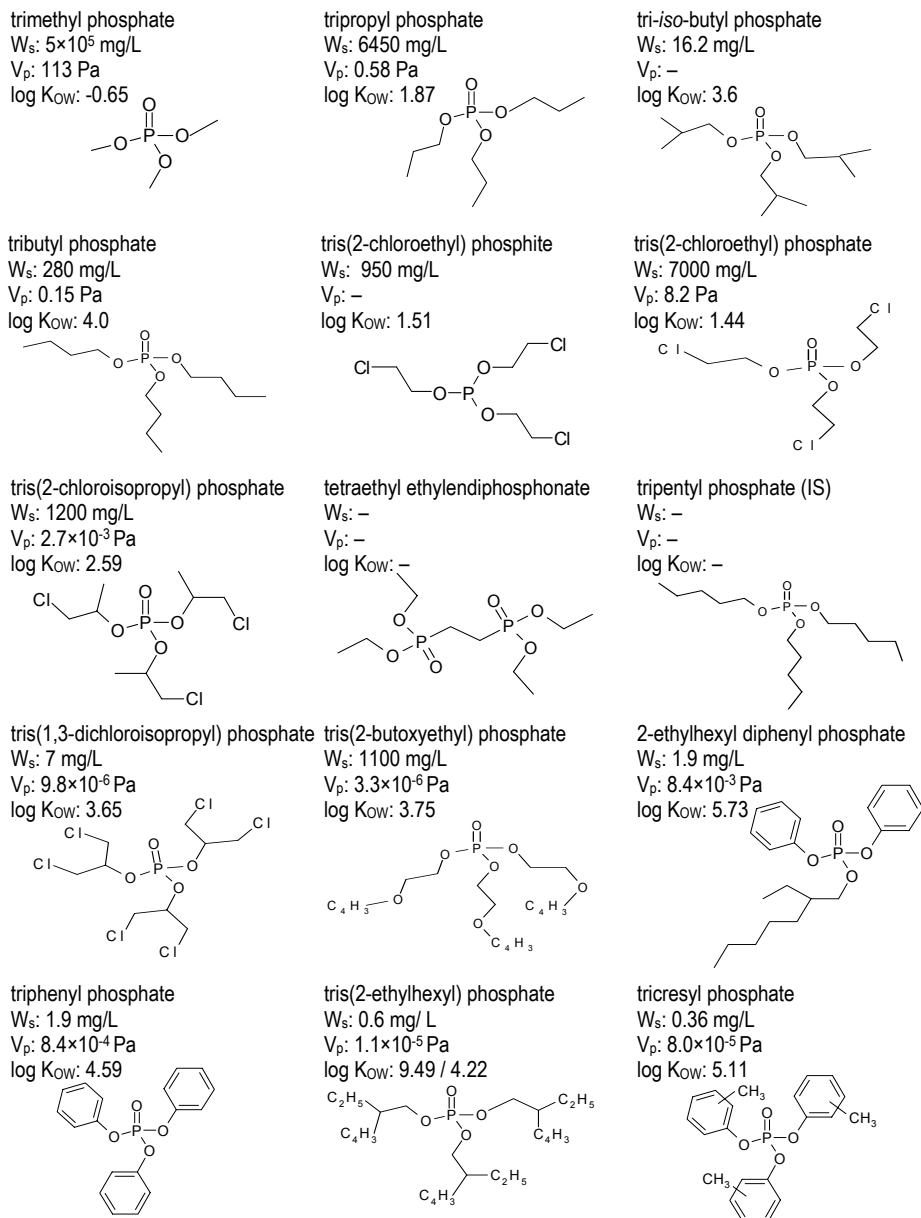


Figure 2. Structure and physical characteristics of organophosphate esters^[11,24]. W_s = water solubility, $\log K_{OW}$ = octanol-water partition coefficient, V_p = vapour pressure.

Apart from being used as flame retardants, some OPs (*e.g.* TBP, TPP and TCP) are utilized as extreme pressure additives and antiwear (EP/AW) agents in hydraulic fluids, lubricants, transmission oils and motor oils to prevent surface damage^[25]. TBP is one of the main ingredients (up to 79%) in several aircraft hydraulic fluids, while TPP is usually added at lower levels (1–5%). TBP is also used as an anti-foaming agent in concrete, in antifreeze solutions and as a component in cotton defoliants^[9,10,23].

Flame Retardant Mechanisms

Fire is a gas-phase reaction involving several stages; heating, ignition, decomposition and flame spread. Thus, in order for a substance to burn it must first become gaseous. Flame retardants are added to combustible materials with the principal aims to increase their resistance to ignition and to suppress the combustion process when the material is ignited. Flame retardance is a complex process that may involve physical and/or chemical action in the solid, liquid or gas phase at one or more stages of the combustion process^[1].

Physical actions that slow down the combustion process are:^[1]

- (i) cooling, the added flame retardant triggers endothermic processes that lower the temperature below that required to sustain the combustion process.
- (ii) formation of a protective solid or gaseous layer (coating) that shields the combustible layer from the gas phase. This cools the condensed phase, reduces the quantities of pyrolysis gases and limits the oxygen, which is required for the combustion process.
- (iii) dilution, the flame retardant may evolve inert gases during decomposition which dilutes the fuel in the solid and gaseous phase and thus keeps the combustible gas concentrations below the ignition limit.

Chemical actions in the solid and gas phases that retard the combustion process are:^[1]

- (i) reactions in the gas phase, the flame retardant interrupts the radical mechanisms of the combustion process which take place in the gas phase. This stops the exothermic process, cools the system, and reduces the supply of flammable gases.
- (ii) reactions in the solid phase, which may be of two types: (a) the flame retardant may accelerate the breakdown of the polymer, limiting the influence of the flame; (b) the flame retardant may cause the formation of a carbonaceous layer by cyclization and cross-linking, which shields the polymer.

The working mechanisms of the organophosphorus flame retardants vary with the phosphorus compound, the polymer and the combustion conditions^[26]. The phosphate esters function mainly in the condensed phase, but are also reported to act in the gas phase. The halogenated OPs, for example, interfere with the radical mechanisms taking place in the gas phase, but also affect the condensed phase^[1]. In the latter case, OPs promote charring by producing phosphoric or polyphosphoric acids which catalyse the formation of an intumescent carbon char that shields the polymer from the flame^[26]. The flame retardant properties of the chlorinated OPs are enhanced by the combination of the phosphorus group and the halogen^[18]. The vapour pressure and the water solubility are reduced by the halogen, which contributes to the retention of the flame retardant in the polymer.

Occurrence in the Environment

Organophosphate esters do not occur naturally in the environment, but only as a result of anthropogenic activity^[8,9,11,12,14]. They have previously been detected in both indoor and outdoor environments. In indoor environments, OPs have been found in air and dust, but most studies have usually examined only a few OPs or a limited selection of indoor environments, *e.g.* offices, homes and day care centres^[21,27-30]. However, two recently published studies present a number of OPs in several indoor environments^[31,32]. The OPs are normally found at mg/kg levels in dust and at ng/m³ or µg/m³ levels in indoor air. In outdoor environments, OPs have been found in diverse compartments, including river water^[33-37], groundwater^[34,35], wastewater^[33-35,38-41], precipitation^[34,35,42], pine needles^[43], soil^[44], leachates from waste disposal sites^[45,46] and particulate matter collected in Antarctica^[47]. Similarly to the studies of indoor environments, studies of their occurrence in outdoor environments are usually limited to a few OPs and/or a limited number of sampling sites.

In humans, TBEP, TBP and TDCPP have been detected in adipose tissue at levels up to 260 ng/g^[48,49]. TDCPP has also been found in human seminal plasma at concentrations ranging from 5 to 50 ng/g^[50].

Uptake and Elimination

The octanol-water partition coefficient (K_{ow}) of a substance can be used to predict its potential to bioconcentrate – the higher the $\log K_{ow}$ value, the higher its ability to bioconcentrate. As can be seen in Fig. 2, $\log K_{ow}$ values for

OPs range from -0.65 to 9.49, indicating that there are significant differences in bioconcentration potential among OPs. However, to accumulate in an organism the substance needs to be bioavailable. Further, the uptake rate, lipid content, metabolic capacity and metabolic specificity also affect the bioconcentration and, consequently, the actual bioconcentration is species-specific. Killifish and goldfish, for instance, show great variations in bioconcentration when exposed to TBP, TCEP, TDCPP and TPP^[51]. Of the four studied substances, all accumulated in the fish, except for TCEP. The uptake rates varied both between compounds and between species, and killifish seemed to absorb and metabolize TBP more efficiently than goldfish. TPP showed the highest ability to accumulate in both species, which is consistent with its high log K_{ow} (4.59). Further, chironomid larvae accumulate higher concentrations of EHDPP and tri-*meta*-cresyl phosphate than fathead minnows^[52]. After a year in ponds in which the initial concentration of each of these substances was 50 µg/L, the larvae contained 0.4 µg/g and 0.8 µg/g of EHDPP and tri-*meta*-cresyl phosphate, respectively, in the cited study. The distribution of TPP in internal organs of rainbow trout exposed to ¹⁴C-TPP has been studied by Muir *et al.*^[53] The highest amounts were found in liver and kidney tissues, and the liver also showed rapid clearance of TPP, which the cited authors attributed to extensive metabolism of TPP in the liver.

Studies on mammals have shown that OPs can be absorbed via inhalation, digestion and dermal exposure^[8,9,11,12,54,55]. Rats that have been orally exposed to TDCPP show a fast uptake through the digestive system^[56]. The substance is then distributed throughout the body and the highest concentrations have been found in kidney, liver and lung tissues. In rats, TDCPP is metabolised and excreted, primarily as di- and mono-esters via urine^[56,57]. In a study where rats were intravenously exposed to ¹⁴C-TDCPP, 92% of the ¹⁴C was excreted within five days via urine (54%), faeces (16%) and exhalation (22%)^[57]. The main metabolite was bis(1,3-dichloro-2-propyl) phosphate, while other identified metabolites were 1,3-dichloro-2-propyl phosphate and 1,3-dichloro-2-propanol. However, there was no increase in the urinary elimination of TCEP, or its metabolites, in rats repeatedly fed TCEP, indicating that it is not easily metabolized to urinary metabolites in rats^[58].

Soybean plants have been shown to take up tri-*para*-cresyl phosphate^[14]. After 90 days in a soil contaminated with 10 mg/kg of this substance, 34 µg was found in the plants. The stem and leaves contained the highest proportions; 74% and 24%, respectively. No tri-*para*-cresyl phosphate was detected in the seeds. Extensive uptake of OPs from water by duckweed has also been re-

corded^[59]. After 10 h in ponds with 60 µg/L of each EHDPP and TPP, the duckweed had taken up 2980 µg/kg of EHDPP and 2143 µg/kg of TPP.

Degradation

The potential for biodegradation decreases with the chain length for alkyl phosphates, and similarly, with the number and size of alkyl substituents for aryl phosphates^[60]. In addition, the chlorinated OPs are more resistant to degradation than alkyl and aryl phosphates^[8,9,12]. The main path for degradation of phosphate esters is suggested to involve stepwise enzymatic hydrolysis of the ester bonds, with di- and mono-esters and alcohols/phenols as products^[61]. Enzymes involved in the degradation have been found in both fungi and bacteria^[62]. The primary degradation products are suggested to undergo further degradation^[60]. TPP, for example, has been proven to undergo complete degradation, with carbon dioxide, water and inorganic phosphate as the final products. Anderson *et al.* determined the half-life of TPP in soil, under both aerobic and anaerobic conditions, to be approximately 30 days, and further, concluded that the degradation of TPP in soil is primarily of microbial nature^[62]. In contrast, Fries *et al.* concluded that the degradation rate of OPs is slow in anaerobic environments since they detected TCEP, TBP and TBEP in groundwater^[35]. The importance of microbial activity for the degradation of OPs has also been shown by Saeger *et al.*^[60] In Mississippi river water, TBP, TCP and TPP showed complete primary degradation within seven days and EHDPP within 21 days, while there was no detectable degradation or loss of OPs in heat-sterilized water samples. When degradation of TBP in activated sludge was investigated, Saeger *et al.* observed a decrease in the degradation rate when the concentration of TBP was increased from 3 to 13 mg/L. Moreover, it has been noted that OPs are unlikely to be non-biologically degraded by photolysis in water, since triaryl phosphates do not show significant absorbance of light with wavelengths longer than 290 nm^[52].

Biological Effects

The chemical structure of organophosphate esters used as flame retardants and plasticizers is similar to that of organophosphorus insecticides, which are designed to affect the nervous system of insects. Tri-*ortho*-cresylphosphate (TOCP) was recognised as early as the 1890s as a substance that caused delayed neuropathy when it was used as a 15% solution to treat tuberculosis^[63]. The delayed neuropathy, which can lead to irreversible paralysis, associated with

TOCP and other organophosphorus compounds is referred to as OPIDN (organo-phosphate-induced delayed neuropathy)^[14]. Following a delay of 2–3 weeks, after exposure to single or multiple doses of TOCP, various species (cats, dogs, monkeys and chickens) developed paralysis in their hindlegs. The observed nerve degeneration was limited to the spinal cord and peripheral nerve fibres. However, not all organophosphorus compounds are capable of causing OPIDN, and not all species are uniformly susceptible^[63]. For example, in humans, sheep, cats, chickens and a number of other species there is clinical evidence of progressive, irreversible OPIDN, while rats and mice are not affected in the same way after exposure. Nevertheless, when tricresyl phosphate is produced nowadays, it consists mainly of a mixture of the *meta*- and *para*-isomers; the *ortho*-isomer content is usually minor^[14].

TOCP, and some other OPs (TBEP, TBP, TCEP, TPP and TCP), may also inhibit the enzyme acetylcholinesterase (AChE) in humans^[8,9,11,12,14]. The function of AChE under normal conditions is to catalyse rapid degradation of the neurotransmitter acetylcholine and thus terminate nerve signals^[64]. When AChE is inhibited, acetylcholine accumulates and causes excessive stimulation of the synapses. With more than 50% inhibition of AChE, cholinergic toxicity can be observed with symptoms like involuntary movements, changes in heart rate and respiratory depression. Severe cases of poisoning may even lead to paralysis of the respiratory system and eventually death.

Except for their neurological effects there are sparse data on the physiological effects of OPs, or on human exposure to them. Some of the substances have been tested on animals, and there are also a few reports of workers being accidentally exposed to OPs. It is known that TBP, TCP and TDCPP are adsorbed through human skin^[9,14,54], and that TBEP, TBP, TCPP, TDCPP, TPP and TEHP irritate the skin^[8,9,11,12]. TPP has also been reported to cause contact dermatitis and to be a potent inhibitor of the human monocyte carboxylesterase^[65,66]. Further, OPs have been shown to cause haemolysis (rupture of red blood cells), and the haemolytic effect decreases in the order, EHDPP, TCP, TEHP, TPP, TDCPP, TBP, TBEP, TCPP and TCEP^[67]. Finally, carcinogenic effects have been observed for the chlorinated OPs TCEP and TDCPP^[8,68].

The acute toxicity of OPs towards aquatic organisms varies among the compounds as well as between species. Acute toxicity data towards fish and rats for some of the OPs studied are presented in Table 2. OPs also affect plants; TBP is a defoliant that increases plants' drying rates and inhibits their respiration by

damaging their leaf surfaces^[9]. In addition, it has been reported that the growth of algae is completely inhibited at TPP concentrations of 1 mg/L^[12].

Table 2. Acute toxicity and bioconcentration factors (BCF) of OPs

substance	NOEC (mg/L)	96-h LC ₅₀ (mg/L)	LD ₅₀ orally rat (mg/kg)	BCF	Ref
TBEP	10 ^a	24 ^a	3000		[11]
TBP		4.2–12 ^a	1390	11–49 ^a	[9]
TEHP		>100 ^b	37000	250 ^b	[11]
TCEP		90 ^c	1150		[8]
TCPP	9.8 ^d	51 ^d	1017		[8]
TDCPP	0.56 ^a	1.1 ^a	2380	47–107 ^a	[8]
TCP		0.26 ^a		770–2768 ^a	[14]
TPP		0.36 ^a	3800	324–1368 ^a	[12]

^a rainbow trout, ^b zebra fish, ^c goldfish, ^d fathead minnow

Human Exposure

For the general population, the most relevant exposure pathways for OPs are inhalation, ingestion of dust and dermal contact. In addition, children may be orally exposed to fabrics treated with OPs. Intake of water and food (via migration of plasticizers in packaging plastics to the food) may also contribute to OP exposure. However, the relative importance of the various routes of human exposure to, and uptake of, OPs is still unclear. Data regarding the content of OPs in food and drinking water are sparse, but TBP, TBEP and TCEP have been detected in groundwater at concentrations up to 3700, 2010 and 750 ng/L, respectively^[34]. In tap water, TBEP has been detected at levels up to 5400 ng/L, and leachates from synthetic rubbers and seals were suggested to be the likeliest sources^[11]. The dietary intakes of TBP, TPP and TEHP per kg body weight for eight age groups are reported to range between 3.5–39, 0.3–4.4 and 23–71 ng/(kg×day), respectively^[69].

Personnel who handle OPs as pure chemicals, for example, in industries manufacturing OPs, plastics, textiles, oil products, concrete, etc. are suspected to be the most heavily exposed. Other groups that may be more exposed to OPs than the general population include, *inter alia*, personnel who handle large quantities of hydraulic fluids (*e.g.* aircraft and shipyard technicians), aircraft crew, professional drivers, construction workers and workers at recycling plants for electronic goods.

Regulatory Limits

There are no guidelines or threshold limits for OPs in Sweden. In Germany a guideline value of 40 µg/(kg×day) has been suggested for the sum of TBEP, TBP, TCEP, TCPP, TEHP and TPP^[70]. In the United States, threshold limit values (TLV-TWA) of 2.2 mg/m³ for TBP and 3 mg/m³ for TPP are recommended for occupational exposure^[71].

EXPERIMENTAL SECTION

In general, residue analysis of environmental samples involves several steps, for example, sample pre-treatment, extraction, clean-up and instrumental analysis. The illustration below (Fig. 3) outlines how OPs in an environmental sample may be analysed. In this chapter, the sampling technique and analytical procedure used for each group of sample matrixes are briefly described, while detailed descriptions of the methods used are presented in Papers I–IV.

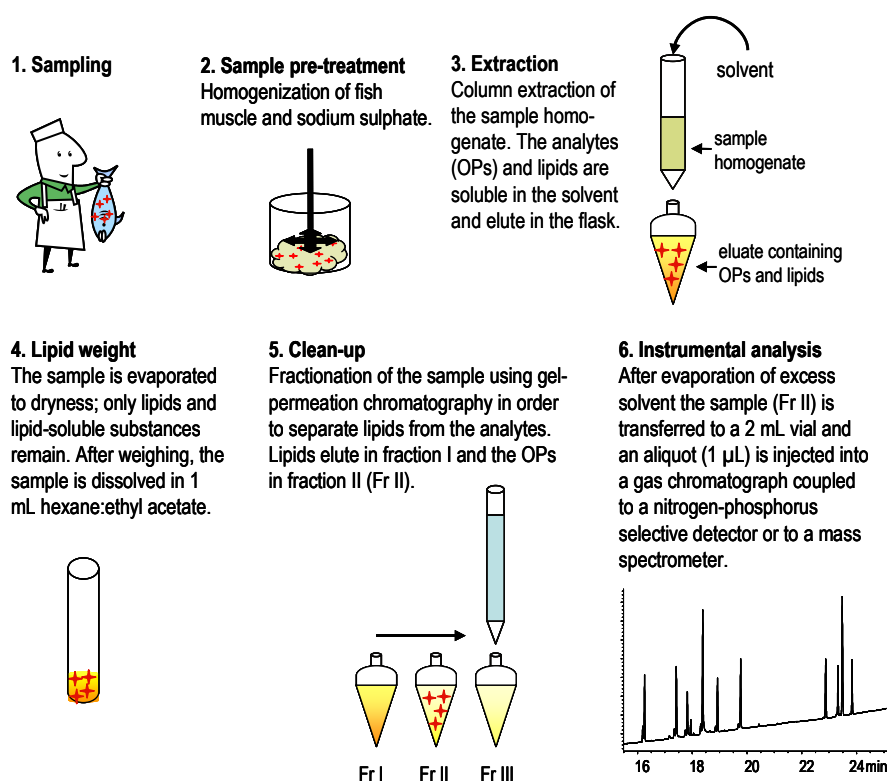


Figure 3. Outline of the analytical method used to analyse OPs in fish. The red crosses illustrate the target analytes, OPs.

Sampling, Extraction and Clean-up

To enable corrections to be made for losses of analytes during extraction and clean-up an internal standard (IS) was added to all samples, generally before extraction.

Indoor Environments

In order to investigate the levels and distribution of OPs in indoor environments, samples of dust, indoor air and wipe samples from vehicles were collected and analysed.

Dust and Windscreens

Dust samples were collected from 15 indoor environments, representing domestic, occupational and public environments (Paper I; Table 4 in Chapter 4). The dust was collected from dust bags of conventional vacuum cleaners except for two of the samples (hospital wards and textile shop), which were hand-picked. The dust bags were made of paper and had been in use for one week on average before sampling. One to two grams of each dust sample (often in duplicate or triplicate) were extracted twice with dichloromethane (DCM) by ultrasonication. The organic layers were combined and filtered.

Wipe samples were collected from the inside of the windscreen of 42 vehicles, representing 15 brands. The sampled vehicles were all 1 to 2 years old except for three, of which one was three years old and two were five years old. Wipe samples were also collected as pooled samples from (a) computer screens and (b) covers. The wipe samples were prepared as described for the dust samples.

Air

Duplicate air samples were collected from 17 buildings, 12 of which had previously been used for dust sampling, hence, the samples represented domestic, occupational and public environments (Paper II; Table 4 in Chapter 4). Solid-phase extraction columns (SPE) with an amino phase were used as sampling devices as they have been shown to be suitable adsorbents for OPs^[72]. In each case, a stationary pump was used to draw approximately 1.7 m³ of air through the sampler at a flow rate of 2.5 L/min.

3. Experimental Section

The SPE columns were eluted with DCM. To ensure that there was no breakthrough of OPs in the sampler, tests were conducted by coupling two SPE columns in series before sampling 2.6 m³ of air. The SPE columns were then separately eluted and analysed.

Human Exposure

An exposure study was performed in which 18 persons, representing five occupations – aircraft technicians (3), prison warders (3), librarians (4), day care centre personnel (3) and taxi drivers (5) – were equipped with personally carried air samplers during an average work day. The aim of the study was to investigate whether there was any correlation between the concentration of OPs in air and the concentration of OPs in blood and urine. The groups were primarily selected on the basis of the results from previous studies in which OPs had been detected in indoor environments, vehicles and oil products (Paper I–III). The personally carried air samplers consisted of a glass fibre filter and a cylindrical PUF adsorbent serially mounted in a sample holder of anodized aluminium^[27], and the air was pumped through the sampler at a flow rate of 2 L/min. Samples of blood and urine were collected from the test persons during the same day as the air sampling. To prevent possible microbial degradation, the samples were frozen immediately after sampling.

The adsorbents were extracted twice with DCM in an ultrasonic bath. The organic layers were combined, evaporated and filtered through a Pasteur pipette containing a plug of glass wool to remove particles before analysis.

Outdoor Environments

In the studies of OP levels in outdoor environments, samples of snow, background air, deposition, wastewater and sludge were analysed. Further, an attempt was made to trace some possible sources of OPs by analysing oils, hydraulic fluids and deicing products.

Snow

Six samples of snow, each of approximately 10 kg, were collected from a municipal airport and from the vicinity of a major road intersection (Paper III). Two of the airport samples were collected at the side of the runway and one at the side of the aircraft parking place. The samples from the intersection were taken at distances of 2, 100, and 250 m, along a line that bisected the angle between the two roads (Fig. 4). As a reference sample, snow was collected in a forested area, 3 km from the nearest road, to reduce the influence of traffic.

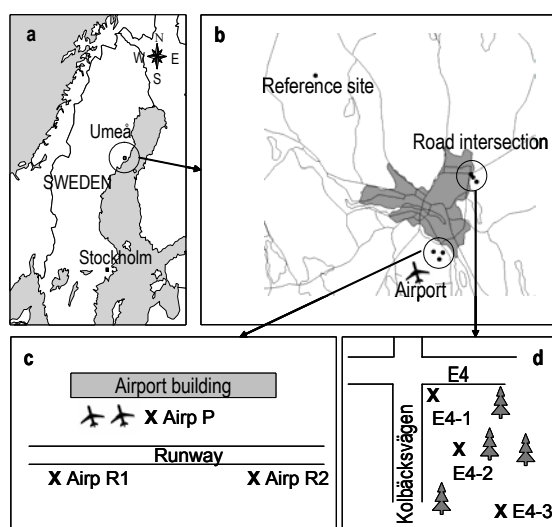


Figure 4. Maps (a and b) showing the snow sampling locations and schematic maps (c and d) showing points, marked by "X", where samples were collected at the parking space for aircraft (Airp P) and by the runway (Airp R1-R2) at the airport (c), and at distances of 2 m (E4-1), 100 m (E4-2), and 250 m (E4-3) from the intersection (d) (Paper III).

The melted snow samples were filtered through filter papers and glass wool plugs after particles larger than 2 mm had been removed. Two litre portions of the water phase were then repeatedly liquid-liquid extracted with DCM. The organic layers were combined, evaporated, dried with anhydrous sodium sulphate, and evaporated into dichloroethane (DCE). The particles (<2 mm) and filters were gently dried in an oven and Soxhlet-extracted with DCM. The Soxhlet extracts were evaporated, dissolved in hexane, and then fractionated using glass columns packed with Florisil and sodium sulphate, and methanol:diethyl ether (83:17) as the eluent^[44].

Product Samples

Samples of lubricants, hydraulic fluids and deicing products were collected at the same airport as the snow samples (Paper III). In addition, samples of oil and waste oil from different types of vehicles were collected from local vehicle repair shops, and pooled according to vehicle type, *i.e.* cars, lorries, tractors and road-construction machines (Table 6 in Chapter 4). Transformer oil and hydraulic fluid were also collected at a hydroelectric power station.

The product samples (4–11 mg) were dissolved in hexane and then fractionated on Florisil columns following the procedure described above for the particle phase from the snow samples.

Background Air and Deposition

In Pallas, a remote area in northern Finland, a 3200 m³ sample of background air and a corresponding dry and wet deposition sample were collected during one week in July 2004 by the Swedish Environmental Research Institute (Paper III). The sampling site was located in an open field, where the air and deposition samplers were positioned at heights of 4 m and 1.5 m above ground, respectively. The air sample was collected using a high-volume sampler (20 m³/h) fitted with a glass fibre filter in front of three cylindrical PUFs in series^[73]. The dry and wet deposition sample was collected in an open Teflon coated sampler, sloping downward to a central opening where three PUFs in series were attached as adsorbents^[74]. During the sampling period, the precipitation amounted to 44.8 mm. Field blanks, consisting of clean PUFs wrapped in aluminium foil, were handled along with the adsorbents. The samples and blanks were stored in a freezer until analysis, Soxhlet-extracted with DCM overnight and evaporated as described for the snow samples. No further clean up was required.

3. Experimental Section

Sewage Treatment Plants

Samples were collected from eleven sewage treatment plants (STPs) spread across Sweden (Paper IV). The STPs were chosen to represent small, medium sized and large STPs, to which various types of industrial facilities were connected (Table 3). Samples of influent, effluent and sludge were collected from STPs 1 through 7, but only sludge from STPs 8 through 11. The samples were collected under normal operating conditions except at STP 5, where we learned disturbances had occurred in the sedimentation process during the sampling week. Thus, the effluent data for this STP were excluded from the study.

Table 3. Descriptive data for the investigated sewage treatment plants (Paper IV)

	influent, effluent and sludge samples							sludge samples			
	1	2	3	4	5	6	7	8	9	10	11
size	small	large	medium	large	small	medium	medium	medium	small	large	medium
treatment ^a	M/C	M/C/B	M/C/B	M/C/B	M/C	M/C/B	M/C/B	M/C/B	M/C/B	M/C/B	M/C/B
sampl. year	2003	2002	2003	2002	2003	2003	2003	2003	2003	2003	2003
sampl. week water	5-6	9	4	5	42	19	40				
sampl. week sludge	5-6	10-12	4	7-9	42	19	40	49	49	49	49
personal equivalents	3,400	257,000	102,000	695,000	1,500	32,500	30,400	24,000	9,800	775,000	104,000
flow (10 ³ m ³ /year)	756	44,900	14,500	88,000	182	3,750	4,730	4,500	1,500	107,000	11,200
sampl. flow (m ³ /day)	4,700	140,900	46,100	317,500	500	10,300	14,900				
sludge dw (tonnes/year)	170	5,800	3,500	13,900	-	790	770	800	240	14,400	1,900

^a M=mechanical, C=chemical and B=biological treatment (activated sludge)

Influent and effluent samples of wastewater, representing weekly averages, were collected flow proportionally using the automatic sampling equipment installed at each STP, except at the two smallest STPs in which the sampling was performed manually. The samples were frozen immediately after sampling, and stored in a freezer until analysis.

One litre of each influent and effluent was filtered, and then repeatedly liquid-liquid extracted with DCM. The first portion of DCM was passed through the same filter as the sample to release OPs that may have been attached to particles trapped by the filter. The organic layers were combined and treated in the same way as the snow samples.

The sludge samples were collected as the final product obtained after the treatment process, except at STP 5, in which the sludge had been stored outdoors for 4–6 months during summertime before collection. Immediately after sampling, the samples were placed in a freezer, where they were stored until analysis to reduce the risk of microbial degradation.

The sludge was freeze-dried and approximately 5 g of each sample (six were analysed in duplicate) was homogenized with diatomaceous earth and then extracted with ethyl acetate using an accelerated solvent extractor (ASE). The extracts were evaporated and then fractionated on a gel permeation chromatography (GPC) column (50 g Biobeads SX-3) using 1:1 ethyl acetate:cyclohexane (v/v) at a flow rate of 5 mL/min. The fraction containing the OPs (20–42 min) was evaporated and then further cleaned up on a 1 g silica column, eluted with ethyl acetate.

Biological Samples

Fish

The muscle tissue of perch collected from eleven Swedish lakes and carps collected from a pond receiving the effluent of a sewage treatment plant were analysed for OPs. Three perches from one lake were analysed individually, while perch from the remaining ten lakes were pooled (2–4 perch per sample) and analysed in duplicate. An average of 27 g of muscle tissue from each sample was homogenized with 150 g anhydrous sodium sulphate for 3×10 s (200 rpm) using a laboratory knife mill. The homogenate was allowed to equilibrate for 3 h and was then rehomogenized. The homogenate was then transferred to a 4 cm wide glass column in which it was extracted with 200 mL of 5:2 ethyl acetate:cyclohexane (v/v) followed by 150 mL of 9:1 cyclohexane:diethyl ether (v/v) and finally by 150 mL DCM. The organic layers were combined and 400 ng IS (TPeP) was added to the extract which was then evaporated, using a rotary evaporator, to approximately 2 mL. A 20-mL portion of ethanol was added to the sample, which was further evaporated to remove water residues. The sample was evaporated to dryness under a gentle stream of nitrogen and the lipid weight was determined before dissolving the sample in 1 mL of 9:1 cyclohexane:ethyl acetate (v/v). The sample was fractionated on a GPC column (70 g Biobeads SX-3) using cyclohexane:ethyl acetate (9:1) as eluent at a flow rate of 5 mL/min. The eluent was directed to waste during the first 26 min, the second fraction (26–63 min) was collected as it contained the analytes of interest, and the GPC system was then rinsed for 15 min. The sample fraction was evaporated into DCE.

Analysis

Instrumental Analysis

Prior to analysis each sample was evaporated into 0.1–1 mL of DCE and transferred to a GC-vial (Papers I–IV). Quantitative analysis of OPs was generally performed using a gas chromatograph equipped with a nitrogen phosphorus detector (GC-NPD), which is highly selective for phosphorus containing substances (Fig. 5). The gas chromatographic separations were carried out using a DB-5 fused silica capillary column. In the GC-NPD analysis, the OPs were identified by comparing the retention times of the sample components with those of the reference standards. To verify the identities of the OPs, selected samples of each matrix were reanalysed by GC-mass spectrometry (MS). Full-scan spectra were collected and the relative retention times and electron impact spectra were compared with those of the reference standards, and additionally, by reverse search using the NIST library. The GC-MS analysis was performed using the same type of column and an identical temperature program as for the GC-NPD analysis.

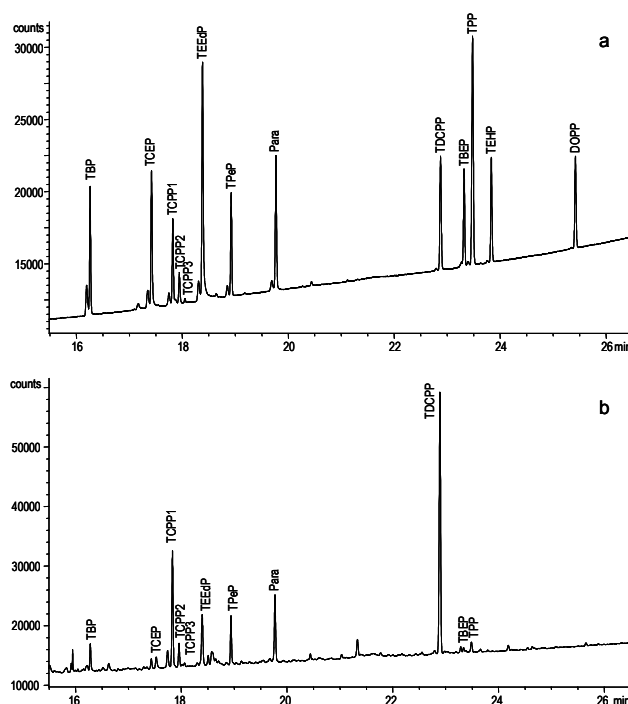


Figure 5. GC-NPD chromatograms of a standard mixture (a); and of the liquid phase of the snow sample E4-2 (b). The standard mixture contained all OPs analysed, at individual concentrations between 350–530 pg/ μ L. The injected amount was 1 μ L (splitless) in both cases (Paper III).

3. Experimental Section

The sludge samples were quantified using GC-MS (Paper IV). The gas chromatographic column used and the settings were similar to those used for GC-NPD. The MS was operated in selected ion monitoring (SIM) mode.

Calibration and Quantification

The GC-NPD quantifications were performed using the internal standard technique (Equation 1), which automatically corrects the data for losses during sample treatment (clean-up) and analysis. To enable the recovery of the internal standard to be calculated (Equation 2), a volumetric standard (ethyl-parathion in most studies) was added to each sample prior to analysis.

Single-point calibration was used after it had been shown that the GC-NPD responses were linear for all analysed OPs over the interval 10 to 1500 pg/ μ L (correlation coefficients ≥ 0.997).

$$\text{Equation 1.} \quad m = \frac{A_{Sample} \times A_{IS Std} \times m_{Std}}{A_{IS Sample} \times A_{Std}}$$

$$\text{Equation 2.} \quad \text{Recovery (\%)} = 100 \times \frac{A_{IS Sample} \times A_{RS Std}}{A_{RS Sample} \times A_{IS Std}}$$

m = amount of analyte
IS = internal standard

A = peak area
RS = recovery standard

Std = reference standard

Quality Assurance and Quality Control

Organophosphate esters are ubiquitous substances that appear to be present in all types of indoor environments, thus, they may contaminate glassware and chemicals used in their analysis^[27]. To prevent contamination by OPs, all laboratory equipment was cleaned extensively; glassware was soaked in 5% (w/w) potassium hydroxide in ethanol, then rinsed with deionised water followed by ethanol. Filters and glasswool were Soxhlet-extracted or extracted by ultrasonication and then carefully wrapped in aluminium foil until use. All solvents were checked for impurities after 800- to 2700-fold concentration by evaporation. The concentrated solvent was then analysed using GC-NPD and the chromatogram obtained was compared with those of the virgin solvents.

3. Experimental Section

To ensure that the samples were not contaminated from the surroundings during the sample treatment, 2 to 11 blank samples were prepared and analysed in the same way as the samples for all matrixes analysed. There were no significant signals from the blank samples for either the dust or air samples. However, the blank samples of the windscreen wipe samples had significant blank contributions of TCPP, ranging from 31 to 72 ng/m², therefore, levels of TCPP below 100 ng/m² should be considered uncertain. The blank levels for snow, wastewater, sludge, background air and deposition samples were low and could be considered negligible, except for the two samples of sludge from the smallest STPs, in which low levels, similar to or slightly higher than those found in the blanks, of TiBP, TBP and TDCPP were detected.

The methods used have been validated for the recovery of the individual OPs and/or the internal standard used. The average recoveries of the IS in the different matrixes were: 97% (dust and oil); 85% (air); 91% (wipe samples); 93% (snow and wastewater); 75% (deposition and background air); 93% (sludge) and 63% for fish. For each matrix studied, replicate injections of the samples (n=3) gave relative standard deviations (RSD) below 18% for the most abundant OPs analysed (TBP, TCEP, TCPP, TDCPP, TPP and TEHP). However, when duplicate, or triplicate, samples of dust and sludge were analysed, the deviations were higher (up to 100%). A possible explanation for the high RSDs is the heterogeneity of the samples, for example, dust is a very inhomogeneous material containing fragments of hair, skin, dandruff, fibres from textiles and papers, particles of soil and sand etc.^[75] Similarly, sludge contains substances and particles of various origins and sizes, which may affect the recovery.

The accuracy of the OP measurements has been validated in an inter-calibration study in which two samples, each containing a standard mixture of TBEP, TCEP, TCPP and TDCPP at different levels, were quantified with the methods validated in-house at three different laboratories (Environmental Chemistry, Umeå University, Akzo Nobel, NL and Rhodia, UK). The results obtained by the different laboratories agreed well.

LEVELS AND SOURCES

Indoor Environments

Dust and Air

Organophosphorus compounds were detected in both dust and air samples from all sampled environments (Papers I and II). The total concentrations found in dust and air ranged from 22 to 5500 mg/kg and from 37 to 950 ng/m³, respectively (Table 4). The indoor environments that showed the highest total levels, in both dust and air, were the prison and the office. Eleven of the 12 analysed substances were found in the environments and eight of them were present in all dust samples and a majority of the air samples. As can be seen in Table 4, TBEP was the most abundant OP in most of the dust samples, followed by TCEP, TCPP and TDCPP, while the chlorinated OPs (TCEP and TCPP), followed by TBP, dominated in the air samples. TMP was not detected in either dust or air in any of the samples.

The distribution of the individual OPs were quite similar among the samples collected from vacuum cleaner bags and those that were hand picked. This suggests that possible contamination by OPs from the various vacuum cleaners used for the sampling did not affect the results significantly.

The levels of TBEP in dust ranged from 0.014 to 5.3 g/kg, the highest level being found in the prison; significantly higher than those in the industrial and public buildings, and 200 times higher than those in the domestic buildings. The prison also had higher atmospheric levels of TBEP than other locations. Other sampled environments with elevated levels of TBEP in dust were the office, the hospital and the public dance hall, probably due to the regular use of floor polishes and waxes on floors in these types of premises. The lower levels of TBEP found in the other locations can be explained by known features of the sampled environments, for example, the dust from the library was vacuumed from books and shelves, the cinema had wall-to-wall carpets, while the university lobby and the radio shop had tiled floors. These findings indicate that floors are the main source of TBEP, due either to the use of floor polishes and waxes or the presence of PVC coverings, in which TBEP may be utilised as a plasticizer.

Table 4. Individual and total concentrations of the most prevalent OPs found in dust (mg/kg) and air (ng/m³) from various indoor environments. For the wipe samples from computer screens and covers, concentrations are given in ng/m² (Papers I and II)

sample site	TBEP		TCEP		TCPP		TDCPP		TPP		TBP		ΣOPs ^a	
	dust	air	dust	air	dust	air	dust	air	dust	air	dust	air	dust	air
home 1	25	0.6	0.27	0.4	0.47	210	0.39	n.d	0.85	8.8	0.21	14	27	230
home 2	18	n.d	0.19	3.0	0.93	38	1.1	n.d	0.99	n.d	0.61	120	22	160
day care centre	31	1.0	0.82	2.5	2.5	28	1.8	59	4.5	1.1	0.20	3.7	41	96
hospital wards	210	1.4	3.8	320	2.3	69	2.1	150	2.0	0.7	0.07	5.4	220	550
hospital office ^b	120		1.0		5.3		0.56		2.2		0.18		140	
radio shop	14	n.d	1.4	29	2.3	10	0.59	n.d	0.93	13	1.8	3.6	21	58
textile shop	31	1.7	0.37	3.4	1.4	32	0.20	n.d	3.1	1.8	0.41	31	37	70
hotel	42	n.d	3.9	2.2	8.9	69	0.91	n.d	1.7	2.3	0.13	5.1	58	81
prison	5300	55	8.2	17	8.9	570	53	6.0	110	n.d	0.35	20	5500	670
university lobby	50	n.d	1.6	2.0	50	440	5.7	1.7	4.9	18	0.32	4.2	110	470
office	270	n.d	48	730	73	160	67	35	6.8	7.1	0.35	8.2	470	950
library	16	n.d	94	590	2.9	40	0.84	n.d	24	n.d	0.59	7.8	140	640
aircraft ^b	18		4.2		2.2		0.86		4.4		2.2		34	
cinema ^b	21		0.85		2.4		7.0		1.1		0.12		33	
public dance hall	120	1.8	1.0	16	1.5	79	1.1	n.d	3.3	n.d	0.48	12	130	110
plastics factory 1 ^c		3.2		8.9		32		0.4		6.3		7.8		73
plastics factory 2 ^c		1.7		3.8		27		n.d		23		3.8		65
bowling alley ^c		3.3		460		93		n.d		6.6		n.d		570
furniture store ^c		0.6		11		73		0.8		2.0		68		160
laboratory ^c		n.d		0.7		31		n.d		0.9		0.5		36
computer screens	940		220		370		290		3300		30		5300	
computer covers	170		210		220		170		4000		70		5300	

n.d = not detected

^a TEEpP was excluded from the total amount due to unsuccessful verification by GC-MS.

^b Dust samples only

^c Air samples only

The highest levels of TCEP, 94 mg/kg in dust and 730 ng/m³ in air, were detected in the samples from the library and the office, respectively. The acoustic ceilings in these locations were the likeliest source of these compound, since this type of material may contain high levels of TCEP^[21]. TCPP, TDCPP and TPP were detected in dust from all sites. After the office, the university lobby had the highest level of TCPP in dust (50 mg/kg). The dust from the university lobby primarily originated from vacuumed sofas, and since upholstery is commonly flame retarded by chlorinated OPs, the sofas were most likely the main source of TCPP. Similarly, the elevated level of TCPP in the air sample from home 1 probably originated from a new sofa, which had been installed a couple of weeks before the sampling.

TPP dominated in the wipe samples from computer screens and covers, which is consistent with reports of TPP emissions from computers^[76]. The highest level of TDCPP (150 ng/m³) was detected in the air sample from the hospital ward, which may be explained by the use of this substance in hospital mattresses^[20]. Further, the highest level of TBP in dust was found in the sample from aircraft. TBP is an ingredient in aircraft hydraulic fluids^[9] and may enter the cabin via leakage from the hydraulic system, or spillage on the ground outside the plane and subsequent transfer by the passengers when boarding the plane.

In summary, substantial variations in both individual and total concentrations of OPs in indoor environments were observed. However, the OP profiles generally appeared to reflect materials and products used in the sampled premises, and site-specific patterns were distinguished. Other important factors influencing the levels of OPs in indoor environments are the ventilation rate and, since emissions of OPs decrease with time^[76,77], the age of the buildings and the products used in them. The indoor environments that had the highest levels of OPs in dust turned out to have high concentrations in air as well, although there was almost a year between the dust and air samplings. Prisons and public buildings like office buildings and hospitals are subject to strict fire safety standards, which may explain the approximately 10-fold higher levels of total OPs in dust, and about 3–4-fold higher levels in their indoor air, compared to domestic buildings. Differences in concentrations of OPs between premises have also been observed by Hansen *et al.*, who detected significantly higher levels of TCEP and TBEP in samples of dust and air from school buildings than from homes^[28].

A compilation of results from previous studies of OP-levels in various indoor environments is presented in Table 5. In general, these levels are of the same magnitude as those presented in Paper I and II, and summarized in Table 4.

Table 5. Concentrations (ng/m³) of OPs in indoor air collected by stationary samplers

sampling site	TBP	TBEP	TCEP	TCPP	TDCPP	TPP	Ref.
3 schools (n=4)	9.8–64	1.4–3.0	18–250	19–58		0.5–0.8	[27]
day care centre (n=4)	13	5.9	144	53		detected	[27]
office (n=4)	18	2.2	11	44		0.7	[27]
dismantling hall (n=12)	9–18	20–36	15–36	14–28		12–40	[78]
shredder (n=2)	15–19	17–19	28–34	25–33		160	[78]
6 homes	n.d–100	n.d–30	n.d–30			n.d–10	[30]
50 indoor environments			5–6000				[21]
lecture hall (n=3)	1.9	3.3	48	450		3.2	[79]
above computer (n=3)	7.6	8.1	7.6	8.7		560	[79]
14 public buildings		<10–30	<10–3900			<10	[28]
room (n=4)	<0.3	4.2	4		3	3.3	[29]
room (n=4)	<0.5	5.0	2		<0.5	2.0	[29]
2 furniture stores	14–17	n.d– 2.5	6.3–12	45–57	n.d	0.56–1.1	[31]
3 offices	4.5–8.1	n.d	23–56	n.d–130	n.d	2.0–3.1	[31]
theatre	29	n.d	36	63	n.d	3.4	[31]
4 cars, turned off	2.5–14	n.d	n.d–9.4	n.d–260	n.d	0.4–0.9	[31]
lecture hall (n=5)	5		n.d	760	n.d	n.d	[72]
computer hall	n.d		3	1100	2	1	[72]
10 homes (n=5)	5–80	n.d–5	1–115	7–160	n.d	n.d	[32]
car, turned off (n=5)	15	2	20	1800	5	3	[32]
bus, turned off (n=5)	6	n.d	n.d	2300	n.d	n.d	[32]
subway, turned off (n=5)	5	n.d	32	2000	n.d	n.d	[32]

n=number of parallel samples in each sample site, n.d = not detected

Windscreens

The chlorinated OPs accounted for more than 54% of the total OPs detected in the wipe samples from windscreens from all sampled vehicles. TDCPP was the most abundant compound in almost all brands sampled, followed by TPP, TCEP and TCPP. The distribution pattern (Fig 6) differed between the brands, indicating that different manufacturers use different materials. However, the results obtained from the analysis of the windscreens are essentially qualitative since the levels found are affected by several factors, such as the age of the vehicle, total distance covered by the vehicle, and distance covered since the windscreen was cleaned before the sampling. Nevertheless, the results give a good indication of the OPs that are present in vehicles.

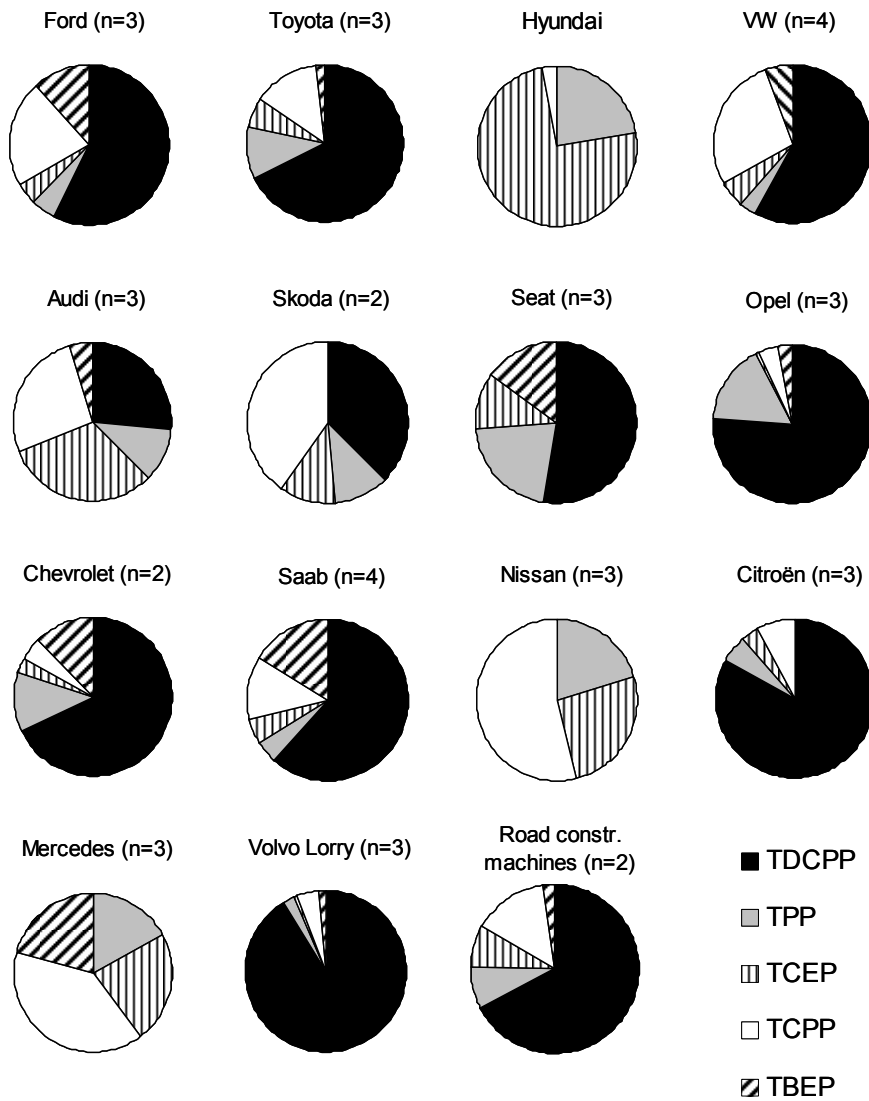


Figure 6. Average distribution of OPs in wipe samples from windscreens. n=number of vehicles of the same brand.

Human Exposure

Exposure through inhalation is dependent on the respiratory volume, duration of exposure, the total concentrations of OPs present in the air, and their distribution between the gaseous, particulate and aerosol phases of the air. Furthermore, the size of the inhaled particles and, of course, the bioavailability of the inhaled OPs also affects exposure and uptake.

In summary, the analysis of the personally carried air samplers confirmed the findings obtained in the previous studies, *i.e.* the substances found to be abundant in the sampled environments in the previous studies were also relatively abundant in the samples collected in the exposure study. TBEP, for example, which was detected at high levels in the prison, accounted for about 50% of the total OPs in the air samplers carried by prison warders (Fig. 7). Another group that was significantly more highly exposed to airborne TBEP than others was the personnel at the day care centre, where the TBEP levels ranged from 41 to 120 ng/m³. This is probably because children playing on the floor whirl up dust particles to which TBEP may be associated, and the personnel spend parts of their work-days on the floor attending to and playing with the children. Further, the indoor environment in which TCEP occurred at the highest levels in both air and dust was the library and, accordingly, the librarians were more heavily exposed to TCEP than any of the other groups.

Personnel working in the previously unsampled environments, *i.e.* the aircraft technicians and the taxi drivers, were the groups who were most highly and most lightly exposed to OPs, respectively. The aircraft technicians were exposed to one order of magnitude more total OPs than the other groups. They were predominantly exposed to TBP, at levels ranging from 270 to 2100 ng/m³, followed by TPP at an average level of 200 ng/m³. Both TBP and TPP are additives in hydraulic fluids and engine oils used at the airport, and the worst exposure scenario was therefore postulated to be when the technicians refill aircraft with such fluids. The air samples collected by the taxi drivers showed the lowest levels of total OPs, which may be due to them spending part of the day outside the car while waiting for passengers, opening doors, carrying luggage etc. Further, the taxi drivers were more heavily exposed to TDCPP than the other groups, which is consistent with previous findings of large percentages of TDCPP in wipe samples from windscreens.

Unfortunately, the analyses of OPs in blood and urine were not completed in time to be included in this thesis. However, two samples of urine were analysed at the department of Analytical Chemistry, Stockholm University, and preliminary data indicate that the metabolite diphenyl phosphate was present in both. In the urine sample from one of the aircraft technicians the level was 80 ng/mL (RSD 11%, n=3), and in the urine from one of the taxi drivers the level was above the detection limit (25 mg/mL), but below the quantification limit (75 ng/mL).

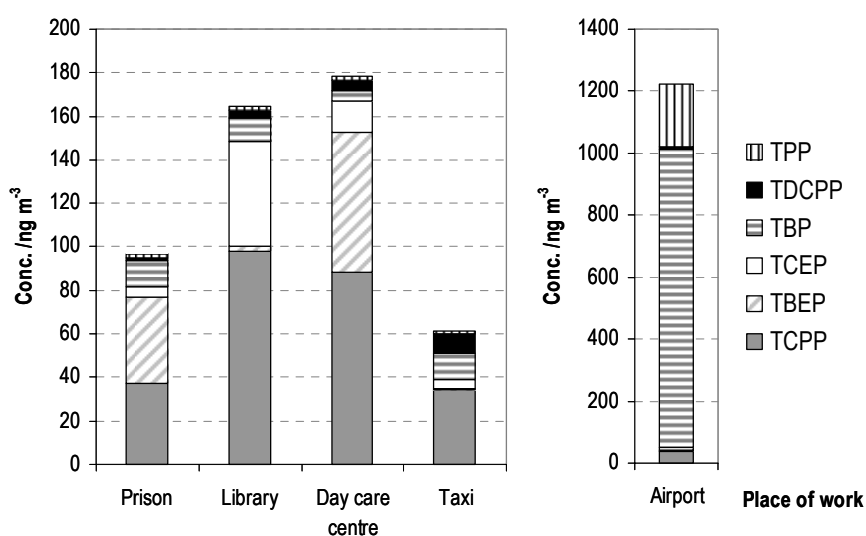


Figure 7. The average exposure, via inhalation, to the most prevalent OPs measured in air for occupational groups at five workplaces.

Prompted by the results of the analysis of OPs in indoor dust and air from various indoor environments, an exposure assessment for children and adults was performed (Paper II). Assuming that adults have a respiratory volume of 19 m³ and spend 21 h per day indoors, adults inhale 0.24 m³/(kg×day) of indoor air and ingest 1.0 mg/(kg×day) of house dust^[80]. Corresponding values for children aged 1–3 years are 0.53 m³/(kg×day) (air) and 10 mg/(kg×day) (dust). Under these conditions, an adult weighing 70 kg and a child would be exposed to 0.04–5.8 µg/(kg×day) and 0.3–57 µg/(kg×day) of total OPs (TBEP, TBP, TCEP, TCPP, TEHP and TPP), respectively, via inhalation and by ingestion of dust. In all but two of the sampled environments, the exposure to OPs via ingestion of dust, for adults, was heavier than by inhalation. For children, ingestion of dust was the most important route of exposure in all sampled environments. However, the suggested guideline of 40 µg/(kg×day)^[70] was exceeded in only one environment, and even there only for children. Since the

environment in question was a prison, this does not pose an alarming risk as children are unlikely to be present, except for brief periods such as visiting hours. Nevertheless, there may be other indoor environments in which the guideline value is exceeded. However, it should be noted that the exposure may be overestimated. OPs associated with small dust particles in the air may be trapped on the air sampler and thus, account for an unknown proportion of OPs in the air sample. Consequently, some of the contribution of OPs associated with dust may be counted twice; via inhalation of air, and via ingestion of dust.

Considering the reported levels of OPs in food and drinking water^[34,69], exposure to OPs by dietary intake seems to be of minor importance, for the population in general, compared to exposure via inhalation of air and ingestion of dust.

Outdoor Environments

Product Samples

Vehicles are sources of OPs, since traces of TPP (0.8–1.9 µg/g) were detected in pooled samples of waste oil samples from (i) cars, (ii) lorries and (iii) road-construction machines (Paper III; Table 6). In the waste oil from cars, TEHP was detected as well. Moreover, TPP (1.9–8.9 µg/g) was detected in the three samples of pure oil collected at the airport, which also contained high amounts of TCP (6.3–12 mg/g). Analysis of a pure sample of the hydraulic fluid (Skydrol 500B4) used in the aircraft showed that it contained 190 mg/g (19%) of TBP. According to the material and safety data sheet for Skydrol 500B4, its TBP, dibutylphenyl phosphate and butyldiphenyl phosphate contents are 19.8%, 40–70% and 10–30%, respectively. None of the OPs analysed were detected in the two samples of deicing fluid used at the airport. However, a trace of TCP was detected in turbine oil from a hydro-electric power station. Thus, leakage and spills of lubricants, motor and transmission oils, as well as leakage of hydraulic fluids, contribute to levels of OPs in outdoor environments.

Table 6. Contents (µg/g) of the OPs detected in product samples (Paper III)

product sample	TPP	TEHP	TBP	TCP ^a
waste oil from cars	1.0	4.2	<0.5	<0.3
waste oil from lorries	0.8	<0.3	<0.5	<0.3
waste oil from road-construction machines	1.9	<0.3	<0.5	<0.3
waste oil from tractors	<0.3	<0.3	<0.5	<0.3
TurboSuper 10W-30 (engine oil)	<0.3	<0.3	<0.5	<0.3
Agrol Mendo 46 Bio (hydraulic fluid)	<0.3	<0.3	<0.5	<0.3
BP 2380 Turbo oil (airport)	6.1	<0.3	<0.5	12 000
BP Turbo oil 2197 engine and accessory oil (airport)	8.9	<0.3	<0.5	6300
Mobile Jet Oil II Synthetic jet engine oil (airport)	1.9	<0.3	<0.5	6500
Kilfroast DF PLUS (80) (de-icing fluid, airport)	<0.3	<0.3	<0.5	<0.3
Skydrol 500B4 (hydraulic fluid, airport)	<0.3	<0.3	190 000	<0.3
Kilfroast ABC-2000 (de-icing fluid, airport)	<0.3	<0.3	<0.5	<0.3
Binol Vegocool (hydro-electric power station)	<0.3	<0.3	<0.5	<0.3
Mobil DTE Heavy medium oil (hydro-electric power station)	<0.3	<0.3	<0.5	160

^a Tricresyl phosphate (TCP) was semi-quantified using triphenyl phosphate.

Snow

The amounts of OPs in the liquid and particle phases in the snow samples were summed and then divided by the specific weight of the respective sample. Nine of the analysed OPs were detected in snow collected from a road intersection (Paper III). The total concentration of OPs declined as distance increased, from 430 ng/kg through 400 ng/kg to 150 ng/kg at distances of 2 m, 100 m and 250 m, respectively, and all of the samples had higher total OP concentrations than the reference sample (130 ng/kg). However, not all of the OPs showed such a gradient; the levels of TBP and TDCPP did not decrease with distance, while those of TCPP, TBEP, TPP, TCEP, TMP and TEHP did, suggesting that traffic was a source of the latter group (Fig. 8). The lack of a concentration gradient for TBP at the intersection and the similarity of the levels detected in the samples from the intersection and the reference sample indicate that this substance originated from diffuse sources or long-range air transport.

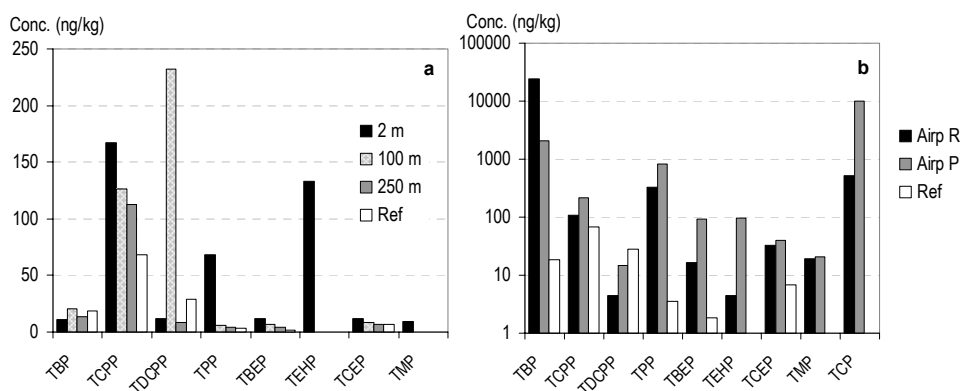


Figure 8. Comparison of concentrations of individual OPs in snow from the reference site (Ref) and in samples collected at distances of 2, 100, and 250 m from a road intersection (a) and in samples collected at an airport (b). Airp R shows the average of two samples collected on the side of the runway and Airp P was collected at the aircraft parking space. TCP was not detected in the snow samples from the road intersection (Paper III).

TCPP has previously been detected in air samples from vehicles at levels of 1800–2300 ng/m³ [32]. In addition, the chlorinated OPs were present in nearly all wipe samples collected from the inside of the windscreens of vehicles. These findings indicate that OPs are emitted from plastic materials used in car fittings and reach the outdoor environment via the ventilation system of the vehicles. Thus, vehicles are a possible source of the chlorinated OPs found in snow collected at the intersection.

In the snow samples collected at the airport, TBP was the most abundant OP. The highest levels (23 and 25 $\mu\text{g/kg}$), found in the samples collected at the runway were three orders of magnitude higher than in the reference sample (19 ng/kg). At the aircraft parking place the level of TBP was 2.1 $\mu\text{g/kg}$. Similarly, the levels of TPP and TBEP were higher in the snow from the airport than in the snow from the intersection and the reference snow. Moreover, TCP was identified and semi-quantified in all snow samples from the airport. The most apparent sources of TBP, TPP and TCP at the airport are leakage and spillages of hydraulic fluid, lubricants and engine oils, which contained significant amounts of these substances, as confirmed by the product analysis (Table 6). The highest level of TBEP was found at the aircraft parking space, which is close to the terminal building. As TBEP is utilized as an ingredient in floor polishes, floor waxes and shoe soles, and is also abundant in indoor dust (Paper I), it may have been transferred by the passengers.

Background Air and Deposition

Analysis of background air and deposition collected in northern Finland confirmed that some OPs are subject to long-range air transport. The concentration of TCEP (87 ng/L) detected in precipitation is similar to the level found by Fries and Püttmann in German rainwater (121 ng/L)^[35]. In background air, the most abundant OPs were TPP, TCP and TBP (12 000, 810 and 280 pg/m^3 , respectively). These findings supported the conclusion drawn from the results of the snow analysis; that TBP, which did not show a concentration gradient at the intersection, is subject to long-range air transport. A finding that is more difficult to explain is that TPP was detected at similar levels in the background air sample to those found in indoor environments. The identity of TPP was confirmed by GC-MS and the blanks were not contaminated.

Sewage Treatment Plants

In most cases both the total and individual concentrations of OPs in (i) the influents, (ii) the effluents and (iii) sludge were similar amongst the studied STPs (Paper IV). These findings indicate that their sources were predominantly diffuse, *e.g.* the use of flame retarded products in both private households and industrial facilities, and that the size of the STPs, in terms of personal equivalents, seems to be of minor importance regarding the OP concentrations.

4. Levels and Sources

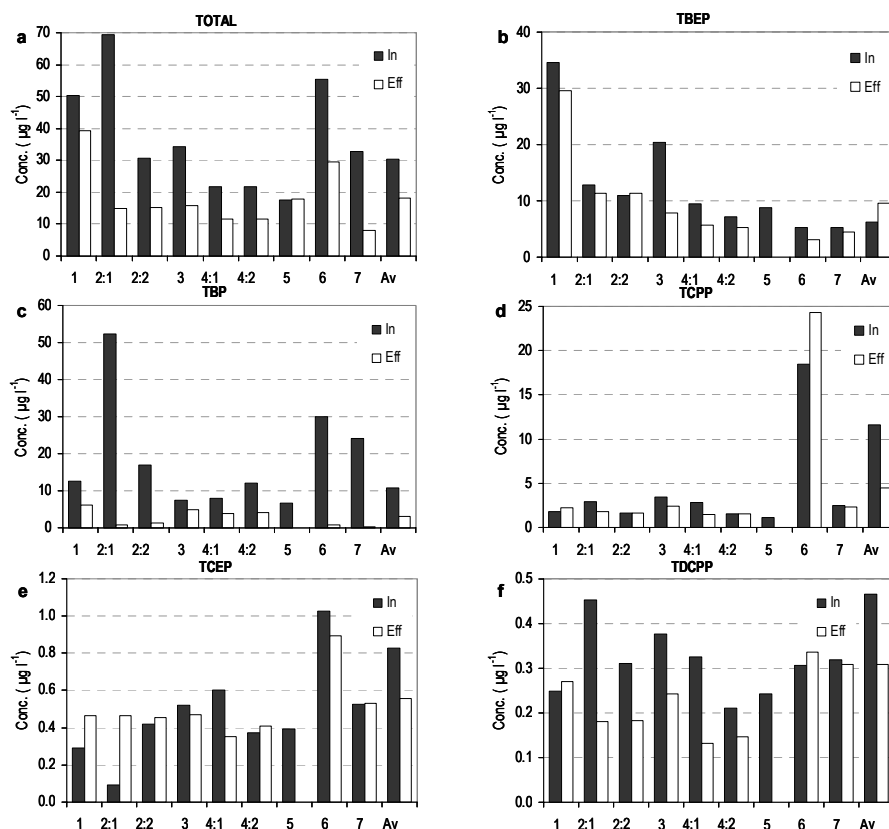


Figure 9. Comparison of total (a) and individual concentrations (b-f) of the most frequently occurring organophosphates in influents and effluents (In and Eff, respectively) from Swedish STPs, “Av” shows the average value (Paper IV). STPs 1–7 are described in Table 3.

In wastewater, TBEP and TBP were the most prevalent OPs in both influents and effluents, followed by the chlorinated OPs; TCPP, TCEP and TDCPP (Fig. 9). TPP was also detected in all samples, at levels similar to or slightly lower than those of TDCPP. The levels of OPs detected in the wastewater samples (Paper IV) are comparable to the levels found in other studies (Table 7) except for TBP and TBEP, which in most cases were higher in both influents and effluents.

4. Levels and Sources

Table 7. Concentrations of OPs ($\mu\text{g/L}$) in influents (in) and effluents (eff) from municipal sewage treatment plants

sampling site	TBP		TBEP		TCEP		TCPP		TDCPP		TPP		Ref
	in	eff	in	eff	in	eff	in	eff	in	eff	in	eff	
Sweden (n=1)	1	0.3	5.8	0.6							0.4	n.d	39
Sweden (n=3)		≤ 3		≤ 28				≤ 4		≤ 3		≤ 3	40
Germany (n=1)	5	1.5	13	0.5	21	34							34
Germany (n=3)	15	0.6	13	3.0	1.0	0.4							35
Germany (n=1)	1.2	0.5	3.7	0.4	0.3	0.4	2.0	3.0	0.1	0.1	0.1	0.07	81
Germany (n=4)		≤ 0.2		≤ 0.5		≤ 0.13		≤ 0.4		≤ 0.12		≤ 0.03	33
Spain (n=1)	0.59	0.13	12	0.07	0.33	0.35	3.1	2.6	0.21	0.18	n.d	n.d	41
Germany (n=1)							0.52	0.38					38

n=number of sampled sewage treatment plants n.d = not detected

The total concentrations of OPs ranged from 0.7 to 7 $\mu\text{g/g}$ in the sludge and the OP profiles were dominated by EHDPP, TBP and TCPP (Fig. 10). The smallest STPs (Nos. 1 and 5) had significantly lower levels of OPs than the medium sized and large STPs.

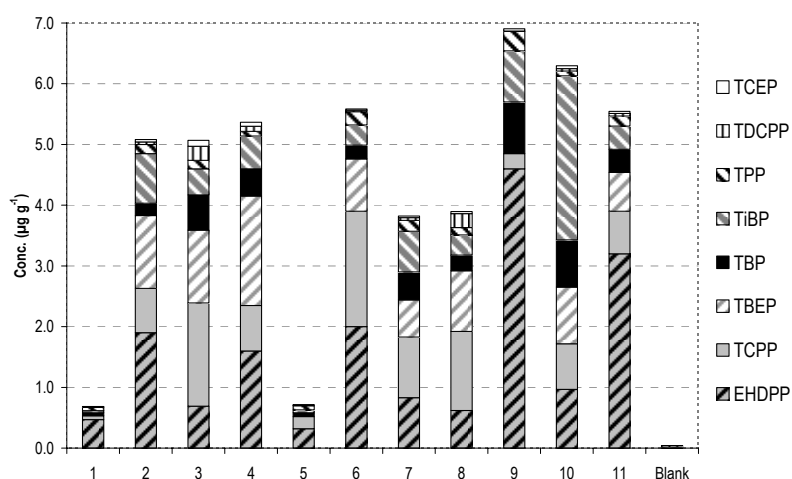


Figure 10. Average levels of OPs in sludge samples collected at 11 Swedish STPs (Paper IV). Descriptive data for STPs 1–11 are given in Table 3.

As mentioned above, most OPs reaching the STPs are probably emitted from OP-containing products in general use. TBEP, for example, is utilized as a levelling agent in floor finishes. This substance, which was the major OP found in wastewater and indoor dust (Paper I), probably reaches the STPs via cleaning water from both public and domestic buildings. Other diffuse sources, in cases where STPs receive drainage water from streets (stormwater), are dry and wet deposition.

STP 6 was distinctive, in having one order of magnitude higher levels of TCPP in both its influent (18 $\mu\text{g/L}$) and effluent (24 $\mu\text{g/L}$) than the other STPs, and the highest concentration of TCPP in its sludge. A factory that manufactures flame retardant paint is connected to this STP, which may explain the elevated levels. Similarly, a factory processing flexible PUF, which is commonly flame retarded by chlorinated OPs, may contribute to the elevated levels of chlorinated OPs detected in sludge from STP 3. Analysis of a sample of cleaning water from the PUF factory confirmed the presence of the three chlorinated OPs, with TDCPP as the major compound at 10 mg/L. The highest measured level of an individual OP was 52 $\mu\text{g/L}$ for TBP in influent from STP 2 (Fig. 9c). Since TBP had previously been detected at high levels in snow and hydraulic fluid collected at an airport (Paper III), a major airport connected to STP 2 presumably contributes to the elevated levels of TBP.

The primary function of STPs is to clean wastewater in order to protect recipients and their associated ecosystems from being affected by harmful substances. This study showed, however, that OPs were poorly removed from the wastewater, and the chlorinated OPs especially tended to pass through the STPs without being removed or degraded. Alkyl-OPs, such as TBP were, however, more successfully removed. Of the total amounts entering STPs, 50% are emitted to the recipients.

Biological Samples

Fish

OPs are taken up by both perch and carp. As can be seen in Fig. 11, the distribution patterns of OPs were quite similar among the perches collected from all eleven sampled lakes, whilst the average total concentrations varied between 4 and 45 ng g^{-1} (ww). Variations in concentrations in perch collected from the same lakes were also noticed. For example, the three perches from Lake 1 were of similar size (each weighing 66–92 g), but their total concentrations of OPs ranged from 13 to 28 ng/g (ww). The highest level was detected in the largest fish and, thus, bioaccumulation may explain some of the differences in concentrations. However, their local habitat and feeding preferences may also be important.

4. Levels and Sources

In all perches, TPP and TCPP contributed more than 73% of the total OPs. TCEP was also detected in all perches, and both TBP and TDCPP in most of the samples. The two carps showed a different OP distribution from the perches, and also had higher total concentrations of OPs (140 and 230 ng/g). As in the perch, TPP was the major OP in carp, while TBEP was the second most abundant (average 69 ng/g), followed by TCPP. In perch, TBEP was only detected at low levels (0.3 ng/g), and only in perch from Lake 1.

All lakes from which the perches were collected are considered to be background locations, *i.e.* not influenced by direct emissions from industrial sites or cities. In the sample of background air (Paper III) TCPP and TPP were the most abundant OPs. Thus, the origin of the OPs detected in perch is most likely dry and wet deposition. For carp, however, the source is obvious; the pond in which they lived, receives OP-containing effluent from an STP (Paper IV).

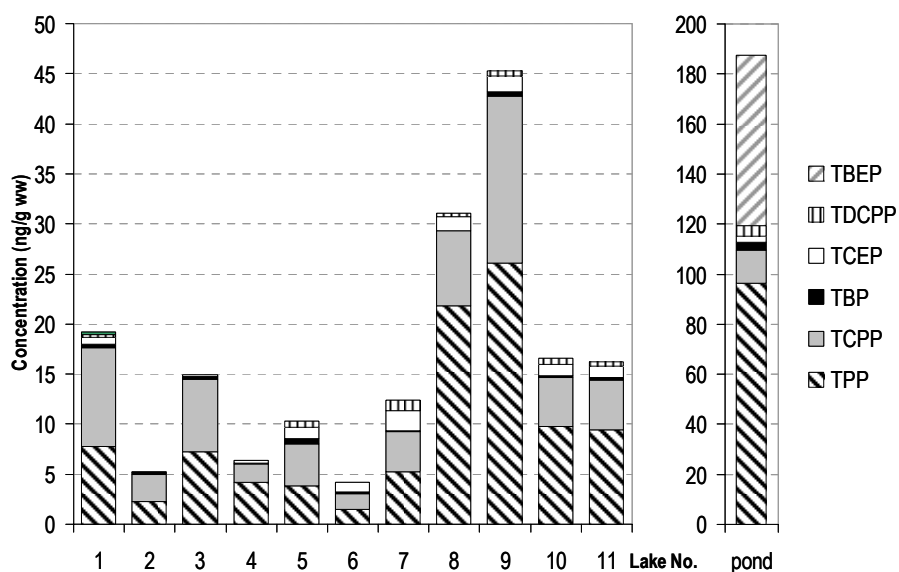


Figure 11. Average OP concentrations in perch collected from 11 Swedish lakes, and carp collected from a pond receiving the effluent of a sewage treatment plant.

ESTIMATION OF MASS FLOW

The total flow of OPs in Sweden was roughly estimated using the concentrations of OPs found in indoor air, deposition, and STP samples (Papers II–IV), and various supporting data. The imported and exported quantities of OPs were obtained from the Chemical Inspectorate of Sweden^[5]. The emissions of OPs via ventilation from households and public buildings were calculated using the average concentrations of total OPs in the different types of buildings, the total area of domestic buildings, and the total area of non-residential buildings, excluding industrial sites^[82]. The ventilation rate was estimated to be 0.5 air changes per hour and the ceiling height was assumed to be 2.4 m in domestic buildings and 2.6 m in non-residential buildings. According to the Swedish Water and Wastewater Association, Swedish STPs annually treat approximately 1.5 km³ of wastewater and produce 240 000 tonnes of sludge^[83]. Using this information and the average concentrations of total OPs found in the influents, effluents and sludge of the examined STPs, the mass flow of OPs to and from STPs in Sweden was estimated (Fig. 12). When calculating the amount of OPs deposited annually, the precipitation was normalised to average levels because rain fell continually during the sampling week, resulting in a precipitation level of 45 mm, compared to an average level of 13 mm per week in 2004^[84].

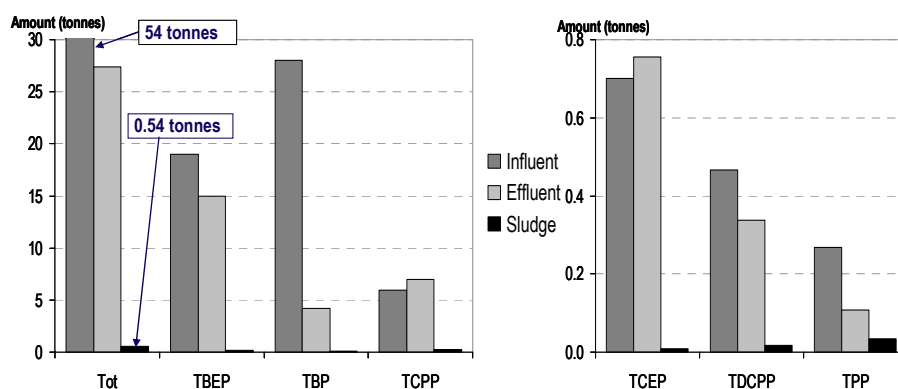


Figure 12. Annual amounts of OPs in influents, effluents and sludge in Swedish STPs. The OPs occurring at higher levels in influents and effluents are presented to the left, and the OPs at lower levels to the right.

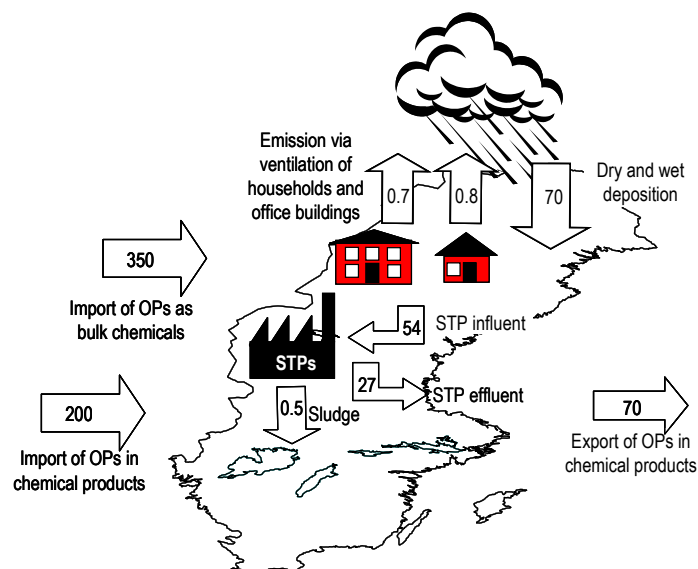


Figure 13. Rough estimation of the annual flow, in tonnes, of OPs in Sweden. The import and export figures represent the total amounts of TBP, TBEP, TCEP, TCPP, TDCPP, TEHP and TPP imported and exported in 2003, according to information from the Chemical Inspectorate in Sweden. Emission and deposition data are calculated on the basis of the results presented in Papers II–IV. Aryl- and chlorinated phosphates are not produced in Sweden.

Approximately 550 tonnes of OPs are imported into Sweden annually, either as raw material or as ingredients in chemical products (Fig. 13). Of these, 70 tonnes are exported. However, the figures do not include OPs incorporated into consumer products and semi-manufactured articles. A substantial amount of OPs may also be imported that are not reported to the authorities, for example, ingredients accounting for less than 5% of the total content in chemical products do not have to be reported unless they are classified as harmful. Furthermore, of the OPs discussed in this thesis, TBP and TCEP are the only substances that are officially classified and labelled. Moreover, chemicals and chemical products that are not officially classified as harmful do not have to be reported to the authorities by importers who annually import quantities less than 100 kg. There may also be unrecorded amounts due to importers neglecting to report data to the authorities.

The quantity emitted from households and industries via the sewage system to STPs represents 10% of the imported quantity of OPs. The corresponding value for deposition is 13%. Of the total amount of OPs emitted via STP effluents (27 tonnes), TBEP accounts for the largest proportion; 55% (Fig. 12).

Since TBEP is widely used as an ingredient in floor polishes and waxes, it is not surprising to find high levels in the wastewater. Similarly, the levels of the other OPs seem high, considering that their intended use is as flame retardants. For a flame retardant to function properly, it must be present in the material it is supposed to protect. However, the estimated mass flow indicates that a large proportion of OPs are emitted from the materials.

Given that the air and deposition sampling was performed in a remote area in northern Finland, the deposition of OPs also appears to be high. A possible explanation for this finding is that substantial amounts of OPs are transported long distances in air. Air parcel back-trajectories calculated 168 h back in time during the sampling period showed that the air masses had been mainly transported over urbanised and industrial areas before reaching the sampling location (Paper III). However, the deposition data should be handled with caution since they were based on only one sampling occasion. It should also be noted that the deposition sample was collected in July, and the volatility of any compound decreases with decreasing temperature. Consequently, during the winter season when temperatures are lower, the amounts of gaseous OPs in the atmosphere are likely to be lower than in summertime. A more reliable estimate of the annual deposition would have been obtained if more samples had been collected, preferably evenly distributed throughout the year and at various geographical locations, and as separate samples for dry and wet deposition.

CONCLUSIONS AND FURTHER PERSPECTIVES

Organophosphorus flame retardants and plasticizers are used in high volumes and are incorporated in various products from which they may be emitted throughout the products' entire lifetimes. The studies underlying this thesis have proven that OPs are ubiquitous in indoor environments, where they were found in air and dust. They were also frequently detected in samples from outdoor environments including snow, background air, deposition and fish, as well as in finished products and samples from sewage treatment plants. The results of the analysis of wastewater and sludge indicate that the main sources of OPs are of diffuse character; probably emission of OPs from products containing OPs in general use in households and industries. Similarly, emissions via ventilation of buildings are sources of OPs in the atmosphere. Oil products were also shown to be sources of OPs, both directly, via leakage and spillage in relatively large quantities, and diffusely, through emissions from vehicles. Furthermore, analytical methods for determining OPs in the various sample matrices were developed and validated. These methods could, however, be improved. It would be especially desirable to reduce the overall solvent consumption and to change dichloromethane for a more "environmentally friendly" alternative.

The substantial amounts of OPs that are emitted from STPs annually are alarming. Although the levels of the most abundant OPs in the effluents were up to three orders of magnitude lower than their documented acute toxicity levels, the possibility that long term exposure to them may cause adverse effects in aquatic organisms cannot be excluded. Similarly, in cases where sludge from STPs is used in filling materials or fertilizers, the concentrations of OPs may cause adverse effects in earth-dwelling organisms. Moreover, in some of the studied indoor environments, the exposure to OPs, via inhalation and ingestion of dust, was close to the suggested guideline value. However, since these studies include only a limited number of samples and sampled sites, and information on the health and environmental effects of OPs are sparse, there is insufficient information to draw definitive conclusions about the likelihood that they represent significant threats.

In my opinion there is an urgent need for further studies to find out if OPs pose environmental risks. For example, the release of 50% of the total OPs entering STPs calls for analysis of recipient waters and sediments. Toxicological studies of OPs' long term effects on both aquatic and earth-dwelling organisms are also required. Depending on the awaited results of the blood and urine analysis in the human exposure study, there may be a need for more extensive studies. One approach could be to monitor the dermal exposure to OPs for airport technicians and other personnel who regularly handle OP-containing hydraulic fluids and lubricants.

The physico-chemical characteristics of OPs suggests that they have low solubility in water, low volatility and relatively high affinity to organic material. Therefore, OPs entering STPs would be expected to be primarily associated with particles and end up in the sludge rather than being present in the water phase. However, as shown in Paper IV, almost 100% of the chlorinated OPs tend to pass through the treatment process without being removed or degraded. A possible explanation for this is that other substances present in the wastewater, such as surface-active agents, may affect the water solubility of OPs. It would be interesting to study OP sorption to particles in some detail to elucidate why the OPs do not behave as expected in wastewater. The results of such a study could also be used to improve the wastewater treatment processes at STPs in order to reduce the amounts of OPs emitted to the recipients. It would also be interesting to study degradation rates of OPs, and their degradation products in sludge. This might be done by collecting sludge, homogenizing it and dividing it into sub-samples, which could be analysed at regular time intervals.

New chemicals are constantly being introduced to the market, some of which may replace the OPs considered here. Hence, there is also a need to study other OPs that have not previously been analysed. Moreover, as long as the additives are compatible with the polymer to be flame retarded, the ones chosen to flame retard plastics are usually the cheapest. By monitoring sewage sludge at regular intervals, changes in the usage pattern of OPs may be revealed.

The most effective way to reduce OP levels in the environment would be to decrease their usage, by increasing the use of materials that do not require flame retardants for example. For most people, it is extremely difficult to find out what types of flame retardants or plasticizers are incorporated in commercially available products and construction materials. It would be preferable if products containing OPs had a more detailed declaration. Unfortunately, this would conflict with the interests of the manufacturer, who want to avoid com-

peting companies obtaining knowledge about the composition of their products. However, some products *e.g.* insulation blocks used in road constructions^[4] are flame retarded solely to reduce the risk of fire during their storage, rather than during their final use. It must be possible to develop alternative practices for such materials. However, even if a chemical has been proven to be toxic, authorities cannot simply ban it, since various economic and political issues have to be considered, notably its costs, benefits and risks. Finally, of course, we must not forget that the use of flame retardants may save lives and reduce the destruction of properties by fire.

ACKNOWLEDGEMENTS

Det sägs ju att det, med undantag av handledare, opponent och betygsnämnd, är väldigt få som läser en hel avhandling. Så nu när det är dags att skriva den här sidan, som för övrigt brukar höra till de lite mer populära delarna i en avhandling, ska jag försöka att skriva något läsvärt!

Först och främst vill jag tacka Peter, min huvudhandledare, som trodde att jag, med min bakgrund från MHS och inte som "riktig kemist", kunde genomföra forskarutbildningen på Miljökemi. Det har gått alldeles utmärkt och nu känner jag mig som en riktig Miljökemist! Tack för all vägledning, manuskriptgranskning, kloka råd och analytisk expertis.

Barbro, tack för att du varit min biträdande handledare under den här tiden. Dina erfarenheter och kunskaper om luftprovtagning och inomhusmiljöer har varit en välkommen resurs, men framförallt har du en härligt positiv inställning och en unik förmåga att komma med hejarop när det behövs som bäst.

Det känns lite överkligt att man tagit sig ända hit. Tiden har gått snabbt och till största delen har det varit en mycket bra period i mitt liv. Framförallt har jag trivts väldigt bra med alla arbetskamrater och den goda stämningen på Miljökemi. Jag vill passa på att tacka alla arbetskamrater jag har haft under den här tiden, jag har verkligen uppskattat alla trevliga samtal vid fika och lunch och att folk tagit sig tid att lyssna och komma med goda råd när man kört fast med något på labbet. Speciellt tack till Micke som särskilt i början fick agera som GC-konsult. Malin, min rumskompis i drygt 4 år, det har varit jätteroligt att dela rum med dig, vi har hunnit med att analysera mycket, även utanför labbet!

Nu har inte allt varit en dans på rosor, men det enda som varit tråkigt är alla trassel av olika slag med både analysinstrument och datorer. Även om mitt motto sedan en lång tid tillbaka varit "allting ordnar sig alltid till det bästa" så är jag fullt övertygad om att det ligger något i Murphy's lag... För att försöka se det positiva i alla instrumentella motgångar har jag haft en liten skylt med de kloka orden "Problems are opportunities in disguise" på GC:n. Denna lilla skylt kan jag nu med varm hand överlämna till Kicki.

7. Acknowledgements

För att genomföra en forskarutbildning behövs även finansiering. Tack till Naturvårdsverket som finansierat en stor del av projektet. För att jag fått möjligheten att delta i flera internationella konferenser och dessutom kunnat tillbringa några veckor på universitetet i Duisburg-Essen där jag labbat tillsammans med andra fosforbaserade flamskyddsmänniskor har stipendier från Kempe-och Wallenberg stiftelserna, Civilingenjörsförbundets Miljöfond och Ångpanneföreningen mottagits tacksamt. Utan prov blir det inga analyser, därför vill jag även rikta ett varmt tack till personalen på de arbetsplatser där jag fått göra provtagningar samt till de som hjälpt till med själva provtagningen. Ett särskilt tack går till de personer som deltog i exponeringsstudien och som stod ut med att bära surrande luftpumpar på sig en hel arbetsdag. Tack även till Ingvar Bergdahl som hjälpte till med den etiska ansökan för exponeringsstudien samt till Gerd Lindén som tog blodproven.

Tack till Mamma och Pappa, även om ni inte alltid varit så insatta i vad jag gjort under min tid här så har ni alltid varit uppmuntrande. Roger och Carina har även de bidragit med support i formen av fraser som "äcklig klibbhjärna". För utomstående låter det kanske inte så trevligt, men jag vet att de menar väl. Margareta och Arne, de bästa svärföräldrar man kan önska sig, har varit till stor hjälp under den hektiska tiden där avhandlingsskrivning och husbygge krockade. Utan er hjälp skulle huset fortfarande vara omålat, eller så hade inte avhandlingen blivit klar i tid.

Erik, min sambo, förtjänar massor med tack. Tack för att du uppmuntrat mig när det gått trögt. Tack för att du tagit på dig så mycket med husbygget när jag skrivit på min avhandling och tack för att du är världens finaste och alltid finns där för mig.

REFERENCES

- 1 Troitzsch J. *International plastics flammability handbook: Principles, regulations, testing and approval*, 2nd ed. Hanser Publishers, Munich, Germany, 1990.
- 2 SRI Consulting. Consumption of flame retardants. 2004; <http://www.cefic-efra.com/content/Default.asp?PageID=7> (accessed 1 November 2004).
- 3 Green J, 1996. A review of phosphorus-containing flame retardants. *Journal of Fire Sciences* 14: 353-366.
- 4 Westrop N. EFRA (European Flame Retardant Association). Personal communication, 2004.
- 5 KemI. The Products Register, National Chemical Inspectorate of Sweden. Sundbyberg, Sweden, 2002 and 2004.
- 6 European Commission. Regulation (EC) No 2268/95 of 27 September 1995 concerning the second list of priority substances as foreseen under Council Regulation (EEC) No 793/3. European Chemicals Bureau.
- 7 European Commission. Regulation (EC) No 2364/2000 of 25 October 2000 concerning the fourth list of priority substances as foreseen under Council Regulation (EEC) No 793/3. European Chemicals Bureau.
- 8 World Health Organization. *Flame retardants: tris(chloropropyl) phosphate and tris(2-chloroethyl) phosphate, Environmental Health Criteria 209*. Geneva, Switzerland, 1998.
- 9 World Health Organization. *Tributyl phosphate, Environmental Health Criteria 112*. Geneva, Switzerland, 1991.
- 10 Lanxess Energizing Chemistry. *Antifoam T*. Product description, 2004. Lanxess Deutschland GmbH, Leverkusen, Germany. http://phosphor-chemikalien.de/p/english/products/alkyl_phosphates/ (accessed 31 October 2005)
- 11 World Health Organization. *Flame retardants: tris(2-butoxyethyl) phosphate, tris(2-ethylhexyl) phosphate and tetrakis(hydroxymethyl) phosphonium salts, Environmental Health Criteria 218*. Geneva, Switzerland, 2000.
- 12 World Health Organization. *Triphenyl phosphate, Environmental Health Criteria 111*. Geneva, Switzerland, 1991.
- 13 National Toxicology Program, 2000. *Chemical Repository Database*. <http://ntp-server.niehs.nih.gov>. (accessed 11 April 2002).

8. References

- 14 World Health Organization. *Tricresyl phosphate, Environmental Health Criteria 110*. Geneva, Switzerland, 1990.
- 15 Barashkov OK, Barshtein RS, Bil VS, Kavun MS, Lykov VN and Ryzhakova LV, 1987. Fire resistance and freeze resistance of PVC composites containing plasticizer mixtures. *Plasticheskie Massy* 5: 61-62. [abstract]
- 16 Travkin VF, Kravchenko AN and Miroevskii GP, 1993. Extraction of arsenic and antimony from sulfate solutions by organophosphoric mixtures. *Tsvetnye Metally* 4: 14-18. [abstract]
- 17 Osberhaus R and Blum H, 1977. Use of alkane diphosphonic acid esters as deodorants. Patent 2607225.
- 18 World Health Organization. *Flame retardants: A general introduction, Environmental Health Criteria 192*. Geneva, Switzerland, 1997.
- 19 Green, J. *Flame Retardants and Smoke Suppressants*. Ch. 6 in *Polymer modifiers and additives, Vol 62*, Eds. Lutz, JT and Grossman, RF. Marcel. Dekker Inc. New York, NY, 2001.
- 20 KemI. *The flame retardant project - Final report*. National Chemical Inspectorate of Sweden, Stockholm, Sweden, 1996.
- 21 Ingerowski G, Friedle A and Thumulla J, 2001. Chlorinated ethyl and isopropyl phosphoric acid triesters in the indoor environment - An inter-laboratory exposure study. *Indoor Air* 11: 145-149.
- 22 Sellström U and Jansson B, 1987. Mass-spectrometric determination of tris(1,3-dichloro-2-propyl)-phosphate (TDCP) using NCI-technique. *International Journal of Environmental Analytical Chemistry* 29: 277-287.
- 23 Akzo Nobel. *Functional Chemicals, Phosphorus Chemicals. Phosflex® Flame Retardant Plasticizer, Phosflex T-BEP, Tributoxylethyl Phosphate*. Product description, 1998. Akzo Nobel Chemicals Inc. New York.
- 24 SRC, 2000. *SRC PhysProp Database*. Syracuse Research Corporation. <http://esc.syrres.com/interkow/physdemo.htm>. (accessed 17 October 2005).
- 25 Agency for Toxic Substances and Disease Registry. *Toxicological profile for hydraulic fluids*. U.S. Department of Health and Human Services. Atlanta, GA, 1997.
- 26 Green J, 1992. A review of phosphorus-containing flame retardants. *Journal of Fire Sciences* 10: 470-487.
- 27 Carlsson H, Nilsson U, Becker G and Östman C, 1997. Organophosphate ester flame retardants and plasticizers in the indoor environment: Analytical methodology and occurrence. *Environmental Science & Technology* 31: 2931-2936.

8. References

- 28 Hansen D, Volland G, Krause G and Zoltzer D, 2001. Determination and occurrence of phosphororganic compounds (POV) in dust and indoor air. *Gefahrstoffe Reinhaltung der Luft* 61: 13-17. (in german)
- 29 Nagorka R and Ullrich D, 2003. Determination of organophosphorus flame retardants in indoor dust: Screening method with GC/NPD. *Gefahrstoffe Reinhaltung der Luft* 63: 79-84. (in german)
- 30 Otake T, Yoshinaga J and Yanagisawa Y, 2001. Analysis of organic esters of plasticizer in indoor air by GC-MS and GC-FPD. *Environmental Science & Technology* 35: 3099-3102.
- 31 Hartmann PC, Burgi D and Giger W, 2004. Organophosphate flame retardants and plasticizers in indoor air. *Chemosphere* 57: 781-787.
- 32 Staaf T and Östman C, 2005. Organophosphate triesters in indoor environments. *Journal of Environmental Monitoring* 7: 883-887.
- 33 Andresen JA, Grundmann A and Bester K, 2004. Organophosphorus flame retardants and plasticisers in surface waters. *Science of the Total Environment* 332: 155-166.
- 34 Fries E and Püttmann W, 2001. Occurrence of organophosphate esters in surface water and ground water in Germany. *Journal of Environmental Monitoring* 3: 621-626.
- 35 Fries E and Püttmann W, 2003. Monitoring of the three organophosphate esters TBP, TCEP and TBEP in river water and ground water (Oder, Germany). *Journal of Environmental Monitoring* 5: 346-352.
- 36 Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB and Buxton HT, 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999-2000: A national reconnaissance. *Environmental Science & Technology* 36: 1202-1211.
- 37 Gomez-Belinchon JI, Grimalt JO and Albaiges J, 1988. Analysis and persistence of tributyl phosphates in riverine and marine coastal waters. *Chemosphere* 17: 2189-2197.
- 38 Bester K, 2005. Comparison of TCPP concentrations in sludge and wastewater in a typical German sewage treatment plant - comparison of sewage sludge from 20 plants. *Journal of Environmental Monitoring* 7: 509-513.
- 39 Paxeus N, Robinson P and Balmer P, 1992. Study of organic pollutants in municipal waste-water in Göteborg, Sweden. *Water Science and Technology* 25: 249-256.
- 40 Paxeus N, 1996. Organic pollutants in the effluents of large wastewater treatment plants in Sweden. *Water Research* 30: 1115-1122.

8. References

- 41 Rodil R, Quintana JB and Reemtsma T, 2005. Liquid chromatography-tandem mass spectrometry determination of nonionic organophosphorus flame retardants and plasticizers in wastewater samples. *Analytical Chemistry* 77: 3083-3089.
- 42 Laniewski K, Boren H and Grimvall A, 1998. Identification of volatile and extractable chloroorganics in rain and snow. *Environmental Science & Technology* 32: 3935-3940.
- 43 Aston LS, Noda J, Seiber JN and Reece CA, 1996. Organophosphate flame retardants in needles of *Pinus ponderosa* in the Sierra Nevada foothills. *Bulletin of Environmental Contamination and Toxicology* 57: 859-866.
- 44 David MD and Seiber JN, 1999. Analysis of organophosphate hydraulic fluids in U.S. Air Force base soils. *Archives of Environmental Contamination and Toxicology* 36: 235-241.
- 45 Yasuhara A, Shiraishi H, Nishikawa M, Yamamoto T, Uehiro T, Nakasugi O, Okumura T, Kenmotsu K, Fukui H, Nagase M, Ono Y, Kawagoshi Y, Baba K and Noma Y, 1997. Determination of organic components in leachates from hazardous waste disposal sites in Japan by gas chromatography mass spectrometry. *Journal of Chromatography A* 774: 321-332.
- 46 Yasuhara A, Shiraishi H, Nishikawa M, Yamamoto T, Nakasugi O, Okumura T, Kenmotsu K, Fukui H, Nagase M and Kawagoshi Y, 1999. Organic components in leachates from hazardous waste disposal sites. *Waste Management & Research* 17: 186-197.
- 47 Ciccioli P, Cecinato A, Brancaleoni E, Montagnoli M and Allegrini I, 1994. Chemical composition of particulate organic matter (POM) collected at Terra Nova Bay in Antarctica. *International Journal of Environmental Analytical Chemistry* 55: 47-59.
- 48 LeBel GL and Williams DT. 1983. Determination of organic phosphate triesters in human adipose tissue. *Journal of the Association of Official Analytical Chemists* 66: 691-699.
- 49 LeBel GL and Williams DT, 1986. Levels of triaryl/alkyl phosphates in human adipose tissue from eastern Ontario. *Bulletin of Environmental Contamination & Toxicology* 37: 41-46.
- 50 Hudec T, Thean J, Kuehl D and Dougherty RC, 1980. Tris(dichloropropyl) phosphate, a mutagenic flame retardant: frequent occurrence in human seminal plasma. *Science* 211: 951-952.
- 51 Sasaki K, Takeda M and Uchiyama M, 1981. Toxicity, absorption and elimination of phosphoric acid triesters by killifish and goldfish. *Bulletin of Environmental Contamination & Toxicology* 27: 775-782.

8. References

- 52 Muir DCG, Lint D and Grift NP, 1985. Fate of three phosphate ester flame retardants in small ponds. *Environmental Toxicology and Chemistry* 4: 663-675.
- 53 Muir DCG, Grift NP, Blouw AP and Lockhart WL, 1980. Environmental dynamics of phosphate esters. I. Uptake and bioaccumulation of triphenyl phosphate by rainbow trout. *Chemosphere* 9: 525-532.
- 54 Gold MD, Blum A and Ames NB, 1978. Another flame retardant, tris-(1,3-dichloro-2-propyl)phosphate, and its expected metabolites are mutagens. *Science* 200: 785-787.
- 55 Hughes MF, Edwards BC, Mitchell CT and Bhooshan B, 2001. *In vitro* dermal absorption of flame retardant chemicals. *Food and Chemical Toxicology* 39: 1263-1270.
- 56 Nomeir AA, Kato S and Matthews HB, 1981. The metabolism and disposition of tris(1,3-dichloro-2-propyl) phosphate (Fyrol FR-2) in the rat. *Toxicology and Applied Pharmacology* 57: 401-413.
- 57 Lynn RK, Wong K, Garvie-Gould C and Kennish JM, 1981. Disposition of the flame retardant, tris (1,3-dichloro-2-propyl) phosphate, in the rat. *Drug Metabolism and Disposition* 9: 434-441.
- 58 Burka LT, Sanders JM, Herr DW and Matthews HB, 1991. Metabolism of tris(2-chloroethyl) phosphate in rats and mice. *Drug Metabolism and Disposition* 19: 443-447.
- 59 Muir DCG, Grift NP and Lockhart WL, 1982. Comparison of laboratory and field results for prediction of the environmental behavior of phosphate esters. *Environmental Toxicology and Chemistry* 1: 113-119.
- 60 Saeger VW, Hicks O, Kaley RG, Michael PR, Mieure JP and Tucker SE, 1979. Environmental fate of selected phosphate esters. *Environmental Science & Technology* 13: 840-844.
- 61 Barrett H, Butler R and Wilson IB, 1969. Evidence for a phosphoryl-enzyme intermediate in alkaline phosphatase catalysed reactions. *Biochemistry* 8: 1042-1047.
- 62 Anderson C, Wischer D, Schmieder A and Spiteller M, 1993. Fate of triphenyl phosphate in soil. *Chemosphere* 27: 869-879.
- 63 Ehrich, M. and Jortner, B. S. *Organophosphate-induced delayed neuropathy*. Ch. 2 in *Handbook of neurotoxicology, Vol 1*, Ed. Massaro, EJ. Humana Press Inc. Totowa, NJ, 2002.
- 64 Pope, C. and Liu, J. *Nonesterase actions of anticholinesterase insecticides*. Ch. 3 in *Handbook of neurotoxicology, Vol 1*, Ed. Massaro, EJ. Humana Press Inc. Totowa, NJ, 2002.

8. References

- 65 Saboori AM and Newcombe DS, 1990. Human monocyte carboxylesterase - purification and kinetics. *Journal of Biological Chemistry* 265: 19792-19799.
- 66 Mandel JS, Berlinger NT, Kay N, Connett J and Reape M, 1989. Organophosphate exposure inhibits non-specific esterase staining in human blood monocytes. *American Journal of Industrial Medicine* 15: 207-212.
- 67 Sato T, Watanabe K, Nagase H, Kito H, Niikawa M nad Yoshioka Y, 1997. Investigation of the hemolytic effects of various organophosphoric acid triesters (OPEs) and their structure-activity relationship. *Toxicological and Environmental Chemistry* 59: 305-313.
- 68 Beth-Hübner M, 1999. Toxicological evaluation and classification of the genotoxic, carcinogenic, reprotoxic and sensitising potential of tris(2-chloroethyl)phosphate. *International Archives of Occupational and Environmental Health* 72: M17-M23.
- 69 Gunderson EL, 1988. FDA Total diet study, April 1982-April 1984, dietary intakes of pesticides, selected elements, and other chemicals. *Journal of the Association of Official Analytical Chemists* 71: 1200-1209.
- 70 Sagunski H and Roskamp H, 2002. Richtwerte für die Innenraumluft: Tris(2-chloroethyl)phosphat. *Bundesgesundheitsblatt - Gesundheitsforschung - Gesundheitsschutz* 45: 300-306. (in german)
- 71 ACGIH and American Conference of Industrial Hygienists. *Documentation of the threshold limit values and biological exposure indices*. 7th ed., 2001.
- 72 Staaf T and Östman C, 2005. Indoor air sampling of organophosphate triesters using solid phase extraction (SPE) adsorbents. *Journal of Environmental Monitoring* 7: 344-348.
- 73 Brorström-Lundén E, Lindskog A and Mowrer J, 1994. Concentrations and fluxes of organic compounds in the atmosphere of the Swedish west coast. *Atmospheric Environment* 28: 3605-3615.
- 74 Brorström-Lundén E and Löfgren C, 1998. Atmospheric fluxes of persistent semivolatile organic pollutants to a forest ecological system at the Swedish west coast and accumulation in spruce needles. *Environmental Pollution* 102: 139-149.
- 75 Macher JM, 2001. Review of methods to collect settled dust and isolate culturable microorganisms. *Indoor Air* 11: 99-110.
- 76 Carlsson H, Nilsson U and Östman C, 2000. Video display units: An emission source of the contact allergenic flame retardant triphenyl phosphate in the indoor environment. *Environmental Science & Technology* 34: 3885-3889.
- 77 Salthammer T, Fuhrmann F and Uhde E, 2003. Flame retardants in the indoor environment - Part II: release of VOCs (triethylphosphate and halogenated degradation products) from polyurethane. *Indoor Air* 13: 49-52.

8. References

- 78 Sjödin A, Carlsson H, Thuresson K, Sjölin S, Bergman A and Östman C, 2001. Flame retardants in indoor air at an electronics recycling plant and at other work environments. *Environmental Science & Technology* 35: 448-454.
- 79 Sanchez C, Ericsson M, Carlsson H, Colmsjö A and Dyremark E, 2002. Dynamic sonication-assisted solvent extraction of organophosphate esters in air samples. *Journal of Chromatography A* 957: 227-234.
- 80 Stubenrauch S, Hempfling R, Doetsch P and Grünhoff D, 1999. Vorschläge zur Charakterisierung und quantifizierung pfadübergreifender Schadstoffexpositionen. *Umweltwissenschaften und Schadstoff-Forschung Zeitschrift für Umweltchemie und Ökotoxikologie* 11: 219-226.
- 81 Meyer J and Bester K, 2004. Organophosphate flame retardants and plasticisers in wastewater treatment plants. *Journal of Environmental Monitoring* 6: 599-605.
- 82 Swedish Energy Agency and Statistics Sweden. *Summary of energy statistics for dwellings and non-residential premises for 2000 - 2003*, Statistics Sweden, Stockholm, Sweden, 2005.
- 83 Svenskt Vatten. *Fakta om vatten och avlopp*, Svenskt Vatten, Stockholm, Sweden, 2001. (in swedish)
- 84 Swedish Meteorological and Hydrological Institute. *Nedebörds klimat*; http://www.smhi.se/kund_t/klima/sveklm/nederbord.htm (accessed 28 September 2005). (in swedish)