Engineering for Sustainability –
*Development of a Methodology to Solve Problems
with Organic Pollutants in Urban Areas*

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ABSTRACT

Sustainable development is a challenge for engineers and scientists every sector. The greatest challenge now is to implement practical ways of living and engineering that are environmentally sustainable. This masters thesis deals about ways of solving problems associated with organic pollutants that are transported by stormwater to aquatic environments. Organic pollutants will cause problems in aquatic systems because most of them are toxic to aquatic organisms and they are also able to bioaccumulate in organisms. There are usually no defined ways of solving problems with organic pollutants, and consequently important aspects are often missed or not known in the engineering methodology used when dealing with the problems.

This thesis is composed of two parts. One part with an extensive literature study to identify the fate of organic pollutants in the environment and to find a sustainable methodology for measurements of these pollutants. A methodology was then deduced from the literature, and case studies were used to verify the validity of the methodology in real life-based situations. As a result a sustainable development-orientated methodology has been developed, a method that can be used as a basis for decision-making in public authorities in the building sector and companies. The developed methodology is divided into three important parts with focus on measurements, risk assessment and decision-making.

The main focus in this thesis has been on the measurements part and the aim has been to find and apply environmentally friendly methods, to ensure achievement of sustainable development. Scientists and engineers dealing with environmental analysis usually encounter a paradoxical situation; whilst trying to analyse traces of harmful substances left in the environment, they harm the same environment by the traditional methods they use. Traditional sample preparation methods are time and labour intensive, have multi-step procedures that lead to loss of analytes, and require the use of toxic chemicals. In this project the solid phase microextraction (SPME) methodology was described and successfully applied in case studies to meet these demands.

MEASUREMENTS

RISK ASSESSMENT

DECISION-MAKING

ECOTOXICOLOGY

Contaminated Sediment

Indicators

Screening

Quantification

Partitioning and Transport Processes

Sources

Exposure

Bioavailability/Bioaccumulation

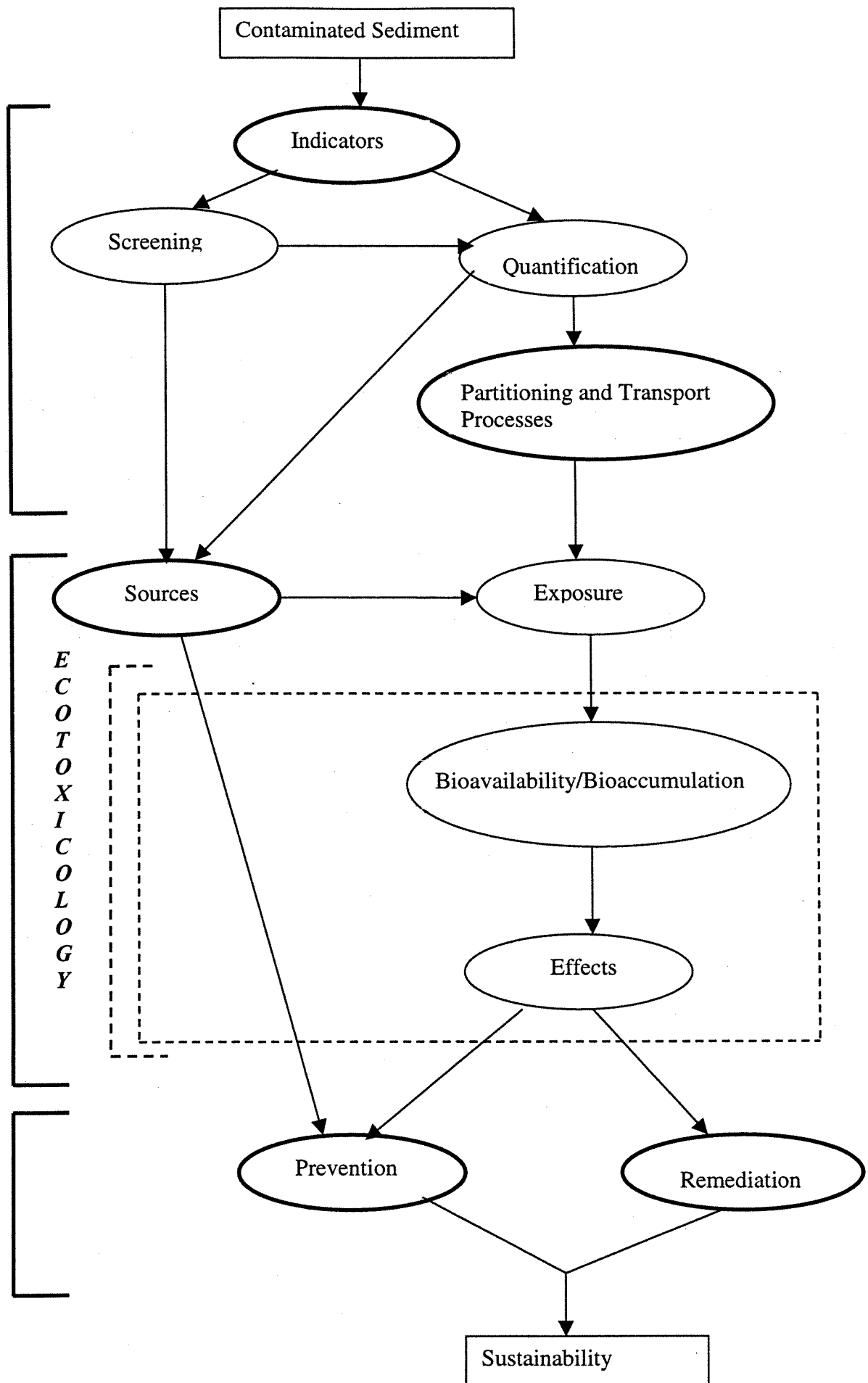Effects

Prevention

Remediation

Sustainability

ACKNOWLEDGEMENTS

GLOSSARY OF ABBREVIATIONS

ABM: active biomonitoring
ADI: acceptable daily intake
AEMT: Appled Environmental Measurement techniques
BCF: bioconcentration factor
BHT: butylated hydroxy toluene
BMF: biomagnification factor
BSAF: biota-soil (or sediment) accumulation factor
DBP: dibutyl phthalate
DDT
DEHP: diethylhexyl phthalate
DIBP: diisobutyl phthalate
DNA: dioxyribonucleic acid
DOC: dissolved organic carbon
EPA: Environmental Protection Agency
EPT: Equilibrium Partitioning Coefficient
EROD: ethoxyresofurin O-deethylase
GC: gas chromatography
GCT: gas chromatography time-of-flight mass spectrometer
HPLC: high pressure liquid chromatography
HRGC – HRMS: high resolution gas chromatography-high resolution mass
                  spectrometer
HSSPME: Headspace solid phase microextraction
K_{ow}:   octanol-water partition coefficient
K_p: partition coefficient
LC: liquid chromatography
LLE: liquid liquid extraction
LOAEL: lowest observed-adverse-effect-level
MS: mass spectrometer
NOAEL: no observed adverse effect level
NP: nonylphenols
NPE: nonylphenol ethoxylate
PA: poly(acrylate)
PAH: polyaromatic hydrocarbons
PBM: Passive Biomonitoring
PCB: polychlorinated biphenyls
PDMS: poly(dimethylsiloxane)
PDMS-DVB: poly(dimethylsiloxane)-poly(divinylbenzene)
POP: Persistent organic pollutants
RfD: reference dose
SARA: soil (or sediment) availability ratio
SHQ: Sediment Health Quotient
SOC: semivolatile organic compounds
SPME: solid phase microextraction
SPE   Solid Phase Extraction

SQC: sediment quality criteria
STF: stormwater treatment facilities
TOC: total organic carbon
TOF   Time-of-flight
WET: Water Environment Transport
WQC: water quality criteria

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Chapter 1

Introduction

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1.1 Description of the problem

Stormwater runoff from highways and commercial, industrial, and residential areas contains a wide spectrum of pollutants including heavy metals, petroleum hydrocarbons, pesticides, herbicides, sediment and nutrients. A considerable amount of these pollutants are transported by the stormwater and finally reach receiving waters such as lakes, rivers or creeks. A significant amount percolates down to groundwater thereby causing damage in drinking water systems and the environment. Most of these pollutants are toxic to the environment, especially to aquatic organisms. Significant research has been done mostly on the control of heavy metal pollution in stormwater (at least at the Department of Water Environment Transport, WET), and little attention has been paid to stormwater organic pollutants. Therefore this study is aimed at monitoring the impact of stormwater organic pollutants on watercourses, sediments and soils in urban areas. Organic pollutants are usually hydrophilic, resist degradation, can remain in sediments for years and may have adverse effects on aquatic life.

In many environmental cases, pollution problems are unnoticed or hardly identified, and no ecotoxicological or risk quantification is made to evaluate the magnitude of the damage and severity of the pollution effects. Hence, it is of importance to study the fate of organic pollutants in the environment, to do risk assessments in order to estimate the severity of the contamination, and to use indicators for identifying the presence and toxicology of organic pollutants in watercourses. There are usually no defined methods for carrying on these assessments, and many important aspects are undermined. Development of a methodology covering all the steps that should be taken into account when dealing with land and water polluted with organic chemicals is a prerequisite for sustainable development.

1.2 Aims and Objectives

The objective of this study is multi-fold:

- To develop a sustainable development-orientated methodology, that is, a methodology focused on limited use of substances/technologies that have adverse effects on the environment.
- To introduce the methodology so that it can be used as a basis for decision-making in public authorities and among companies in the building sector.
- To explain the necessity of considering issues like risk assessment and pollution indicators when solving organic pollutant-related problems in the environment.
- Illustration of how the methodology can be used in real life, by applying it in case studies.

1.3 Relevance of the study

Urban stormwater runoff is a matter of concern because of the potential of stormwater to contaminate downstream lakes, streams, and reservoirs. Engineers and scientists globally are faced with a challenge of ensuring sustainability of their activities, and that necessitates the use of environmentally friendly technologies. Since many organic pollutants, usually found in stormwater, remain in the environment for a long time, they are of utmost concern in sustainable development, because if not taken care of, they can be a threat to the coming generations. Therefore, it is important to equip engineers with a methodology to follow when facing problems with organic pollutants in the environment.

1.4 Presentation of the Thesis

This study is an introduction to a major research project that will be carried out by Department of Water Environment Transport (WET) at Chalmers University of Technology, Sweden. The vision is to develop civil engineering that favours sustainability and the main ambition is to develop sustainable engineering within the areas of water and transport.

The thesis is composed of a literature review of organic pollutants in urban environment, laboratory and field measurements of organic pollutants. The experimental part of the thesis covers laboratory analysis of sediment and water samples. The results are presented as case studies, which demonstrate how the methodology can be applied in real-life situations. The case studies, which are reviewed in the last part of the report, are:

- Environmental monitoring of nonylphenols in the Mölndal river
- Organic pollutants leached by stormwater from asphalt storage
- Brief investigation of sediment health in the river Viskan.

1.5 The Hypothetical Methodology

As a starting point for the project, a preliminary methodology was proposed by Ann-Margret and the WET group, as an engineering tool for sustainability. The following steps were proposed:

- Measurement techniques for organic pollutants in land and water environments in urban areas
- Partition, chemical reactions, spreading and transport processes for organic pollutants in water, sediment and soil
- Ecotoxicological impact assessment of organic pollutants in land and water environments in urban areas
- Impact assessment and indicators of sustainability of land and water in urban areas contaminated with organic pollutants
- Identification of sources in urban areas and plans for strategies

- Preventive actions and preventive techniques for taking care of soil and water in urban areas contaminated with organic pollutants

The major part of this study was to improve the above steps in order of importance for environmental monitoring. A model was to be developed, which is an easy-to-interpret tool even for engineers with limited knowledge in chemistry and environmental issues. In building the model, the information gained from literature review was used as a foundation. The model was then tested in the case studies and the results are later reported in chapters 11-13.

Chapter 2
Background

2.1 Urban Stormwater and Sediments

Rainwater gets polluted during precipitation and during its transport over urban surfaces (e.g. roads and parking lots) and is named stormwater when leaving the surface. Runoff is caused by rainfall and snowmelt events. Urban stormwater runoff is a matter of environmental concern because of the potential of stormwater to contaminate downstream lakes, streams and reservoirs with urban pollutants. It is known that stormwater pollution can damage the biological life in the receiving waters and thus destroy the ecosystems. There is a toxic threat to the receiving water if no treatment, concerning stormwater improvement is undertaken; therefore pollutant reduction is a key issue. A significant portion of pollutants may be present as dissolved and may be bioavailable to organisms (Pettersson, 1999).

The chemistry of urban stormwater runoff, however, depends on factors other than the direct input of contaminants into the flow system by urban activities. A strong relation has been established between the chemical characteristics of urban stormwater and the concentration of suspended solids in stormwater. The implication of this relationship is that the chemistry of urban stormwater runoff is affected directly by the chemistry of urban sediments (Parker, et al, 2000).

In the urban environment, sediment is transported from streets, parking lots, rooftops, construction sites, vacant lots, and landscaped grounds during rainstorms. Sediment can be transported by flow through gutters, storm drains, sewers, and stream channels across urban flood plains, and can be deposited at any point along the stormwater flowpaths as flow velocities decrease. Deposition also occurs in natural or artificial basins, such as ponds, detention basins, or any depression in the topography. Unlike urban stormwater, urban sediment can be stored upstream from its eventual destination for significant periods of time. Sediment deposited directly in flow paths may be stored only until the next storm produces sufficient run-off to transport the material farther downstream. Sediments deposited in urban flood plains might be stored for several years or decades until a sufficiently large flood erodes flood plains. Sediments can be stored in detention basins indefinitely (Parker, et al, 2000).

Because sediment can be stored, it presents environmental managers and engineers with different issues than does stormwater. Dissolved contaminants in stormwater are transported rapidly downstream and generally are diluted as they enter larger streams that receive runoff from non-urban areas. If sediments are contaminated or composed of naturally occurring toxic elements their storage upstream also can represent an environmental hazard at the site of deposition or can represent a future threat to aquatic environments if they are abruptly released into the stormwater flow paths by human activity of large floods (Parker, et al, 2000).

2.2 Sources of Stormwater Pollutants

Contamination of urban sediments can occur through a variety of processes, including spillage, leaching of hydrocarbons from asphalt, construction materials, car exhaust, unburned fuel, rubber from car tyres, atmospheric fallout, and application of pesticides and fertilizer. In rapidly urbanizing areas, sediments can show residual contamination by past land-use practices, such as agricultural spraying.

Pollutants enter stormwater in many ways, among which are the following (Urbonas and Stahre, 1993):

- Pollutants are absorbed as the raindrops pass through the atmosphere.
- Pollutants are washed off the paved and unpaved surfaces by stormwater runoff
- Pollutants that have accumulated since the last storm in sewers, ditches, and channels are picked up by the new stormwater. This source can be also aggravated by illegal wastewater connections to the stormwater conveyance system

Some studies show that the pollutant concentrations are largest early in the runoff process. This is explained by speculating that the paved surfaces are most polluted before rain begins. As rainfall continues, the surface pollutant accumulation is depleted and pollutants are diluted by larger flows in the transport system. Also, it is speculated that the so-called first flush also depends on the intensity and the duration of rainfall (Urbonas and Stahre, 1993).

Stormwater contains a variety of pollutants originating from anthropogenic actions such as corrosion of materials from buildings, erosion of streets and roads from vehicular traffic and other activities. Elements significant in polluted stormwater are metals, organic pollutants and nutrients such as nitrogen and phosphorus. Heavy metals are usually present in particulate and dissolved phases. Organic pollutants are mostly attached to suspended solid-associated organic matter (Pettersson, 1999). To narrow the scope of this report, focus will be on organic pollutants.

Organic pollutants originate from different activities. There are natural and anthropogenic sources of organic pollutants. Some organic pollutants, such as polyaromatic hydrocarbons (PAH), are formed by incomplete combustion processes. Natural combustion processes such as forest fires and volcanic eruptions are therefore also sources of organic environmental toxins. Another natural source is enzyme formation in organisms. The major sources of PAHs in the air are wood burning, traffic, coal and coke plants, aluminium smelters, energy production, and waste combustion.

Several organic pollutants have been banned in some countries many years ago. For instance, the use of polychlorinated biphenyls (PCB) was banned in Sweden in 1973, except for sealed systems. However, sealed is a relative concept in this context, and it is now known that most so-called sealed systems leak to some degree. As a result, fifteen years after the banning of PCB, there is still a discharge to the environment.

Another source of environmental pollutants that is more difficult to deal with is the diffuse discharges from various human activities, such as traffic, household, or garden use of chemicals. Another source is products containing environmentally harmful compounds such as PCB and brominated flame retardants, which are spread to the surrounding environment either during the products lifetime or as a refuse. It is clearly of fundamental importance to identify the dominant sources to the environment if source reduction measures are to be effective (Jones, et. al, 1999).

2.3 Persistent Organic Pollutants

Persistent organic pollutants (POPs) are organic compounds of natural or anthropogenic origin that resist photolytic, chemical and biological degradation. As their name suggests, POPs may persist in the environment for years and even decades. They react slowly or not at all by processes such as biodegradation, photolysis, oxidation and hydrolysis. Typical criteria for classifying POPs are degradation half-lives in excess of 2-5 days in air, 2-6 months in water and 6-12 months in soils and sediments, there being a sense that if the half-lives exceed these values the substance is persistent enough that it can be expected to accumulate in the environment and become subject to long-range transport. Some POPs persist much longer than these criteria. For example, PCBs and certain other organochlorinated substances are preserved virtually indefinitely in marine and fresh water sediments (Wania and Mackay, 1999).

POPs are characterised by low water solubility and high lipid solubility, resulting in bioaccumulation in fatty tissues of living organisms. POPs are transported in the environment in low concentrations by movement of fresh and marine waters and they are semi-volatile, enabling them to move long distances in the atmosphere, resulting in widespread distribution across the earth including regions where they have never been used.

As mentioned in the section 2.2, many POPs have been banned in some countries, due to their damage to the environment. Most, if not all, POPs are still in use or existing in many countries, especially in developing countries. For agrochemical POPs the source is clear, the deliberate application to crops and soils. Other POPs have been deliberately manufactured but have multiple diverse and diffuse uses, for example PCBs. Thus, both humans and environmental organisms are exposed to POPs around the world, in many cases for extended period of time.

Chapter 3
Indicators of organic pollutants

An ecosystem population that is under stress due to some anthropogenic changes in its environment is frequently characterised by a limited distribution, low abundance of its individuals and/or reduced reproductive potential (Diamant and Westernhagen, 1999). A useful indicator will flag the occurrence of stress-induced changes in a specific population and help in predicting whether such changes will lead to serious damage. The greater the indicator reliability and the earlier the warning provided by it, the more useful it is. In such a programme multiple measures of effects are essential and measurements should include those indicative of both exposure and pathology. Many indicators that can be used for organic pollutants include sediments, biota and water.

3.1 Environmental Biomonitoring

Biomarkers are also promising tools for biomonitoring, both in marine and freshwater environment. It is however clear that much more information is needed about the exact relation between biomarker responses and the health and fitness of organisms, and even more so between biomarker responses and risks for the ecosystems. In order to address these questions, it is important to realise that the possibilities for the application of a biomarker depend on the concept that is chosen for environmental monitoring. The purpose of monitoring varies from simple screening to risk characterisation of the ecosystem level. Different concepts for environmental monitoring and for the application of biomarkers are summarised in Table 1.

As shown in table 1, it is important to realise that, depending on whether biomonitoring is performed with the intention to signal, to control or to predict pollutants and/or their effects, each concept brings specific requirements for the implementation of biomarkers. It is therefore useful to distinguish between the application of biomarkers for screening, as diagnostic tools, as parameters in trend analysis or as predictive markers (risk indicators) (Besten, 1998). In the case of screening, the biomarker may be used as a first and cost-effective measurement in a stepwise approach intended to signal the presence or the effects caused by pollutants (referred to as early-warning system). Biomarkers used for screening may be only biomarkers of exposure (with specificity for certain contaminants) or also markers of toxic effect. Their function is to trigger further research. In some cases, the biomarker is the endpoint in a bioassay, performed in the laboratory or *in situ*.

The term diagnosis refers to the application of a suite of biomarkers which can signal the cause of observed effects in a population of organisms in the field. In this concept biomarkers are used to determine whether or not organisms are physiologically 'normal'. It is required to know at what point a departure from the normal, healthy state (homeostasis) is likely to affect the performance of the organism (survival, growth or reproduction). With this knowledge these biomarkers can be used as early warning signals for effects on the population level that have not yet become eminent (Besten, 1998).

Table 1: Concepts for the Implementation of Biomarkers in Environmental Monitoring *(adopted from den Besten, 1999)*

Concept	Purpose	Use of Biomarkers	Specific requirements for further Implementation of biomarkers
Screening	-Cost-effective use of biomarkers as a first screening step; -Signaling effects (early-warning system)	-Simple biomarkers measurements in a tiered approach (in combination with bioassays and chemical analyses). -Biomarkers of exposure and biomarkers of toxic effect -Biomarkers incorporated in bioassays which are used to test environmental samples (water, sediment)	-Sensitive biomarkers with specificity for certain types of contaminants or certain types of effect mechanism
Diagnosis	-To signal the possible cause for observed adverse effects in populations of certain species	-Large batteries of biomarkers (indicators of toxic effect) are applied in studies on animals from affected populations (in comparison with reference populations)	-Development of a suite of biomarkers which cover all relevant modes of action by contaminants -Insight in the relation between departure from homeostasis (healthy state), biomarker response and fitness or performance of the organism
Trend monitoring	-To study changes of biomarker responses in time; to compare biomarker responses with quality objectives; or to assess improvement after remedial action	-Repeated sampling and biomarker measurements in time	-Knowledge of the influence of modifying factors -Translation of existing quality objectives in biomarker response criteria
Monitoring of spatial variation	-Assessment of site-specific biomarker responses (gradients)	-Comparison of biomarker responses between sites	-Biomarkers must be applicable in common species (at least common in the area under investigation) -Knowledge of modifying factors; reference values
Site-specific risk Assessment	-Determination of the bioavailability of contaminants and the resulting risk in polluted sites (hot spots) -Signaling effects at higher levels of organizations	-Biomarkers as indicators of exposure -A selection of biomarkers is used as early warning signal of adverse effects on the individual, population or community level	-Biomarkers must be applicable in locally available species, or in *in situ* bioassays. -For predictive biomarkers: responses must be related to effects on higher levels of organization
Risk assessment: ecosystem structure and ecosystem function	-Predicting effects on ecosystem level	-Application of selected biomarkers in a range of species -Estimation of the % potentially affected species - Application of selected biomarkers in key organisms	-Biomarkers must be applicable in different species (incl. key organisms). -Sensitivity comparisons between species

Another concept for the application of biomarkers is seen in trend monitoring (both in time and space). For this type of approach, specific research needs arise from the lack of knowledge of modifying factors. Furthermore, an important issue is the translation of quality objectives for the environment in criteria for biomarker responses (e.g. defining the range for a biomarker value that is characteristic for an unpolluted environment).

Finally, information from biomarkers may be used in risk characterisation procedures. Environmental monitoring is often started after performing chemical analyses (or triggered by the results of the screening methods), when site-specific risk assessment is needed. This is often done on the basis of a comparison of information from biotic parameters (field studies on abundances and health of selected species, bioassays performed in the laboratory demonstrating toxicity of water or sediment samples) with expected effects based on an interpretation of chemical data (den Besten, 1998). The result of such risk assessment is the indication whether or not organisms are exposed to pollutants at unacceptable high levels (determination of the bioavailability). In this concept, biomarkers may be useful tools, indicating bioavailability of contaminants and adverse effects at the same time. Biomarkers could also be used to detect subtle effects on the population or community level.

The inhibition of specific enzymes has proven to be a popular biomarker and with justification. A suite of biomarkers can be used including, stress proteins, EROD (ethoxyresorufin *O*-deethylase activity), liver and spleen somatic indexes and DNA adducts. DNA repair enzymes can also be measured and their induction is an indication of DNA damage and associated genotoxic effects (Landis and Ming-Ho, 1999).

In a study done by Schilderman et al (1999), DNA adducts in crayfish were used as indicators of PAH. Detection of PAH in organisms is difficult since these compounds are easily metabolised into more polar, readily excretable metabolites. For example, in eels living in PAH polluted water no high-molecular-weight PAHs could be detected but high levels of liver-DNA adducts were observed (Schilderman et al, 1999). Determination of PAH-DNA adducts has been successfully applied in environmentally exposed fish and mussels. Interaction products with DNA may therefore be used as indicators for the biologically available dose. Also, PCBs are assumed to induce their toxic effects after metabolic activation, as has been demonstrated for polycyclic aromatic hydrocarbons and numerous other compounds and it has been found that in vivo and in vitro activation of PCBs resulted in formation of metabolites capable of forming DNA adducts (Schilderman et al, 1999).

Furthermore, in a study conducted by Arinc and Sen (1999), the degree of induction of cytochrome P4501A-associated 7-ethoxyresorufin *O*-deethylase (EROD) activity and immunochemical detection of cytochrome P4501A in leaping mullet (*Liza saliens*) and common sole (*Solea vulgaris*) were used as biomarker for assessment of PAH and PCB type organic pollutants along the Izmir Bay on the Aegean Sea coast, Turkey.

Biosensors are a new analytical tool that may hold promise in ecological monitoring. In this new class of sensors, a biological entity such as the receptor molecule or an antibody

for a particular xenobiotic is bound to an appropriate electronic sensor. A signal can then be produced as the material bound to the chip interacts with the toxicant.

3.2 Aquatic Organisms as Indicators

Aquatic biota, sediments, and water samples may be used for pollution-monitoring purposes. The determination of organic micro contaminants having a low log Kow (5-7), such as chlorinated biphenyls, hexacholorobenzene, DDT, toxaphene, etc. in water is very difficult, because of their extremely low concentrations (Boer and Brinkman, 1994). Quality-control data for this type of analysis are very scarce. An alternative approach such as the determination of these analytes in sediments or biota is, therefore, attractive. A number of conditions have to be fulfilled for both types of matrices, prior to using data from the related monitoring programmes. For example, for sediments, the sedimentation rate at the sampling location, the type of sampling device, the homogeneity of distribution of the contaminants in the sediment, the total organic carbon content, and the particle size of the sediment should be studied in detail before hand (Boer and Brinkman, 1994).

The relevance of the sediment measurements is limited, since the contaminants bound to the substrate by adsorption may not be bioavailable for immediate uptake by aquatic organisms. In addition, varying concentrations on the sediment may reflect changes in the binding properties of the sediments rather than variations in the pollution levels of the sediments (Schilderman, et al., 1999). The relevance of direct analysis of water is also limited in the case of hydrophobic contaminants, whereas contaminant levels are usually below detection limits. Therefore living organisms should also be used to monitor environmental contamination, since they may reflect the contamination history of a particular location because they have been exposed during their entire lifetime and are capable of accumulating these toxic substances in their tissues.

The determination of persistent organic pollutants is usually hampered by their extremely low solubility in water. Because they are strongly lipophilic, these compounds are concentrated in the fat of aquatic organisms and it is much easier to determine them in these lipid fractions. Aquatic organisms can be used as biomonitors if they can reflect the contaminant levels at a certain location and their variations over a period of time. Non-migratory species are therefore essential (Boer and Brinkman, 1994). Also, sampling of a class of restricted size is essential, in order to reduce the contribution of biomagnification to the contaminant levels in fish. Yellow eel and cod liver can serve as biomonitors, because the reductions in concentration in the water body are reflected by these fish through growth dilution (Boer and Brinkman, 1994).

Utilization of biochemical factors to evaluate biological responses to pollutants, especially to carcinogenic compounds such as PCBs and PAHs, has increased considerably over the past 15 years (Boer and Brinkman (1994), Arinc and Sen (1999), Besten (1998), Schilderman, et al, (1999)).

3.3 Conditions for biomonitoring

The use of aquatic organisms to monitor contamination in freshwater and marine ecosystems can involve active (ABM) or passive biological monitoring (PBM). Fish, yellow eel and cod liver have been used in several studies for biomonitoring. When site-specific aquatic organisms are used for PBM, it is essential that they should be non-migratory. This condition is normally fulfilled by bottom organisms, such as blue mussels (Mytilus edulis) or freshwater mussels (Dreisserna polymorpha). The disadvantages of using these organisms are their very low fat contents, the restricted amount of available tissue, and the difficulty and labour involved in selecting specific tissues. Moreover, such site-specific species may not be available at many locations. Therefore, the use of fish is a better alternative. Although many fish species show distinct migration, this is not the case for the yellow eels once they have arrived at their destination. The yellow eel has a wide geographical distribution in inland waters of many countries, which enables it for the use in international studies. Silver eels are different from yellow eels since they are known of strong migratory behaviours, so sampling should be done in spring when silver eels are absent because they are sometimes difficult to distinguish from yellow eels (Boer and Brinkman, 1994). Cod is also widely distributed, especially in the North Sea and does not show migratory behaviour. Many data indicate that there is virtually no migration of cod over long distances.

Attention should also be paid on the spawning behaviour of the fish. The life cycle of the eel is unique because spawning only occurs at the end of its life, in its destination. Therefore the loss of organic pollutants during spawning does not confound the use of yellow eel during the period of its life cycle in freshwaters. When sampling is confined to a specific period of the year, the variations in fat content are minimized. Sampling during and shortly after the spawning period should be avoided, the best period being later in the year (between September and December) when fat contents have returned to a constant level. Bioaccumulation experiments have shown that uptake of organochlorine compounds by fish occurs within several days or, at most, a few weeks. Therefore concentration increases will normally be reflected in the fish more or less immediately. The elimination of organochlorine compounds from larger fishes such as cod and eel will, however occur very slowly or not at all (Boer and Brinkman, 1994).

The suitability of aquatic organisms as biomonitors in passive biomonitoring (PBM) can be validated by comparing concentrations of contaminants in the organism with those in sediments and water from the same locations. Active biomonitoring (ABM) uses aquatic organisms from a clean reference location: these are held in cages, deposited in the water at a sampling site, and sampled after several weeks. Freshwater mussels are often used but fish can also be used. ABM has an advantage that instantaneous picture of the actual contamination can be made. An important condition is that organisms from a sufficiently clean reference location must be used. For relatively clean water bodies the PBM approach will therefore be preferred to ABM. It is possible that cultivated eel, in which very low concentrations of organic micro-contaminants are normally found, could be a good alternative for use in ABM.

PBM using fish as biomonitors must certainly be considered as a valuable method complementary to ABM. The selection of the method, ABM or PBM, will depend on the availability of sufficiently clean reference organisms, the type and expected level of compounds to be analysed and the amount of material required for analysis (Boer and Brinkman, 1994).

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Chapter 4
Measurement Techniques

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Measurement is the cornerstone for environmental monitoring. Before any risk assessment or decision-making can be done, pollutants have to be measured. Measurement is a critical step in sustainable development, because it is a step in which traditional methods usually pollute the environment by use of toxic chemicals for analysis. Environmentally friendly measurement techniques are therefore the necessary to assure sustainability. The analytical procedure has several steps: field sampling, field sample handling, laboratory sample preparation, separation and quantitation, statistical evaluation, decision-making and finally action. Each one of these steps is important for obtaining correct results. If an instrument could perform all the analytical steps in the field, without human intervention, then no problems of human error would arise.

Presently, several sophisticated instruments such as gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS), are available to separate and to quantify very complex mixtures.

Traditional sample preparation methodologies involve the consumption of enormous quantities of clean organic solvents, which are subsequently dispersed into the environment or disposed of at high costs. Thus, especially chemists dealing with environmental analysis encounter a paradoxical situation: whilst trying to analyse traces of harmful substances left in the environment, they harm the same environment by the methods they use. Moreover, traditional sample preparation methods are time and labour intensive, have multi-step procedures that lead to loss of compounds. The result is that over 75% of the analysis time is spent on sampling and preparation steps. The phasing out of solvents constitutes a challenge for sustainable civil engineering and for sustainable development. Consequently a great change in analytical methodology is necessary. These needs have driven the development of a solvent-free preparation technique, solid phase microextraction (SPME) and chromatographic methods (GC and HPLC) that can detect environmental pollutants even at trace concentrations (Alpendurada, 2000).

Chromatographic methods such as GC and HPLC are widely used for the detection of organic pollutants in the environment. For these applications, they are considered complementary to each other, with neither of these two separation techniques presenting an overall advantage. However, for polar, thermally labile and high molecular weight compounds, HPLC methods are generally preferred over GC methods. SPME coupled to GC is however, better suited for the analysis of volatile and semi-volatile organic compounds of low to intermediate polarity. Quite a few semi- or non-volatile, thermally labile, or very polar compounds, e.g. pharmaceutical products, drugs, peptides, proteins, and some polar pesticides such as carbamates are better suited to HPLC method.

4.1 The Analysis Procedure

Traditional methods are time consuming; and the result is that about three thirds of the analysis time is spent on laboratory methods such as for example extraction and clean up of sediment samples. Development of faster and reliable methods, as explained above, has led to a decrease in the time required for analysis of organic pollutants in the laboratory. It has also helped minimize loss of analytes, and use of toxic solvents. SPME can be used for both sediment and water samples, followed by direct GC or HPLC injection. This leads to faster solutions of environmental problems and decision-making. Figure 1 illustrates the steps required in the analysis of organic pollutants in sediment and water. The measurement techniques involved in each step are discussed below.
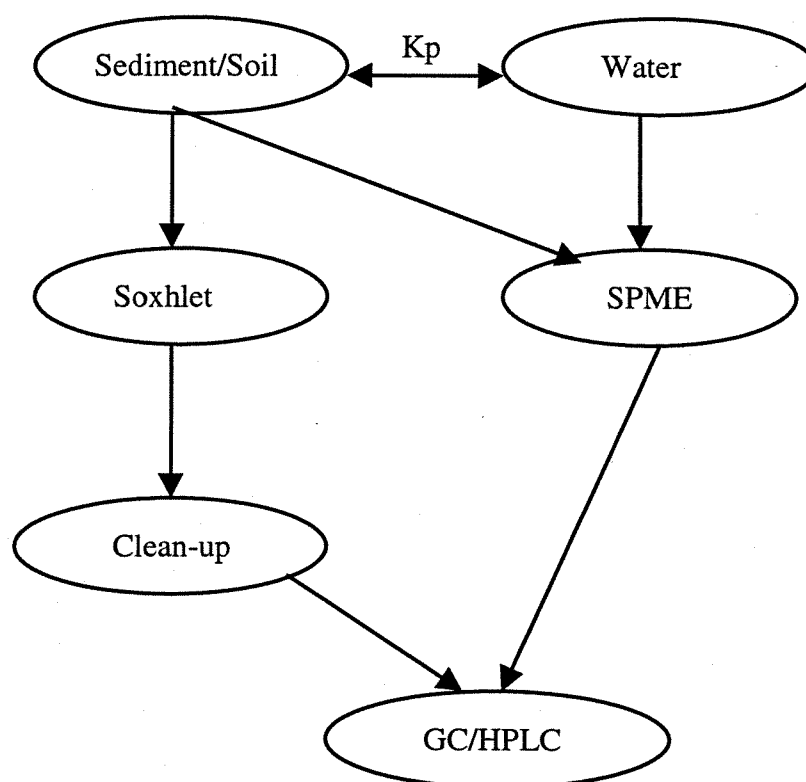
Figure 1: The steps for analysis procedure of organic pollutants

4.2 Solid Phase Microextraction

SPME is a sustainable technique since it prevents the use of toxic chemicals and is fast. Significant research has been invested in improving current methods as well as alternative methods development for analysis of organic compounds. SPME as a sample preparation technique has several apparent advantages over conventional methods for

specific environmental applications. This technique was first introduced by Pawliszyn in 1990 to analyse relatively volatile compounds in the environmental field, but now its use has been extended to the analysis of a great variety of matrices: gas, liquid and solid, and to a wide range of analytes from volatile to non-volatile compounds (Alpendurada, 2000).

SPME was developed to address the need to facilitate rapid sample preparation both in the laboratory and on-site where the investigated system is located. Solid-phase micro extraction was originally named after the first experiment using an SPME device which involved extraction on solid fused-silica fibres, and later as such, as a reference to the appearance of the extracting phase, even though the extraction phase is not always technically a solid (Lord and Pawliszyn, 2000). Figure 2 shows the different parts of the SPME device.
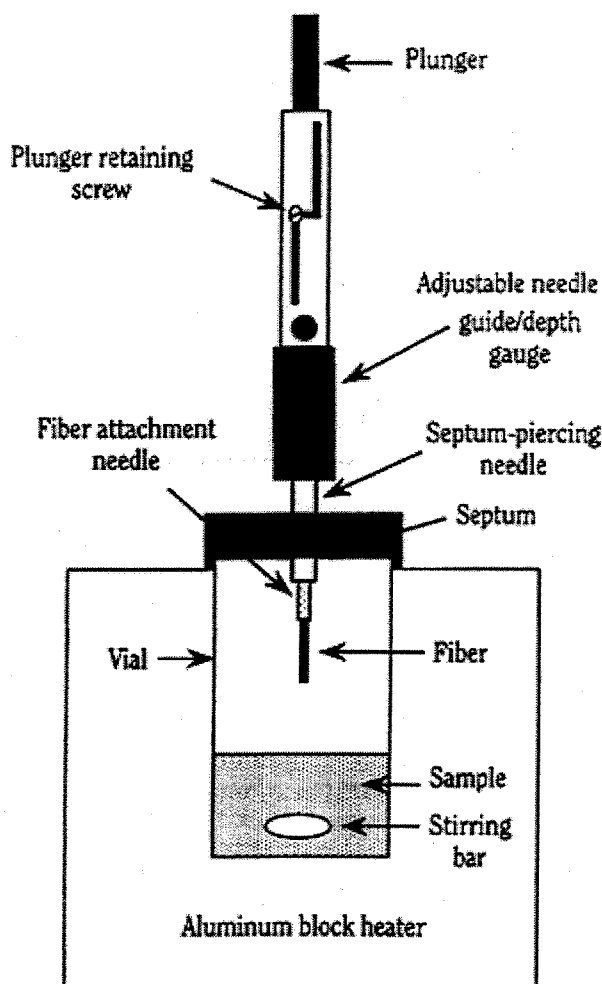
Figure 2: Solid Phase Microextraction device (Start GC, 2000)

In the technique a small amount of extracting phase dispersed on a solid support, is exposed to the sample for a well-defined period of time. In one approach a partitioning equilibrium between the sample matrix and extraction phase is reached. In this case convection conditions do not affect the amount extracted. In a second approach utilizing

short time pre-equilibrium extraction, if convection/agitation are constant, then the amount of analyte extracted is related to time.

In SPME a small amount of extracting phase associated with solid support is placed in contact with the sample matrix for a predetermined amount of time. If time is long enough, a concentration equilibrium is established between the sample matrix and the extraction phase. When equilibrium conditions are reached, then exposing the fibre for a longer time does not accumulate more analytes. Typically SPME extraction is considered to be complete when the analyte concentration has reached distribution equilibrium between the sample matrix and the fibre coating. In practice, this means that once equilibrium is reached, the extracted amount is constant within the limits of experimental error and it is independent of further increase of extraction time. The equilibrium conditions can be described as:

$$n = (K_{fs}V_fV_sC_o)/ (K_{fs}V_f+V_s) \quad ... (1)$$

where n is the number of moles extracted by the coating, K_{fs} is a fibre coating/sample matrix distribution constant, V_f is the fibre coating volume, V_s is the sample volume, and C_o is the initial concentration of a given analyte in the sample.

This discussion is limited to partitioning equilibrium involving liquid polymeric phases such as poly(dimethylsiloxane) (PDMS). The method of analysis for solid sorbent coatings is analogous for low analyte concentration, since the total surface area available for adsorption is proportional to the coating volume, if constant porosity of the sorbent is assumed. For high analyte concentrations, saturation of the surface can occur.

In addition when the sample volume is large, equation 1 can be simplified to

$$n = K_{fs}V_fC_o \, ...(2)$$

which points to the usefulness of the technique for field applications. In equation 2 the amount of analyte is independent of the volume of the sample. In practice, there is no need to collect a defined sample prior to analysis as the fibre can be exposed directly to the ambient air, water, production stream, etc. The amount of extracted analyte will correspond directly to its concentration in the matrix, without being dependent on the sample volume (Lord and Pawliszyn, 2000).

Extraction Modes of SPME

SPME has two steps: in the first step, the coated fibre is exposed to the sample or its headspace and the target analytes partition from the sample matrix to the coating. In the second step, the fibre bearing the concentrated analytes is transferred to the analytical instrument where desorption, separation and quantification of the extracted analytes take place. The desorption step is normally attained by placing the fibre into a hot injector in a GC.

Three modes of SPME can be considered: direct extraction, headspace extraction and membrane-protection approach (Alpendurada, 2000). In direct extraction, the coated fibre

is directly immersed in the sample and the analytes are transported from the sample matrix to the fibre coating. To facilitate rapid extraction, some level of agitation is required to transport analytes from the bulk of the solution to the vicinity of the fibre. For gaseous samples, natural convection of air is sufficient to facilitate rapid equilibration. For aqueous matrices, more efficient agitation techniques, such as fast sample flow, rapid fibre or vial movement, stirring or sonication are required. These conditions are necessary to reduce the effect caused by the "depletion zone" produced close to the fibre as a result of fluid shielding and slow diffusion coefficients of analytes in liquid matrices (Lord and Pawliszyn, 2000).

In the headspace mode, the analytes need to be transported through the barrier of air before they can reach the coating. This modification helps primarily to protect the fibre coating from damage by high molecular mass and other non-volatile interferences present in the sample matrix, such as humic materials or proteins. The headspace mode also allows modification of the matrix, such as a change of the pH without damaging the fibre. Amounts of analyte extracted into the coating from the same vial at equilibrium using direct and headspace sampling are the same as long as sample and gaseous headspace volumes are the same. This is caused by the fact that the equilibrium concentration is independent of fibre location in the sample/headspace system. The membrane-protected SPME is used in order to protect the coating from damage, similar to the use of headspace SPME, for the extraction of analytes in very polluted samples. However, membrane protection is advantageous for the determination of analytes having volatiles too low for the headspace approach. In addition, a membrane made from appropriate material can add a certain degree of selectivity to the extraction process. The use of thin membranes and increased extraction temperatures will result in faster extraction times (Lord and Pawliszyn, 2000).

The choice of particular coating is chemical structure dependent. The general selection rule "like dissolves like" is often applied (Alpendurada, 2000). The most popular coatings to date are poly(dimethylsiloxane) (PDMS) fibres, and whenever possible they should be used as they are very rugged liquid coatings that are able to withstand high injector temperatures up to about 300°C. The PDMS coating is very effective in extracting aromatic hydrocarbons and PAHs from water (Pawliszyn, 1999). PDMS is a nonpolar phase which extracts nonpolar analytes very well, but it can also be used to extract more polar compounds after optimising extraction conditions such as pH, salt concentration and temperature. In the case of PDMS fibres which are commercially available in different thickness, the thinnest coating which achieves the required limit of detection should be chosen. For direct aqueous extraction with magnetic stirring, a 100μm PDMS coating provides equilibration times of less than an hour for compounds which have estimated distribution constants less than 1000. For compounds with higher constants, thinner PDMS coatings should be used since the equilibration time is shorter (Alpendurada, 2000).

Applications and Advantages of SPME

SPME can be used in different fields including environment (water, soil, air), food, natural products, pharmaceuticals, biology, toxicology, forensics and theory (Alpendurada, 2000). It requires no solvents and permits sample transfer and analysis with little or no modifications to existing chromatographic equipment (MacGillivray, 1999). As a result implication costs can be kept low. SPME can also be used in ecotoxicological studies, for partition and bioavailability tests (see section 6.5). Key advantages of utilising SPME for environmental work include its simplicity, amenability to automation, and suitability for field and on-site applications due to its portability. The possibility of errors associated with the handling and storing steps are reduced, as well as costs. In addition, a faster and better characterization of the problem is possible, as the analytical information can be given immediately for evaluation and decision-making (Alpendurada, 2000).

The method has been used for extracting organochlorine pesticides, phthalate esters and other selected semivolatile organics. The advantages of hot water extraction and SPME have led to the more recent development of coupling hot water extraction with SPME. In this approach, the sample (usually soil or sediment) placed in an extraction cell is constantly swept with fresh hot water, and the analytes removed are collected and extracted by SPME fibre from water. Hot water acts as an extraction solvent, facilitating the release of analytes from the solid matrix. SPME fibre on the other hand is used to isolate and concentrate the analytes simultaneously from water into the coating.

Headspace solid phase microextraction (HSSPME) has been used in various studies for the determination of pollutants in soil (Llompart et al, 1999; Santos, et al, 1999). In the study by Llompart et al, SPME fibre was suspended in the headspace above slurry of a soil sample. After GC analysis, it was found that simple addition of water is adequate for the purpose of analysing the target volatile organic chemicals in soil. For soil samples, the application of SPME is limited to sampling the headspace over the soil or soil water to avoid the contact between the fibre and the soil. HSSPME is well suited for the rapid quantification of residual volatiles in landfill or spill samples (Llompart et al, 1999).

Santos et al added water to chlorobenzene-contaminated soil and placed the vial containing the sample in a thermostatic bath for 10 minutes. The sample was then extracted with SPME and injected in GC-MS for analysis. The chlorobenzenes in this soil were quantified by standard addition, for quality assurance, which led to good reproducibility and adequate detection limits (Santos, et al, 1999). Analysis of sediments has also been done with SPME (Millan and Pawliszyn, 2000).

4.3 Gas Chromatography

Environmental organic chemists have now incredibly sensitive and selective analytical methods at their disposal for the analysis of organic pollutants. Current high-resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) techniques allow detection of organic compounds at trace levels on column. Because of the great

sensitivity of electron capture and MS detectors, organic compounds can now be routinely detected in the full array of environmental media at trace levels. Most SPME methods developed until now are used in combination with Gas Chromatography and suitable detection. The detection of low levels of analytes in GC-MS is primarily limited by the presence of chemical interference ions close to the mass of the target ion. Chemical background comes from a variety of sources including source contamination, column bleed and sample matrix. The contribution, from these background ions, to the reconstructed ion chromatogram for a particular target ion, can lead to poor signal and noise ratios. By decreasing the mass window specified for the reconstructed ion chromatogram, a significant proportion of this background interference can be removed from the chromatogram, leading to higher signal to noise ratios (Green and Newton, 1999).

Recently a sensitive, reproductive and faster GC-MS time-of-flight (TOF) [GCT] mass spectrometer has been introduced to solve these problems. GCT is a compact, high performance, bench-top time-of-flight mass spectrometer designed to allow identification of volatile sample components from accurate determination of their molecular weights. The acceleration of time of flight mass spectrometer allows fast acquisition of full spectra, with high sensitivity and resolution, from continuous ionisation sources. GCT may be configured as a fully integrated GC-MS system, or may stand alone allowing analysis of samples by direct introduction. In this instrumentation volatile and semi volatile compounds can be analysed, and alternatively solid samples maybe volatilised directly from a heated insertion probe. GCT provides elevated mass resolution, high mass measurement accuracy (to within 5ppm) and excellent sensitivity – maximising the chemical information obtained from a single GC-MS injection.

As laboratories demand higher sample throughput, fast GC-MS systems are rapidly becoming an industry requirement. TOF technology offers the capability for extremely rapid analyses as well as some unique characteristics to reduce data processing time. TOF systems utilise automated algorithms that automatically detect chromatographic peaks, including those components buried beneath the base line of the total ion chromatogram and coeluting analytes. Once a coelution is defined, automated algorithms separate the overlapped mass spectra for easy analyte identification.

Besides higher throughput, other advantages of faster analyses in the laboratory include faster method development, faster response to emergency samples, the ability to handle unstable samples more easily, and the elimination of errors. Replicate analyses are also feasible to improve accuracy and precision. The net result of all these features is at least a 20-fold decrease in overall analysis and processing time (Leco Corporation, 2000).

Recently a field portable SPME Fast GC has been developed. SPME coupled to high speed GC is a good combination to perform rapid and cost-effective investigations in the field, even of complex organic samples. As discussed above, SPME is particularly suited for fast GC, as it is solvent-free and the thin coatings can provide very fast desorption of analytes at high temperatures. Some instrumental modifications have been performed recently in order to achieve successful fast separations. A portable system was optimised from SPME-fast GC field investigations (Lord and Pawliszyn, 2000).

4.4 High-Pressure Liquid Chromatography

Until recently, the application of SPME has almost exclusively relied on the effective combination of SPME and GC. However many environmental pollutants, such as surfactants, are not sufficiently volatile to enable GC analysis without derivatization. Attempts have been made to incorporate derivatization reagents in the SPME device, but these methods are in the developmental stages (Cela, et al, 2000). A simple alternative for many applications is the use of HPLC and SPME. It is only the desorption technique that must be modified for the HPLC analysis. Coupling of SPME to HPLC was first introduced by Chen and Pawliszyn in 1995. The first application of HPLC-SPME to the analysis of nonionic surfactants, specifically, the alkylphenol ethoxylates, was investigated by Boyd-Boland and Pawliszyn (1996). This method was shown to be ideally suited for the analysis of different types of alkylphenol ethoxylates of varying ethoxylate chain length.

Nonionic surfactants of the alkylphenol ethoxylate class are relatively non-volatile analytes that are typically analysed by Liquid-liquid extraction (LLE) and HPLC or GC after derivatization. LLE and solid phase extraction (SPE) methods are generally combined with chromatographic methods for the separation and resolution of nonionic surfactants. The limitations of these current methods for surfactant analysis include the need for concentration of analytes after extraction to achieve the required sensitivity, the large volumes of often toxic solvents that are required for LLE methods, low breakthrough volumes of analytes in SPE methods, and the plugging of SPE cartridges by particulate matter that is often present in wastewater. As mentioned above, SPME eliminates the separate concentration step from the SPE and LLE methods because the analytes diffuse directly into the coating of the SPME device and are concentrated there. The device is then transferred to the injection port of the HPLC via an interface, where all the analytes are desorbed in the eluent stream and deposited at the head of the HPLC column. Conventional HPLC injection ports are unsuitable for SPME but can be easily modified by replacing the injection loop with a specially designed desorption chamber.

The SPME – HPLC method has been used in various studies including the determination of herbicides (Cela, et al, 2000) and analysis of *Allium* plant volatiles. The *allium* plant volatiles could not be determined by GC as GC is unusable for these labile substances and HPLC seemed to be a good method for these compounds. The new SPME-HPLC can be used for both qualitative and quantitative analyses, and has been found good in analysis of *Allium* volatiles (Jaillais, et al, 2000). The SPME technique has found limited use in HPLC applications because of the unavailability of fibres that are stable and durable in strong organic solvents (xylene and methylene chloride). Gbatu et al (1999) investigated the preparation of fibres that are stable in strong organic solvents as well as acidic and basic solutions using the sol-gel process. These fibres have been subsequently used to extract organo-arsenic, organo-mercury and organo-tin compounds from aqueous solutions followed by separation using HPLC with UV absorbance detection. SPME has been investigated for the analysis of semi- and non-volatile organic compounds in water by HPLC.

In-tube SPME is an automated version of SPME that can be easily coupled to a conventional HPLC autosampler for on-line sample preparation, separation and quantitation. It has been termed "in-tube" SPME because the extraction phase is coated inside a section of fused-silica tubing rather than coated on the surface of a fused-silica rod as in the syringe-like SPME device. The new in-tube SPME technique has been demonstrated as a very efficient extraction method for the analysis of polar and thermally labile analytes. The heart of the interface is a custom-made desorption chamber used for solvent desorption of the extracted analytes instead of thermal desorption in the GC injector. Polycyclic aromatic hydrocarbons (PAH) and nonylphenol ethoxylated surfactants have been successfully analysed with this manual SPME-HPLC method (Gou et al., 2000).

To date there are four types of SPME fibres available for HPLC analysis: PDMS, poly(acrylate)(PA), poly(dimethylsiloxane)-poly(divinlybenzene) (PDMS-DVB) and Carbowax templated resin (CW-TPR). Coating bleeding under harsh solvent conditions can be a concern for manual interface SPME-HPLC method. The limited selection of commercially available fibre coatings for LC analysis may result in poor selectivity for the analysis of very polar compounds with this method. The inherent disadvantages with the manual operation technique are: lower productivity and reproducibility. Those disadvantages could be overcome by automating the SPME-HPLC method. Since there is a large range of coatings available for the GC capillary columns than for the SPME syringe devices, the in-tube SPME-HPLC system can be used with various coated capillaries for different analytes (Gou at al, 2000).

Chapter 5

Environmental Fate and Transport Processes

5.1 Equilibrium Partitioning Theory (EPT)

The equilibrium partitioning approach is an attempt to model the tendency of a chemical to move from one environmental compartment to another. EP is based on the premise that the distribution of a contaminant in an environmental phase (e.g. sediment) is controlled by a continuous exchange with other environmental phases (water and biota). These biogeochemical exchange processes must be sufficiently rapid and reversible to have reached equilibrium (or a steady state) at the time of sample collection. If the partition coefficients for a given contaminant are known, then measuring its concentration in one environmental phase (e.g., sediment) and the concentration of that phase allows determination of its concentration in the other phases (water and biota). Potential biological effects of a certain contaminant concentration in the sediment can be estimated using appropriate chronic water quality criteria (WQC) and the partition coefficient for the contaminant between the aqueous and sediment phases. Though the WQC have been useful in improving and maintaining the environmental quality of water, there is a need for sediment-based criteria. One reason for this is that WQC are usually based on a limited toxicological database. Contaminant accumulation by direct ingestion can be a significant source, but it is also highly dependent on the organism and its local environment. This is usually not accounted for in the original toxicity studies. Therefore WQC may be inadequate to ensure protection of those life forms not included in the original toxicity studies. Sediment quality criteria (SQC) will facilitate the evaluation of severity of sediment contamination, and can be used to distinguish three classes of sediments with concentrations below, above and near the level of adverse impact. Potential benefits and applications of SQC include disposal site designations; permit evaluation for dumping and discharging; disposal site monitoring; site cleanup and restoration; and environmental impact assessment (Shea, 1988).
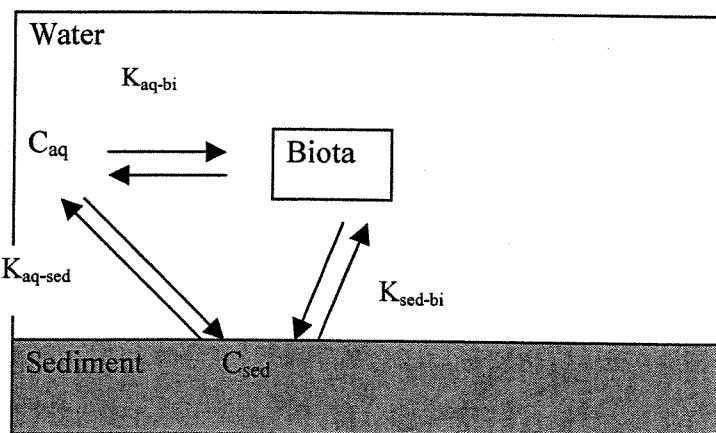
Figure 3: Overview of the partitioning phases of organic pollutants in the aquatic environment

Figure 3 illustrates the partition coefficients of an organic pollutant in aquatic environment. There are different partitioning coefficients for each phase; K_{aq-sed}, (partition between water and sediment), K_{aq-bi} (partition between water and biota, and K_{sed-bi} (partition between sediment and biota. According to one study, if the concentration of a pollutant is known in one phase and if the partitioning coefficient between this phase and another is known, then the concentration of the contaminant in the second phase can be deduced (Shea, 1988).

A general mathematical description of the partitioning of a contaminant between sediment and water can be expressed as a sum of surface interactions that bind or associate a contaminant (C) with a sediment (S).

When deriving a model for determining partition coefficients for organic contaminants in the environment many factors have to be taken to account.

Hydrophobic organic contaminants are generally base neutral compounds and do not undergo significant acid/base or metal complex equilibria that would lead to formation of multiple species. The most important sediment component that binds these nonpolar organic contaminants is organic carbon (OC). The partition has been attributed to hydrophobic exclusion from bulk water (and into the OC) as opposed to association reactions at the sediment-water interface. Therefore it is totally assumed that there is only one sediment component of significance: total organic carbon (TOC). If nonfilterable dissolved organic carbon (DOC) is eliminated by dialysis or taken into account by measuring adsorption constants as a function of DOC, then the assumption of only one contaminant is probably valid. Based on the above factors a model for equilibrium partitioning can be given by the equation below. Derivation of the model can be obtained from Shea, 1988.

$$[C_{org}S] = K_{Corg} / [TOC]$$

where C_{org} represents the organic contaminant, and K_{Corg} is the intrinsic absorption constant for the contaminant.

Values for K_{Corg} can be derived theoretically, empirically from solvent water partition constants or chromatographic data; or preferably from measurements on actual sediments in the laboratory or field (see case study 1). Previous studies have shown that adsorption/desorption of hydrophobic contaminants on sediments may require more than a month to reach equilibrium (Shea, 1988).

5.2 Environmental Cycling of Organic Pollutants

The bulk of the burdens of POPs in the environment reside in soils and sediments where they primarily partition into organic matter. Small changes in the mass of soils/sediments would have a major impact on concentrations in 'adjacent' media such as water and air (Jones, et al., 1999).

Air-surface exchange of POPs occurs in response to temperature changes. Persistent, semi-volatile compounds can participate in repeated air-surface exchange events and as a consequence, move from one area of the globe to another. Emission to air will tend to

occur primarily in 'global source areas' where the POP is used or released. Under cool conditions, gas phase POPs can partition back to the earth's surface, while in rainy areas wet deposition will deposit POPs to the surface. Rates of re-release from the surface will be slower in colder polar or high altitude regions. Hence it has been proposed that on a regional or global scale, POPs can potentially migrate from warmer to colder areas and become 'fractionated' on latitudinal or altitudinal gradients (Jones, et al., 1999) (see next section). Concern has been expressed that the polar regions become 'global sinks' for POPs released/used elsewhere on earth.

Soil is a primary reservoir of semivolatile organic compounds, (SOC) such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in the terrestrial environment. The atmosphere is a major transport medium for these compounds and is suspected to be a major sink. Consequently, exchange between soil and the atmosphere is a key process governing the environmental fate of these compounds. Transfer of chemical from the atmosphere to the soil can occur via wet deposition, via dry deposition of particles, or via diffusive transport from the gas phase to the soil surface. For the reverse process, namely transfer of the chemical out of the soil reservoir into the atmosphere, diffusive transport is the only pathway of significance. Diffusive exchange is driven by the gradient in chemical potential between the soil and the atmosphere. Thus gradient is determined by the soil/air equilibrium partition coefficient K_{SA}. As a result, the exchange of many SOCs with the atmosphere will be determined by the properties of a very thin surface layer of soil; it is the equilibrium partition coefficient in this surface layer that must be known (Hippelein and Mclachlan, 2000).

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Chapter 6
Ecotoxicological Impact Assessment

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6.1 Environment

If analysed in tissues or environmental samples, some POPs will almost always be found. As is the case with many environmental pollutants, it is most difficult to establish causality of illness or disease that is directly attributable to exposure to a specific persistent organic pollutant or group of POPs. This difficulty is further underscored by the fact that POPs rarely occur as single compounds and, individual field studies are frequently insufficient to provide compelling evidence of cause and effect in their own right (IOMC, UNEP, 1995).

Experimentally, POPs have been associated with significant environmental impacts in a wide range of species and at virtually all trophic levels. While acute effects of POPs intoxication have been well documented, adverse effects associated with chronic low level exposure in the environment is of particular concern. Of importance in this context is the long biological half-life of POPs in biological organisms thereby facilitating accumulation of seemingly small unit concentrations over extended periods of time (IOMC, UNEP, 1995).
Concentrations of such POPs as polychlorinated biphenyls (PCBs) are high in certain arctic animal species. This was confirmed in a study performed by Brunstrom and Halldin (2000) which showed that the polar bear, arctic fox, and glaucous gull may be exposed to PCB levels above lowest observed-adverse-effect-level (LOAEL, explained in chapter 7) values for adverse effects on reproduction in mammals and birds.

6.2 Bioaccumulation Factors

For each route of exposure, a bioaccumulation factor can be distinguished, i.e. for water it is the BCF, for food it is the biomagnification factor, BMF, and for soil or sediment it is the biota-soil (or sediment) accumulation factor (BSAF). Most of the information on bioaccumulation is obtained for neutral organic substances. For those substances, log BCF generally increases with low Kow, until log Kow 5-6 where the BCF may not further increase, or even drop. BMF and BSAF are generally much lower than 0.1 for substances with a log Kow less than 3, and may reach values up to approximately 10, for substances with a higher log Kow.
Organic chemicals which sorb to soil or sediment are in equilibrium with the aqueous phase or pore water, the same aqueous phase to which benthic and terrestrial organisms are exposed. For an organic substance, the equilibrium between the concentrations in soil or sediment and pore water can be described by the sorption coefficient (Kp). The relationship between the organism and pore water is described by the bioconcentration factor (BCF). The resulting relationship between the soil or sediment and the organism is then described by the biota-to-soil (or sediment)-accumulation factors (BSAF). There are neutral one-to-one relationships between, on the one hand, the octanol-water partition coefficient (Kow) and Kp, and on the other hand between Kow and BCF for neutral

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organic chemicals. Since the BSAF can be regarded as the ratio between BCF and Kp, it is expected to be independent of Kow (Sijm et al, 2000).
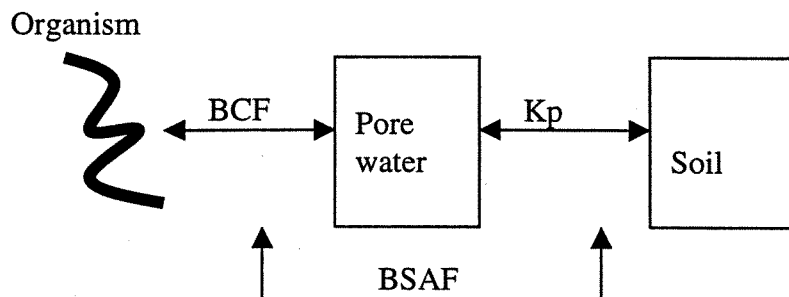
Organism

Figure 4: Relationships among the concentrations in pore water, soil-sediment and the organisms (Sijm et al, 2000).

Figure 4 shows the relationship between the concentrations in the soil and the organism, shown by the bioconcentration factor (BCF), between the concentrations in pore water and the soil, shown by the sorption coefficient (Kp), and between the concentrations in the soil and the organism, shown by the biota-to-soil-accumulation factor (BSAF). Analogous processes are described for benthic organisms and sediment.

EPT that assumes that when either the concentration in the soil, the pore water, or the organism is known the concentrations in the other two can be estimated.

6.3 Bioavailability

Soil and benthic organisms maybe exposed to contaminants via different routes: (pore) water, soil or sediment and food. Depuration of the contaminant from the organisms may take place via the same routes and, additionally, via biotransformation, reproduction, etc. Bioavailability is difficult to define. For each environmental compartment, i.e., water, sediment, soil, and air, bioavailability plays a role. The bioavailability of a hydrophobic organic substance in water is regarded as temporarily reduced when it is bound to suspended particles or to the sediment. In air, polycyclic aromatic hydrocarbons (PAHs) that are bound or even incorporated in particulate matter may not be bioavailable for uptake by respiratory surfaces, e.g. lungs of mammals, while gaseous PAHs are. Bioavailability is thus a complex process which includes all kinds of relationships between the concentration in the ambient environment and the portion of that concentration an organism experiences with regard to uptake. When it comes to bioavailability in soil, one has to evaluate physical, chemical, and biological properties in that compartment (Sijm, et. al, 2000).

6.4 Uptake and Depuration processes

The various uptake and depuration processes can be used to explain deviations from the EPT. Figure 5 shows how a benthic or soil organism may become exposed to contaminants in the sediment or soil, and how it can depurate the contaminants. Whereas there are only three routes of uptake for most of the organisms, e.g. uptake from pore water, food and soil or sediment, there are many different routes through which the organism can either dispose of the chemicals, or can dilute the concentration by for example, growth.
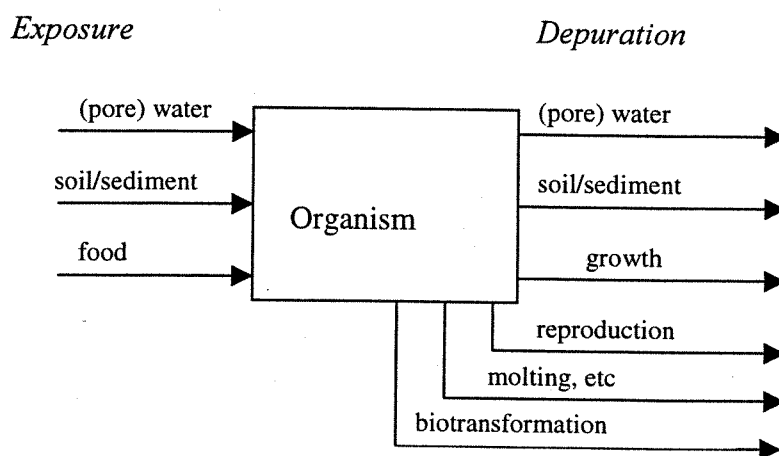
Figure 5: *Uptake and depuration processes in soil and sediment organisms (Sijm et al, 2000)*

Many of the depuration routes can be regarded as passive diffusion processes, and are reversible processes. However some processes are active. One depuration process, biotransformation, even converts the contaminant into another, mediated by enzymes. Those active and biotransformation processes are in general irreversible processes.

When related to EPT, biotransformation may explain why the concentration of a substance in an organism is lower than predicted from equilibrium partitioning. For example some PAHs are being transformed by soil organisms that subsequently result in relatively low BSAF values.

Low BSAF values may also be caused by other factors. Compounds that are not likely to be biotransformed to a high extent, e.g., PCBs and benzenes, also show relatively low concentrations in organisms compared to those in the soil. Thus, biotransformation cannot always explain the observed relatively low BSAF values. In other cases, relatively high BSAF values may occur, e.g. due to food-chain accumulation (Sijm et al, 2000).

Uptake

Most of the information and relationships are obtained from bioconcentration studies in which aquatic organisms are exposed to contaminants in water. These studies have shown that for organic chemicals, the uptake rate constant from water increases with the octanol-water partition coefficient (Kow) for substances that have a log Kow between 0 and 3,

and are relatively constant for substances with a log Kow between 3 and 6. Furthermore, the uptake rate constant decreases with the weight of the organism, and with the molecular weight of the substance.

Uptake from soil and sediment is the least clear and the least studied uptake process. Few studies show that uptake from sediment does occur and this results in higher concentrations than in non-feeding organisms. The uptake rate constant from sediment may vary several orders of magnitude for similar substances. In general, concentrations in aquatic, benthic and terrestrial organisms that are exposed to each route, i.e., water, food, and sediment or soil, seem to be fairly good predicted from the aqueous route of uptake, although additional uptake from other routes may contribute up to 50% of the concentration in the organism (Sijm et al, 2000).

Depuration

Depuration rates have not been and cannot be simply studied individually like the uptake routes. Depuration to water depends highly on the hydrophobicity of the substance, usually expressed by Kow, and further by lipid content of the organism, the molecular weight of the substance and the weight of the organism. The dependence of depuration to soil or sediment to biological and/or physical-chemical processes is less clear. Although the same processes that relate to depuration to water are important for depuration to soil or sediment, also the organic matter content of the soil is important for the depuration to soil. All other depuration routes depend on the biological properties of an organism and further depend on physiology, age, habitat, season etc. Depuration of hydrophobic organic substances from earthworms in soil seems to proceed faster initially than in water, although at later stages, depuration in soil and water are more similar (Sijm et al, 2000).

6.5 Methods to Study Bioavailability

No theoretical approach can adequately estimate the bioavailability of a substance in soil or sediment. Therefore, either organisms need to be used to study bioaccumulation from soil to sediment, or a biomimetic approach needs to be taken. The most recent and relevant methods used to estimate bioavailability are, (SPME) and C18-disks, and one method that uses organisms, i.e. soil (or sediment) availability ratio (SARA) .

The SPME and C18-disc approaches mimic the partitioning of contaminants between the pore water and the organism. SPME uses a fibre that contains, for example, hydrophobic material, and extracts hydrophobic contaminants from aqueous phase in a non-depletive manner. Because only a small fibre is used, with a very slow amount of hydrophobic material attached to it, only a very small amount of contaminant will be extracted from the aqueous phase (see section 4.1). The SPME has the advantage that only the freely dissolved contaminants will partition between the aqueous phase and the fibre, and that the fibre offers a surrogate for the freely dissolved and bioavailable concentration in the (pore) water.

The C18-disk uses a somewhat similar approach, in that again the partitioning of the freely dissolved contaminant is of interest. However, since the volume of the disk and the corresponding volume of the hydrophobic C18-material, is much larger than that of the SPME fibre, also a much larger volume of water is required to avoid depletion.

Both biomimetic approaches assume that the freely dissolved contaminant concentrations will present bioavailability. In particular for neutral organic compounds, the methods maybe of value. However, for substances that may be biotransformed in the organism, the methods will overestimate the concentration in the organism.

SARA uses organisms to estimate the bioavailable concentrations, no matter which route of uptake is relevant or whether or not the substance of interest is biotransformed. It can also measure the bioavailable fraction of chemicals that are aged in soil or sediment by exposing organisms to the soil or sediment, to which a freshly added 'like' chemical is added. The ratio of the concentration in the organism divided by the concentration in soil or sediment of the aged chemical to that of the 'like' chemical reveals the bioavailable fraction. A combination of SARA and one of the biomimetic approaches will reveal the actual potential bioavailable concentrations of the substances from sediment or soil respectively (Sijm, et al., 2000).

6.6 Human Health

As noted for environmental effects, it is also most difficult to establish cause and effect relationships for human exposure of POPs and incident disease. As wildlife species, humans encounter a broad range of environmental exposures and frequently to a mixture of chemicals at any one time.

For some POPs, occupational and accidental high-level exposure is of concern for both acute and chronic worker exposure. The risk is greatest in developing countries where the use of POPs in tropical agriculture has resulted in a large number of deaths and injuries. In addition to other exposure routes, worker exposure to POPs during waste management is a significant source of occupational risk (IOMC, UNEP, 1995).

Laboratory and field observations on animals, as well as clinical and epidemiological studies in humans, and studies on cell cultures collectively demonstrate that overexposure to certain POPs may be associated with a neurological deficitis, reproductive anomalies, behavioural abnormalities and carcinogenesis. The scientific evidence demonstrating a link between chronic exposure to sublethal conditions of POPs (such as that which could occur as a result of long-range transport) and human health impacts is more difficult to establish but gives cause for serious concern.

Swedish investigations have reported that dietary intake of PCBs, dioxins and furans may be linked to important reductions in the population of natural killer cells (lymphoytes). The developing foetus is particularly vulnerable to POP exposure due to transplacental transfer at critical periods of development.

<div align="right">

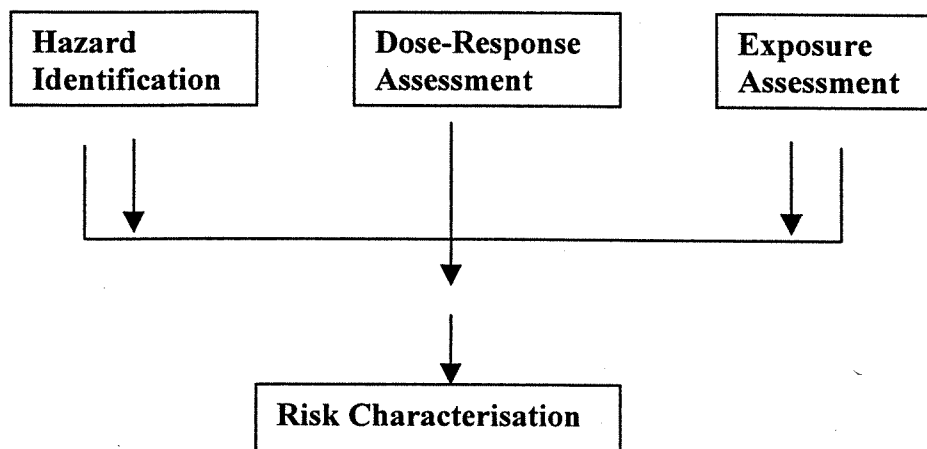Chapter 7
Risk Assessment for Chemicals

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The hazards to which human beings have exposed themselves and their surroundings by releasing harmful substances into the natural environment have prompted intense efforts to assess and deal with the problems involved. One of the most important tasks of research into organic pollutants is to determine the dividing line between harmless and harmful levels or doses of any given substance. Therefore, risk assessment is of great demand if the effects of pollutants in the environment are to be researched.

Risk is the probability that an adverse effect will occur, when a person or group is exposed to particular concentrations or doses of a substance for specific periods of time. Therefore risk is basically a function of toxicity and exposure. Risk assessment is the systematic examination of the nature and magnitude of risk. A risk assessment provides a bridge between research and risk management. According to a definition which was first proposed in the United States, risk assessments are typically divided into four distinct portions, hazard identification, dose-response assessment, exposure assessment and risk characterisation. The first segment, hazard identification determines whether exposure to an agent could cause adverse health effects in humans, the second, dose-response assessment, addresses the relationship between the magnitude of exposure and the occurrence of specific human health effects, including the estimated response at doses far below those tested. The next phase, exposure assessment, identifies intensity, frequency, and duration of human exposure. Finally, risk characterisation is a summary of the entire process which should include an estimation of an adverse effect in a human population based on the level of exposure and the results of the dose-response extrapolation (Ahlborg and Grönlund, 1995).

This chapter examines the chemical risk assessment. As the name implies, chemical risk assessment examines the risk of chemicals.
Chemical risk assessment follows four steps, as explained below (Hill, 1997):

1. Hazard identification: What are the reasons for believing that a particular chemical may be causing harm?
2. Dose-response assessment: Animals are evaluated for their responses to progressively higher doses of the chemical.
3. Exposure Assessment: Who is exposed to the substance? What doses are received by exposed individuals? What sources emit the chemical? What is the route of exposure to the chemical? Over what period does exposure occur?
4. Risk characterisation: In this final step, information from the first three steps is analysed and a risk statement is prepared.

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┌──────────────┐      ┌──────────────┐      ┌──────────────┐
│ Hazard       │      │ Dose-Response│      │ Exposure     │
│ Identification│     │ Assessment   │      │ Assessment   │
└──────────────┘      └──────────────┘      └──────────────┘
       │                     │                     │
       ↓                     ↓                     ↓
       └─────────────────────┼─────────────────────┘
                             ↓
                             │
                             ↓
                  ┌────────────────────┐
                  │ Risk Characterisation │
                  └────────────────────┘
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Figure 6: The chemical risk assessment process

Hazard identification. Hazard identification is the first step in chemical risk assessment. Any chemical can have adverse effects if the dose is high enough. The chemicals of most concern are those that could be harmful at low doses or at exposure levels that already exist in the environment. Certain chemicals are seen as potential hazards; pesticides are among these because their purpose is to kill (Hill, 1997).

Dose-response assessment. The aim for dose-response assessment may be to establish the lowest dose which gives rise to appreciable adverse effects – in animals or in people – or better still, the highest dose which does not produce effects. Once it has been decided that a hazard merits a risk assessment, a controlled dose-response study in animals is the next step. This second step is ordinarily carried out in rats and mice, which are used as surrogates for human beings. In a dose-response assessment, one group, the control group of animals doesn't receive the test chemical and other groups are given a dose of the chemical. The highest dose that does not exert an adverse effect on the animal is the no observed adverse effect level (NOAEL) (also referred to as the no observed effect level, NOEL) (Hill, 1997, Ahlborg and Grönlund, 1995). The first dose level that causes adverse effects is likewise called the lowest-observed-adverse-effect level (LOAEL).
The determination of these levels should be based on the dose for which the most susceptible but appropriate species of animals and the most sensitive indicator of toxicity has been used. Where a study shows two or more doses inducing no toxicity, the highest among them is considered the NOEL (Ahlborg and Grönlund, 1995).

Not all biological effects are signs of toxicity, for example changes in intestinal flora, laxative effects due to bulk or osmotic load, and cecal enlargement and diminished growth rate caused by high levels of non-digestible substances. For this reason, the dose that does not give adverse effects, the no-observed-adverse-effect level (NOAEL), is normally used. The animal NOAEL is divided by an uncertainty factor, which typically assumes that the average human is 10 times more sensitive to the chemical than test animals. The uncertainty factors vary with the quality of the dose-response information

from animal experiments, and range between 10 and 1000. Once an uncertainty factor has been selected, the animal NOAEL is divided by that number to arrive at a reference dose (RfD), a dose assumed to be safe to humans over the period of exposure; the RfD is also often called the acceptable daily intake (ADI). The smaller the value of RfD, the more toxic the chemical is (Hill, 1997).

Exposure assessment. In the third step of risk assessment, human exposure to the chemical in question is evaluated. Exposure can occur through the route of water, food, air or soil. Exposure assessment methodology involves indirect and direct techniques, including measurements of environmental concentrations and personal exposures, measurements of biomarkers of exposure and effects as well as the use of questionnaires and modelling. Accurate estimates of human exposure to environmental pollutants are of vital importance for evaluation of dose-response relationships, as a component in the risk characterisation and for the design and implementation of efficient control strategies (Ahlborg and Grönlund, 1995).

The exposure of children is a special case, they breathe more rapidly that adults and therefore inhale more of an airborne pollutant. Children's greater exposure needs to be considered in a risk assessment. Whether considering adults or children there is seldom enough information to evaluate exposure adequately. To account for this lack of information and to assure an extra degree of safety, the degree of exposure is often assumed to be greater than it actually is.

Risk characterisation. To do a risk characterisation, all the information collected from the hazard identification, dose-response, and exposure studies is gathered, analysed and presented in a useful and understandable manner. To do this, the risk characterisation should contain not only a risk estimate for a given exposure scenario but also a summary of the relevant biological information, the assumptions used and their limitations, and a discussion of variabilities and uncertainties in the risk assessment, both qualitative and quantitative. The risk is then calculated and the information given to risk managers, who are responsible for finding means to reduce the risk (Hill, 1997).

The scientific conclusions made by various toxicologists may differ and result in various risk scenarios. Different conclusions can be drawn not only regarding the quantitative part of the evaluation but also regarding the pure existence of a risk. The difference normally reflects various professional interpretations of the same basic data and need not indicate that one scientist is right and one is wrong (Ahlborg and Grönlund, 1995).

Chapter 8
Management of Stormwater

Management of stormwater is the last step of the organic pollution control model. It falls under the prevention step, because that is where the pollution of watercourses by stormwater is prevented. It also fits in the remediation step, because it is easier to treat the organic stormwater pollutants when they are in a pond than when they are diffuse in the environment. Stormwater management is a high priority topic in urban drainage in many countries. The traditional alternatives are to conduct stormwater directly to, for example, lake recipients or to lead the water to wastewater treatment plants. However, new concepts are now combining infiltration, distributed storage and treatment as well as delayed transport. In the sense of sustainable development, ecological criteria are taken into account in these modern drainage plans which are potentially much closer to nature than the traditional approach (Ristenpart, 1999).

Separate transport systems for stormwater (rain and melt water runoff) in the form of open ditches or stormwater sewers are used for conducting the water to open stormwater treatment facilities (STFs). STFs are 'ecotechnological' facilities that employ natural processes for the removal of pollutants and nutrients in stormwater. Examples of STFs are wet and dry ponds (retention and detention ponds), constructed wetlands, open ditches and green structures such as grassed swales, infiltration trenches and infiltration strips. The advantages of using STFs lie in their pollutant treatment and flow compensation capabilities. These are not sustainable alternatives, the former creating negative impacts in the recipient and latter increasing the metal or organic content of the sludge, and leading to intermittent loadings disturbing the reduction efficiency of the plant/pond. In Sweden particularly in the last couple of years, there is a rapidly increasing trend of using STFs (Larm, 2000). However, there are problems that need to be further investigated and solved. So far, there is limited experience concerning the function and reduction efficiency of different STFs. Furthermore, there is a need for more rigorous design criteria for conditions and tools for making proper choices of treatment methods. The location of the STFs should also take site-specific conditions into consideration (Larm, 2000).

Prevention of stormwater pollution reaching receiving waters can be achieved by removing or decreasing the pollutant sources and abatement of the impact of stormwater runoff on receiving waters can be achieved through pollutant removal. Stormwater flows are highly variable as are the pollutant concentrations. Consequently, conventional treatment plants are not suitable for treatment of stormwater due to the difficulties in taking care of the high concentrations of pollutants in stormwater. Measures to treat polluted stormwater before it is released to receiving waters can be of differing character. Various methods have been used for the control and treatment of stormwater. Measures such as vegetative control, infiltration basins, wetlands and wet ponds have been considered effective. These measures can be used alone or in combination to reduce the pollutant load from stormwater (Pettersson, 1999).

A cost-effective strategy is to treat polluted stormwater in open detention ponds, before letting it out into receiving waters. Traditionally open stormwater detention ponds are used to prevent flooding during heavy rain events. However, since the reduced flow prevents erosion and allows sedimentation of suspended materials in the pond, they are increasingly being used on purpose to improve stormwater quality. One important mechanism for pollutant reduction in stormwater is through sedimentation since a considerable proportion of the pollutant load is attached to solids, although chemical and biological processes are also included (Pettersson, 1999).

A number of models are available for quantifying urban runoff, including water quality. Most of these models express the material loading, i.e. the pollutant load rate, in terms of for example, kilograms per year. Pilot studies using models are useful for establishing a monitoring programme. The models may provide indications of expected pollutant concentrations for avoiding analyses below detection limits and may be used for comparisons with sampling results (Larm, 2000).

8.1 Toxicity testing for controlling stormwater pollution

Stormwater runoff has been estimated to supply 4% of the hydrocarbon input to the oceans. While this seems small compared to the total from other sources, run-off water is discharged into fragile nearshore ecosystems which are the nursery for most finfish and shellfish. Studies have shown that urban runoff is a major source of hydrocarbons to the coastal environment. In a study done by Ngabe et al (2000) the levels and sources of PAHs in stormwater were investigated using GC-MS. Sources of PAHs in urban runoff include asphalt leaching; particles from tire abrasion, automobile exhausts, other combustion processes and lubrication oils. One study found out that sediments of tidal creeks with urban/industrial watersheds had significantly higher concentration of PAHs compared to creeks with suburban and forested watersheds --- which implies that high concentrations of PAHs come from urban runoff.

Urban wet-weather pollution poses a great challenge to environmental protection and the pursuit of sustainable development of urban areas. In this respect, demands on urban drainage have changed dramatically during the past 20 years and have expanded beyond the efficient removal of drainage waters to include the protection of receiving waters against drainage impacts. Such impacts include adverse changes in flow and sediment regimes, stream morphology, habitat structure and water quality. Thus, the planning and design of modern wet-weather pollution controls require the assessment of drainage impacts and their mitigation by various measures. To overcome the problems with assessing water quality impacts by chemical protocols, the use of biomonitoring and biotesting (see chapter 1) is recommended.

Ideally toxicity testing is done in situ, in order to account for localized field conditions. However, toxicity testing is typically done in the laboratory on both water and sediment samples in order to control numerous environmental variables that can influence toxicity

results (e.g. temperature, water quality, etc.) While sediments may represent a historical record of water quality conditions at a particular site, the extraction of sediments brings up the issue of chemical partitioning and bioavailability and thereby introduces some additional uncertainty into results. Toxicity caused by more water-soluble compounds or short-term episodes may not be reflected in tests of sediment extracts. The lack of homogeneity in the sediment sample may also confound the toxicity test results. (Marsalek et al, 1999).

With respect to specific sources, much attention has focused on one of the most toxic components of urban runoff, the highway runoff. The toxic effects of highway runoff can be estimated on samples collected both at the edge of the pavement or immediately downstream of drainage outfalls. The major toxicants include heavy metals and several PAHs, including pyrene, flouranthene and penanthrene and chlorides (Pettersson, 1999; Parker at al, 2000).

Detention ponds are shallow depressions constructed to slow the delivery of urban runoff to storm drains and urban stream channels. While it is unlikely that short-duration stormwater detention in ponds would reduce toxicity caused by dissolved contaminants, stormwater settling is the most effective treatment process leading to toxicity reduction (typically by 50% or more) in laboratory studies. Other treatment processes reducing toxicity include screening, aeration and photodegradation. However, further research is needed for adapting these processes for use in stormwater management (Marsalek et al, 1999).

8.2 Sustainable urban drainage

During the last 30 years the principles which guide urban stormwater control have changed. It was noticed that rapidly removing water accumulated in urbanised areas ended up just by transferring the problem either towards other areas or to the future. Other ways of tackling the problem have arisen. Flood plains have become subject to planning, placing constraints upon both their occupation and the types of works to be carried out, mainly aimed at ensuring the necessary flowing cross-sections (Pompeo, 1999). Detention reservoirs have been designed under the principles of compensatory measures for water collection and flood control in urban areas; nevertheless, their costs are too high. Source control, introduced during the 80s, is another technique aimed at temporary storage in urban lots for flow reduction and, when the reduction of volumes is required, it associates infiltration techniques. The use of source control is delicate given that it requires installations in all of the individual properties and permanent maintenance by the residents. Besides this, source control implies not only the execution of diffuse work but, mainly, assuming a new technological attitude with respect to the development of new paving materials, with norms set for utilisation and for occupation of public and private spaces.

The term sustainable urban drainage is of recent origin. For the past three decades the perception of generalised environmental degradation, and the criticism of the styles of

development based on as irrational exploration of nature have motivated numerous discussions and new proposals to allow the survival of human beings. The perspective of sustainability in relation to urban drainage introduces a new way of directing actions, based upon the recognition of the complexity of the relationships among the natural ecosystem, the artificial urban system and society. This position demands that drainage and flood control in urban areas be reconceptualised in technical and managerial terms (Pompeo, 1999).

Urban planning, when it does not exist, usually disregards the fact that historical absence of integrated and harmonious solutions among the urban and the natural systems is also a significant factor for the occurrence of frequent flooding. Planning of urban activities related to water must be integrated into urban planning itself, including the planning of the urban grid and its expansion, the zoning of activities, the road and transport network, landscape aspects and other issues. The institutional integration must be the reflection of a systematic environmental conception. In this way, it is necessary to consider that management of water in urban environments is a special case of water resources management. Institutional action should integrate, on one hand, water resources management, and on the other hand, urban environmental sanitation. Equally important, the participation of society is referred to as an essential ingredient in tracing the route of sustainable development. This means that the technology which accompanies sustainable development should also be socially sustainable, which entails democratic participation of society both in decision-making and in execution of actions.

The discussion of urban drainage form the point of view of sustainability is fragile, and runs the risk of returning to generalities. This is due to the fact that the three dimensions of sustainability, economic, social and ecological allow development of many courses of action the articulation of which is not found exclusively in the drainage and flood control sector but which must be backed by coherence and relationships with broader policies. This means that no model, structure or proposal can be efficient if sustainability is not considered as the result of multi-sectoral efforts.

The social aspect of sustainability can be developed along three lines: citizenship, democracy and culture. In urban drainage, and in many other areas, these three lines should be followed seeking participation as a result of information and communication. Society must have knowledge to participate on the decision-making and executive levels and in the evaluation of results. The knowledge found in the community also needs to be observed within the range of alternatives that are technically considered. Environmental education, in addition to informing and generating knowledge is capable of promoting the mobilisation of society for this participation. Sustainability points out to the reintegration of water in the urban environment, working together with the hydrological cycle, observing ecological, environmental, landscape and recreation opportunities. For this reason, engineering must be more than ingenious; it must be generous. Concerning management, independent from the institutional arrangement, it is necessary to recognise that urban drainage is part of a management system and not only sparse flood control engineering works defined after a problem arises. Sustainability must be on the agenda of every action and thus must be sought in place of including articulation, wherein all our

negotiation capabilities, acceptation of differences and difficulties, rights and duties must be present (Pompeo, 1999).

8.3 Control and Treatment of Stormwater

Detention and retention basins are normally used for control and treatment of stormwater. These basins are used to attenuate runoff peaks and always have some outlet structure. Retention basins are designed to contain all of the runoff within a given area for a design runoff (Parker, et al, 2000). Detention ponds are inexpensive to construct but require a significant surface area per volume. [*More information about the construction of stormwater ponds can be read from Pettersson et al, 1999*].

Stormwater discharge mechanisms include dry wells and engineered basin floors. Control basins (detention and retention basins) for stormwater in residential areas typically collect runoff from an entire neighbourhood. In commercial areas, the basins can collect runoff from a single commercial building or from a complex of commercial sites ranging from small strip malls to larger regional shopping malls. In some cases runoff from both commercial and residential areas can be collected in a single basin. Runoff from industrial areas, however, is collected separately because it is thought to be of poorer quality (Parker, et al, 2000).

The detention of stormwater in constructed ponds and wetlands is a widely adopted strategy for improving stormwater quality. These detention systems are often utilised to serve multiple functions related to urban landscape design, flora and fauna conservation, passive recreation, and stormwater pollution control. In relation to stormwater pollution control, the most important treatment process in these systems is often the removal of suspended solids and associated pollutants. A combination of sedimentation resulting from reduced flow velocities in the system, and infiltration and adhesion of suspended particles by macrophytes, facilitate the removal of suspended solids from the water column (Somes et al, 2000).

The effectiveness of constructed ponds and wetlands in the removal of suspended solids and associated pollutants from stormwater is related to a number of factors, many of which are influenced by the detention period of pollutants. Determination of the probability distribution of pollutant detention period over the operating life of a constructed wetland or pond system is not a simple matter as detention time response to variation in inflow characteristics is often nonlinear. Continuous pollutant tracking, through numerical simulation can provide a realistic representation of the system behaviour. Somes et al (2000) presented a simple simulation and methodology for tracking pollutant detention periods in a stormwater constructed wetland. The results of the simulation can be used as input to a pollutant removal model to determine the probabilistic long effectiveness of the detention system. Many factors contribute to the variation in the detention time of stormwater in constructed wetlands. These factors include meteorological conditions that result in intermittent unsteady inflow conditions, the storage-elevation relationship and the size of the permanent pool in the wetland. A

series of numerical simulations can be used to determine the impact of these factors on pollutant detention times in wetlands (Somes et al, 1999).

To be able to determine the removal efficiency in stormwater ponds, pollutant removal assessments based on an accurate measuring strategy are demanded. To achieve high pollutant removal efficiency, open stormwater ponds need to be designed properly, promoting a favourable flow regime and sufficient residence time during storm events (Pettersson, 1999).

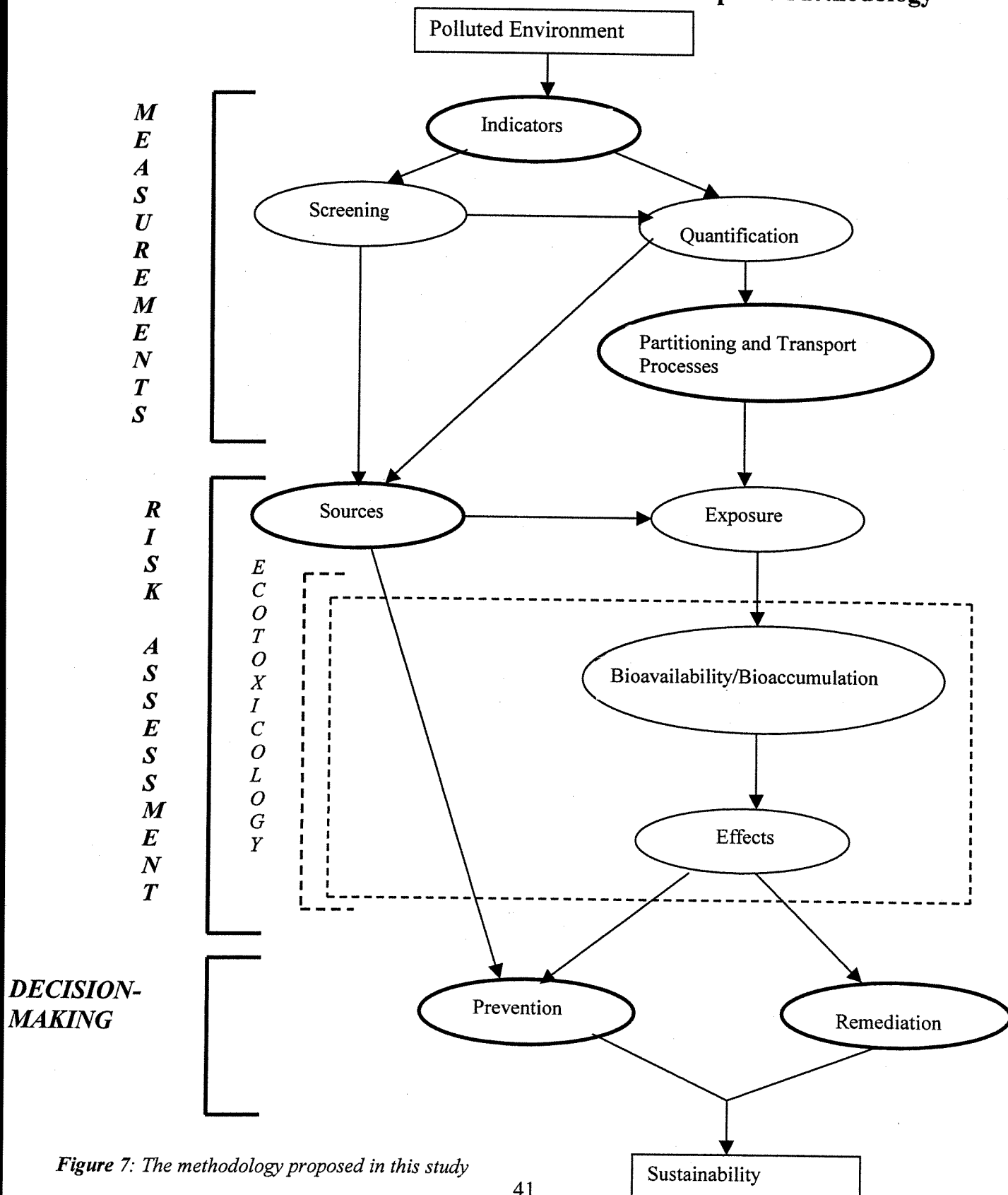Chapter 9
Results: The Proposed Methodology

Figure 7: *The methodology proposed in this study*

41

After a detailed literature review of the chapters discussed above, a model was proposed for solving problems associated with organic pollutants (see figure 7). Not all the steps included in the hypothetical methodology are presented in the model.

The various steps of the model, starting with a polluted environment, are explained individually in the table below:

Indicators are tools that help in identifying a pollution problem (see table 1). Decrease in number of fishes, or aquatic organisms can be an indicator. Use of enzymes can also signal adverse effects of some organic compounds.

Screening. After the problem has been noticed, screening is the most important step, where a sample from the polluted environment is analysed in an analytical instrument to identify the compounds present in the sample.

Quantification is when the concentrations of pollutants in the sample are determined. This step involves both screening and quantification in one step. This is when identification of compounds is carried out as explained above (in screening) and amounts of pollutants present in the sample are determined immediately. Quantification is done by addition of a standard (a chemical containing the compound to be analysed) sample of known concentration, and the difference between the area of the chromatogram of the sample and the area of chromatogram of the standard represents the concentration of the analyte in the sample.

Sources. After screening or quantification has been done, sources of the pollutants can be identified. For instance a chemical that has been found in the screening may be coming from a nearby factory (see case study 1), or the concentration of compounds quantified can determine the major source, depending on which source is expected to be releasing or emitting more of the pollutant.

Partitioning and transport processes can be determined after quantification. Using the equilibrium partitioning theory, the concentration of the pollutant in one environmental compartment can be related to concentration in another compartment by means of the partitioning coefficient (see chapter 5). The information obtained from partitioning theory may not be reliable, since there are deviations like depuration and uptake processes, which are not catered for by the theory. Nevertheless, it can give an idea of how much of the pollutant is in each compartment.

Bioavailability. Presence of organic pollutants in water systems does not necessarily mean that all the concentrations are dangerous to aquatic organisms. Bioavailability determines the fraction of the pollutant that enters and affects the body of the organism.

Exposure. Knowledge of the fraction of the pollutants in each compartment determines which entities of the aquatic system are mostly exposed to the pollutant. Also, sources can help in determining exposure of aquatic organisms in water. For instance, if the

sources are near or far from the river, information on the frequency of the emission or release of the pollutant to the river can be determined, and can explain exposure.

Effects of the pollutant on the organisms can be determined based on the knowledge of the bioavailable concentrations of the pollutant. The concentrations of the pollutant that have adverse effects on the organisms can be determined from the knowledge of bioavailable concentrations.

Ecotoxicology. Summation of information on the bioavailability and effects of the pollutant on the aquatic environment covers ecotoxicological assessment.

Risk assessment. Information on sources of pollutants, exposure of the organisms to the pollutant and the effects of the pollutants can be summed up and a risk characterisation can be done, which finishes up risk assessment.

Prevention of pollution can be done by for example monitoring of the fate of the pollutants from the sources, by blocking the passage of for instance wastewater released from a nearby factory.

Remediation of the aquatic system can be done by for example biological degradation of the pollutant using enzymes.

Decision-making. All the information obtained from the above steps leads to discussions on how to decrease the pollution, by for example setting concentrations of pollutants that are allowed to be released from each factory, or implementation of the 'polluter pays principle'. This all depends on decision-makers.

Sustainability. After a decision has been taken, monitoring performed, and if the pollution has been prevented successfully and remediation has been accomplished, sustainability can be reached.

<div align="right">Chapter 10</div>

Case One - Environmental Monitoring of Nonylphenols in Mölndal River

Project Performance Date: October 1999, October 2000
Project Name: Assessment of POPs in Mölndal River
Location: South of Göteborg, Sweden
Key Contaminants: Nonylphenols
Project Team: Thabisa and Ann-Margret assisted by AEMT students, Chalmers University, Sweden
Evaluation of Measurement Data and Ecotox. Assessment: Thabisa and Ann-Margret

Project Summary

Mölndal River is situated in Göteborg, Sweden and about 12% of its catchment area is covered by lakes. The upper Mölndal River flows through mostly forested areas, which include various industries and factories. The river's quality has been affected by numerous industries set along the river which emit air pollution and introduce wastewater into the river through various activities, e.g., chemical manufacturing, paper industry etc. Pollutant leakages from the various industries in Mölndal are suspected. Even though some industries have left the area or closed down, sediments containing their products are still likely to be found there. Analysis of nonylphenols was done, to determine how much of the NPs are still in the environment after a NP producing plant, Akzo Nobel had been recently closed. Other possible sources were also investigated.

Water and sediment samples were taken in October 1999 and October 2000 in five different locations near the potential sources, by two different groups of students, including the author of this thesis. Results from both groups were compared.

The Study Area and Suspected Sources

The Mölndal River starts from the lake Stensjön, flows through urban and suburban areas of Göteborg and is connected to the Göta River. The catchment area of the river includes the municipalities of Gothenburg, Mölndal, Partille, Lerum, Landveter, Härryda and Borås. Along the banks of the river there are various factories, inhabitation areas, roads and farmlands which may be the sources of organic pollutants. Industrialisation in Mölndal started in late 17th century. Factories developed along the river where the water was used as a natural source of energy for the various industries. The paper production demanded raw material, pulp, which started to be chemically produced in the 19th century. This lead to severe damage of Mölndal River because of the effluents it was exposed to. Among the industries that are or have been located in the banks of the river are:

- McWorther Technology AB, a manufacturer of water-based dispersible resins for paints and methyl esters from vegetable oil.
- Stora Enzo AB, a paper mill for white coated and coloured paper

- Akzo Nobel Surface Chemistry AB, producers of nonylphenols (closed down)
- Anders Hillertz, recycling company
- Textile industries (closed down)

These industries are suspected to be the main contributors to the pollution of the river. Although their liquid wastes are biologically treated and recycled at Ryaverken in Hisingen, suspected accidental leakages may pollute the river. Some of the textile industries that have been in the area closed about 15-20 years ago. A total of about 10 000 tons of NP per year were produced in Akzo Nobel and then sent to the main factory north of Göteborg. About a year ago, the production of nonylphenols was stopped in this plant. Nevertheless, there are still high concentrations of nonylphenols in the soil around the factory resulting from past leakages and spills. The area has had floods for several times, and this might have led to stormwater runoff, washing the pollutants from soil into the river. Therefore, the main source of nonylphenols is suspected to be the Akzo Nobel plant. However, both Mc Worther and Stora Enso have also been using nonylphenols in their production processes.

Traffic is also a potential contributor to the Mölndal River pollution. A big road-building project was performed in the study area during the sampling period in October 1999. This is also a potential source of pollution since nonylphenols ethoxylates (NPE) could be used as additives to concrete and asphalt, and the paints used for the culverts could contain some NPEs as additives. Moreover, after rainfall, road sediments and run-offs from gas stations and small garages may be deposited by stormwater into the river and may have introduced organic pollutants to the river. Building materials and electrical equipment were other suspected sources and contributions could also come from the Anders Hillertz factory since they might be using organic chemicals or detergents for cleaning their drums.

In 1960 Mölndal River was considered as one of the most polluted rivers in Sweden but nowadays the water quality has improved significantly. Salmons have been implanted in the river, and a high number of salmons have been observed, with a peak in 1999. This is probably due to less effluents entering the river from the factories.

Measurement Techniques.

Measurement of nonylphenols in water and sediment is done as explained in the following steps:

- *Extraction:* Soxhlet extraction was used for the clean up of sediment samples. The extraction solvent used was heptane, and the extraction lasted for 24 hours.
- Two different fluorinated phenols were used as internal standards, for calculation of extraction recovery and sediment concentrations.
- SPME was used for the extraction of nonylphenols from water. In this method, a fibre coated with PDMS was introduced into the water sample and nonylphenols were adsorbed through the diffusion process. The fibre was let to stand in each sample for ten minutes, to allow partition.

- ***Preconcentration and clean up of sediment samples:*** A preconcentration step for the sediment samples was carried out to remove the solvent from the sample. The extracted volume was concentrated by using an evaporator. The aim of the clean up was to remove interfering compounds. The extract from the sediments samples was further cleaned up by SPE, where all the sediment samples were filtrated through a sulphonic and a silica gel column in series. The extract was then ready for direct injection to the GC.

- ***Analysis:*** A GC-MS was the available analytical instrument in the Chalmers laboratory, and was used for analysis.

Results: For both 1999 and 2000 samples, no nonylphenols were found in water samples, they were detected only in sediment samples, except for the 'beaker experiment' and the 'microwave experiment'. The highest concentrations were found in sediments close to Akzo Nobel, the nonylphenol-producing factory, showing that nonylphenols are still leaching from the soil surrounding Akzo Nobel.

Table 2: Concentrations (μg/g) of Nonylphenols in Mölndal river sediments from 1997 to 2000

Sampling Point	Conc in 1997	Conc in 1998	Conc in 1999	Conc in 2000
Paper Mill, Stora Enso		24		68
Road Project			3.3	22
Akzo Nobel, NP factory	*n.d.	24	65	90
Mechanical trap ~400m downstream	30	57	23	1940
~ 1km downstream from Akzo Nobel		15	1.4	24
Beaker Experiment (μg/l water)			0.8	90
Microwave Digestion (μg/l water)				43

n.d. = not detected i.e. under detection limit

Table 2 shows concentration of nonylphenols in the sediment in Mölndal River in 1999 – 2000 in comparison with measurements in 1997 – 1998 made by previous AEMT students. The analysis was done under similar conditions in all these years, but not all the samples were taken from the same points. In the beaker and microwave experiments, the nonylphenol concentrations were measured in water after partition from sediments.

Generally, concentrations of NP are higher in 2000 than all the other years. This could be explained by the fact that some weeks before sampling, electric cables were installed along the river banks and close to the mechanical trap. The sediments were dug near Mölndal river so that the cables could be installed underground. This might have led to the release of nonylphenols which had been buried in the deep sediments in the river

bank. The microwave digestion was only done in 2000. The sample taken near the paper mill in 1999 was spilt accidentally.

Except for high NP concentration in the mechanical trap in 2000, concentrations are higher in the samples taken near Akzo Nobel, which suggests that there is still NP leaching from the soil around the factory. NP concentrations were high in the sample taken from the mechanical trap. This is a place where a trap for suspended materials used to be situated. Organic pollutants are usually attached to suspended solid-associated organic matter runoffs (Pettersson, 1999), and are transported by stormwater to rivers. NPs from Akzo Nobel might have been transported in this way downstream to the mechanical trap during floods.

Partition

Beaker experiment: Since no nonylphenols were detected in the water samples, in an attempt to verify the equilibrium partition theory and sustainability of nonylphenol analysis, a 'beaker experiment' was carried out for 6 days in October 1999 and 3 days in October 2000. This might be the reason for lower concentrations in 2000, 3 days was probably too short for equilibrium to be reached. Sediment was put in a beaker and covered with nanopure water. The sample was let to stand for a few days to allow equilibrium partitioning. After extraction with SPME, the sample was analysed by GC-MS and nonylphenols were detected (see table 2 above). Also, the partitioning coefficient between water and sediment was calculated using the equation: $K_{oc} = C_{sed}$ /$(C_w * F_{oc})$ where F_{oc} is fraction of organic carbon in the sediment, C_{sed} is the nonylphenol concentration in the sediment and C_w is the concentration in water (Shea, 1988).

Microwave digestion: In the analysis done in October 2000, a microwave digestion was performed to verify the partition between water and sediments, and to find a more sustainable, fast and environmentally friendly way of analysing nonylphenols in aquatic environments without using solvents. Moreover, soxhlet extraction is more time consuming and can lead to losses of analytes. Sediment was put in a beaker, covered with nanopure water and digested in a microwave for 25 minutes. Also in this experiment, the water phase was extracted with SPME and run in the GC and nonylphenols were detected, but at a less concentration than the beaker experiment (see table 2 above). This is perhaps due to the fact that the aqueous phase of the microwave digestion was not analysed directly after digestion due to time constraints and the sample was not stirred before injection into GC with the fear of particles damaging the fibre, since the samples were very 'dirty'. Nonylphenols must have settled back to the sediments.
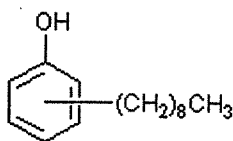
Ecotoxicological Risk Assessment

The chemical, physical and ecotoxicological data of nonylphenols are presented in the table below. This data is important in explaining transport processes of nonylphenols and for risk assessments.
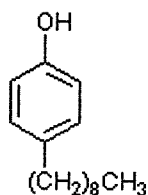
4-nonylphenol   nonylphenols

Figure 8: *Nonylphenol Structural Formulas*

Table 3: Chemical and physical date of nonylphenol

Melting point (oC) :	-
Boiling point (oC) :	~ 315 (293-297)
Vapour pressure (Pa) :	10
Solubility in Water :	insoluble
Log Pow :	3.01-4.2 (6.35 RSC)
BCF :	0.9-3400
Persistence :	medium
Acute toxicity LC50 (μg/l)	17 for zooplankton and 13 000 for fish

Sources. Nonylphenol polyethoxylates (NPEs) have been widely used as non-ionic surfactants in many industrial and household applications. The annual worldwide production of alkylphenol ethoxylates (APEs) amounts to about 500 ktons. This surfactant class is applied to a number of domestic, agricultural, and industrial uses. Surfactants are common water pollutants because of their use in aqueous solutions, which are discharged into the environment in the form of wastewater from treatment plants or sludge stored in landfills. After use, APEs are discharged to sewage treatment plants (STPs) or directly released into the environment. Among APEs, nonylphenol ethoxylates (NPEs) are by far the most commonly used, encompassing about 80% of the world market (Di Corcia, et al, 1998). Either aerobic or anaerobic biotransformation of NPEs leads to the formation of nonylphenols (NPs) in water (Dachs, et al, 1999).

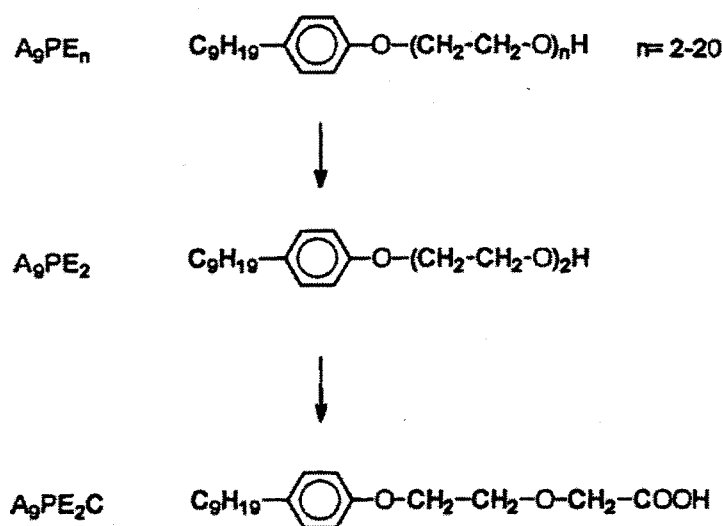*Environmental Fate.* The environmental fate of surfactants has been an issue of concern due to their potential adverse impact on ecosystems. Bioaccumulation and toxicity of 4-nonylphenols (4-NP) in aquatic fauna have been demonstrated in numerous

investigations. Aquatic flora, e.g., macrophytic algae, have also been shown to accumulate 4-NP to levels up to 10 000-fold greater than present in the environment. Toxic effects of 4-NP on the germination and growth of different plant species have also been shown. Thus, phytotoxicity of 4-NP may reduce the yields of crops. As estrogenic effects of 4-NP have been reported, uptake and metabolism of 4-NP in crop plants may have strong impacts on food quality (Bokern and Harms, 1997). The presence of nonylphenols in the environment has recently become of increasing concern since it has been shown to be a strongly estrogenic compound that can cause feminisation of male fish, resulting in a lack of reproductive success. NPs are also linked to fertility problems in men and cancer in humans (Lee and Peart, 1995).

Environmental Degradation of Nonylphenol Ethoxylates

Degradation products of APEs, i.e. nonylphenol (NP), have the potential to bioaccumulate, and are estrogenic, thereby becoming toxic to aquatic and soil micro organisms. To date, NPs have been reported only in aquatic environments (Ejlertsson, et al, 1999, Jones and Westmoreland, 1998, Dachs et al, 1999).

Many studies have shown that NPE metabolites are ubiquitous in the environment, are more toxic than parent compounds, and can bioaccumulate in aquatic organisms (Di Corcia, et al, 1998, Dachs, et al, 1999). Figure 8 shows the degradation of APEs in the environment.

A_9PE_n $\quad$ C_9H_{19}—⬡—O–$(CH_2$-CH_2-$O)_nH$ $\quad$ n= 2-20

↓

A_9PE_2 $\quad$ C_9H_{19}—⬡—O–$(CH_2$-CH_2-$O)_2H$

↓

A_9PE_2C $\quad$ C_9H_{19}—⬡—O-CH_2–CH_2–O-CH_2–$COOH$

Figure 9: Structures and acronyms of nonylphenol polyethoxylate surfactants and their initial most prominent breakdown products

This process leads to formation of short-chain APEs, mainly NPE_2. Complete deethoxylation with formation of nonylphenol has been observed only under anaerobic

conditions. Under aerobic conditions, short-chain NPE biotransformation proceeds via carboxylation of the terminal alcoholic group, with production of persistent NPE_nCs. Here, n indicates the number of ethoxy units plus a terminal CH_2COOH unit. Occasionally, the oxidation process of the ethoxy chain can occur simultaneously and compete with that leading to ethoxy chain shortening. Over one year of monitoring, large amounts of NPECs with long ethoxy chains were constantly detected in secondary effluents of one of the six major STPs in the area of Rome. Further biotransformation of the initial APE metabolites has received very little attention. This oversight may be traced to the general belief that bacterial attack to the branched nonyl side chain is greatly inhibited by steric hindrance (Di Corcia, et al, 1998).
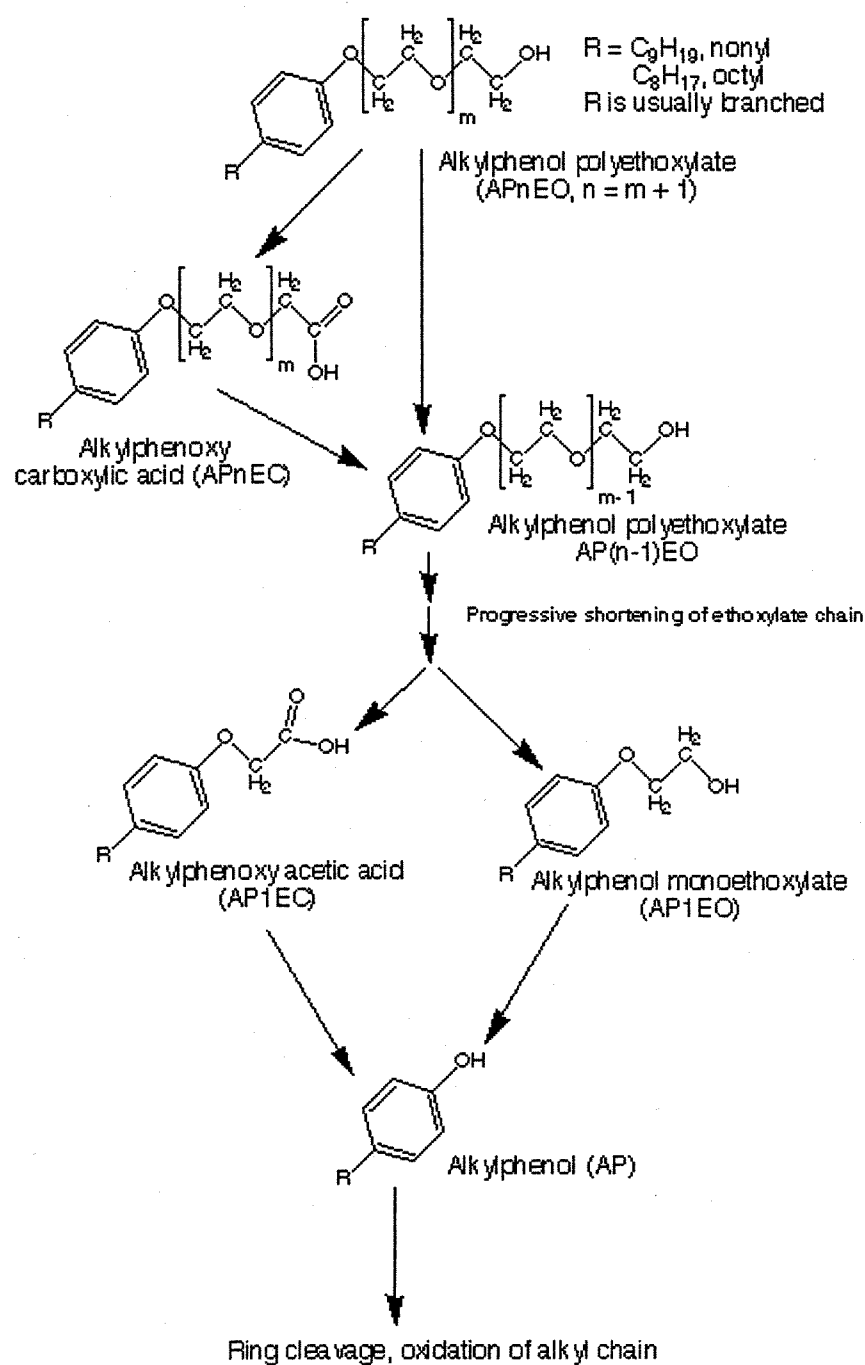
Figure 10. *Degradation of nonylphenols in the environment*

Comments

The results obtained were expected, that is, higher nonylphenol concentrations in sediments than in water. This is because nonylphenols are hydrophobic and tend to accumulate in sediments, as they are insoluble in water. Presence of nonylphenols in sediments does not evaluate the risk for the exposed organisms. In the future it could be

better to perform Sediment Health Quotient tests, as will be explained in chapter 13. Another recommendation would the cleaning of the soil around Akzo Nobel to remove nonylphenol, or bioremediation of the soil around Akzo Nobel.

The partitioning in the 'beaker' and microwave digestion experiments was faster than possible under natural conditions. This may be because nanopure water was used, therefore the results from the beaker experiment cannot be considered directly equivalent to what is happening in real life, but both methods can be used as a starting point in the search for quick, cheap and easy methods of detecting organic pollutants in aquatic environments. The use of solvents for sediment extraction is not environmentally sustainable, because the solvents are toxic. Methods like the beaker and microwave digestion experiments seem to be promising methods for sustainable analyses.

Chapter 11

Case Two - Organic pollutants leached by stormwater from asphalt

Project Performance Date: October 1997 – October 1999
Project Name: Environmental Impact of Asphalt Storage
Location: Härryda, Sweden
Key Contaminants: Butylated hydroxy toluene, diisobutyl phthalate and dibutyl phthalate, naphthalene, diethylhexyl phthalate
Project Team: Geology PhD student Malin Norin, Lecturer Bo Ronge
Evaluation of Measurement Data and Ecotox. Assessment: Thabisa, Ann-Margret, and Malin

Project Summary

The project was performed with the aim to investigate organic compounds that are leached by stormwater from asphalt storages. An experimental site for the project was built in 1997, as presented in figure 10. A leaning plate of asphalt covered with a plastic film was used as a foundation for the experimental site and two different circular storages were placed on the plate, each having a diameter of 10m and area of 113m². The storages were filled up with different asphalt material having different structures: asphalt that was dug from the road surface (R) and scarified asphalt (F). The centre section (R4, F4) of the storage illustrates vertical percolation of water through the storage and the outer section (R1, F1) illustrates water runoff. Each storage was divided into different sections, which contained connection wells. Water leaching through the storage was then collected into bottles. Water samples were taken every month from the bottoms of the collecting bottles. All samples were analysed for metals and 25 of them were taken for the analysis of organic compounds.
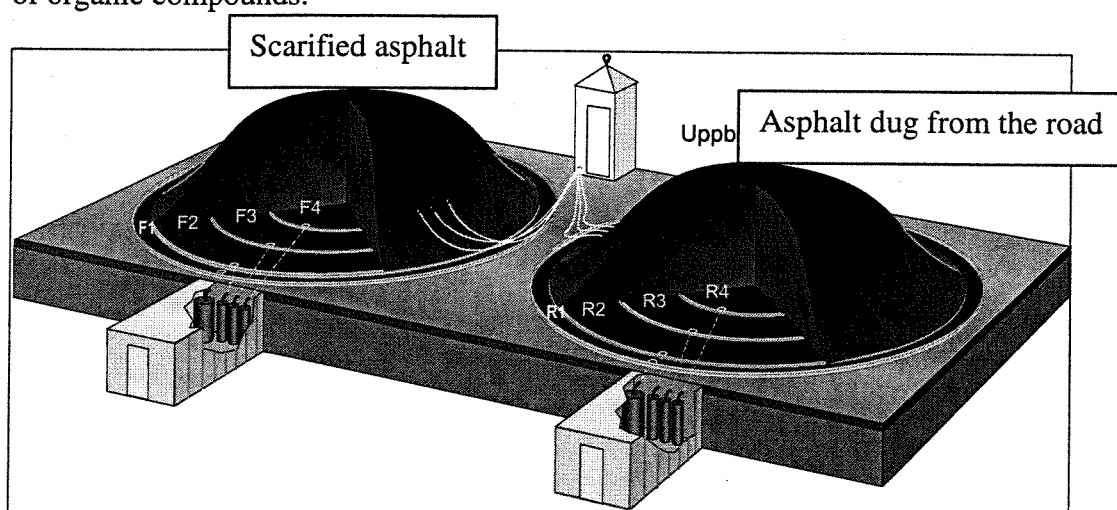
Figure 11: Experimental site for the study of pollutants leaching from asphalt

The Study Area and Suspected Sources

The experimental site is situated in the Härryda community, near Landvetter Airport, Göteborg, Sweden. Since the experiment was done directly on asphalt leachate, a part of organic compounds are suspected to be coming from the asphalt material itself, and another part from traffic, which has polluted the asphalt by worn-out rubber tyres and exhaust emissions.

Asphalt production is dictated by performance specifications rather than by a specific chemical composition. The precise chemical composition and physical properties of asphalt are influenced by the composition of the original crude petroleum oil, which is used in the production, and the manufacturing processes. Crude petroleum oil is composed of paraffinic, naphthenic, and aromatic hydrocarbons as well as heterocyclic molecules containing sulphur, oxygen and nitrogen. The proportions of these chemical components may vary significantly because sources of crude petroleum oil occur in various locations throughout the world involving different geologic formations. Therefore no two asphalts are chemically identical, and chemical analysis defining the precise structure and size of the individual molecules found in asphalt is almost impossible. The organic compounds detected in the screening may be used as additives to asphalt, fuel, rubber and others emitted from car exhaust (Sax and Lewis, 1987). These may have come into contact with the asphalt in road in different ways such as wearing out of rubber from car tyres, or emitted from car exhaust.

Measurement Techniques

The samples were analysed by a geochemistry laboratory in Chester, England. The samples were extracted by SPE and analysed by a GC-MS screen test method for semivolatile organic compounds.

Compounds that were detected in more than one sample and had high probabilities were taken as the 'priority' pollutants leached by stormwater from the asphalt. The compounds were further verified in a few samples by SPME and GC-MS screening test analysis at Chalmers University of Technology. Risk assessments of the compounds that were identified both by the Geochem laboratory and at Chalmers laboratory are given later in this chapter.

With the screen-test method used, the organic compounds were not quantified with standard compounds, making the chemical concentration results less reliable. The mass spectrometer was run in the scan mode, when the instrument is less sensitive, resulting in a relatively high detection limit for the organic compounds. Organic pollutants often occur in extremely low concentrations in environmental samples and can be easily missed in the screening methods. However, the screening methods are useful when samples with unknown compounds are to be analysed, if the results are carefully analysed and followed up with further studies.

Results

Many organic compounds and heavy metals were identified in the samples. In the water leaching from asphalt, high concentrations of PAHs were detected (Norin, 2000) but the PAHs were not identified screening at Chalmers, except for naphthalene. Not all the compounds detected in England were detected again in the screening done at Chalmers. This might be because of the use of different measurement conditions of the GC, since the measurements were done in two different laboratories. Also, the second screening was done after a year, which may suggest that some of the pollutants which were observed previously may have evaporated, or broken down into secondary compounds, or reacted with other organic compounds in samples.

A benzonitrile organic compound was detected in many samples during the analysis in England, but the probability for the given suggestion and chemical structure was low. It was, therefore, not chosen as a priority pollutant in this study.

Quantification of the compounds was done just in England, only identification was done at Chalmers. The concentrations of 'priority pollutants' presented in table 3 below were quantified in England.

Table 3. Concentrations of organic pollutants in asphalt leachate, in stormwater and in groundwater in Göteborg urban area (Norin, 2000).

Concentration (μg/l)	Leachate from scarified asphalt	Leachate from dug asphalt	Urban stormwater pond (Göteborg)	Urban ground water (Göteborg)
Napthalene	[a]n.d. - 15	n.d - <10	n.d - [b]<10	n.d. - <10
BHT	n.d. - 50	n.d. - 40	n.d - 17	n.d. - <10
DIBP	n.d. - <10	n.d - <10	n.d. - <10	n.d. - <10
DEHP	n.d. - <10	n.d. - 10	n.d - <10	n.d - <10
Total Semivolatiles[c]	90 - 460	20 - 260	11 - 26	<10

[a]n.d. = not detected
[b]<10 = compound identified but concentration less than 10 μg/l,
[c]sum of semivilatile compounds less than 10μg/l

Physical and chemical characteristics of the 'priority pollutants' are tabulated in table 4. Structural formulas of the compounds are given in Appendix A. The data given below are important in determining persistence and solubility of organic compounds in aquatic environments. This information is useful for explaining transport processes and ecotoxicological impact of these compounds in the environment. The data on persistence was deduced by the author from the information about degradability of the compounds in the environment.

Table 4: Physical, chemical and ecotoxicological characteristics of the organic compounds leaching form asphalt

Compound	Naphthalene	Diisobutyl phthalate	Dibutyl phthalate	Diethylhexyl phthalate	Butylated hydroxytoluene
Melting point (°C)	80[a]	185[a]	-35[a]	-50[a]	70[a]
Boiling Point (°C)	218[a]	327[a]	340[a]	387[a]	265[a]
Vapour pressure (mmHg)	0.177[a]	20[a]	1.0×10^{-5} [a]	1.32[a]	
Solubility in Water (µg/l)	30 000	20 000[a]	10 000 – [a] 11 200	1×10^{-4} [a]	<1 000[b]
Log Pow	3.3[a]	4.11[d]	4.72[a]		5.0[b]
BCF	430[c]	430[a]	130-8826[a]	20 – 10767[a]	
Persistence	Low	Low	Low	Low	Low
Acute toxicity LC50 (µg/l)	1200-6400 (aquatics)[e] [f] [g]	730 - 3600[a] (aquatics)	0.18-7,5 x 10[5a] (aquatics)	0.34-3x (aquatics)	Not toxic in[a] 400 µg/l

a) *RSC,* b) *BUA* c) *BPS,* d) *BUA Anonymous, 1998,* e) *Korn, et al, 1979,*
f) *Edsall, 1993* g) *Vaishnav, et al, 1990*

11.1 Diisobutyl-, dibutyl- and diethylhexyl phthalates

The sources and risk assessment of phthalates are discussed under the same section since they have similar behaviour in the environment. Dibutyl phthalate was only identified at Chalmers with a high probability. It is discussed in this report because it has same impact on the environment as other phthalates.

Sources: Phthalates are essentially used as plasticisers in the production of polymeric materials such as polyvinyl chloride (PVC), imparting flexibility and workability, both during the manufacturing process and to the end product. They have such varied applications as wire insulation, food packaging and biomedical applications such as tubing and blood containers. When used in this way, they are not chemically bound to the product and may therefore leach into the surrounding medium. They are also used to improve the chemical properties of paints and lubricants and can be found in toys, and food wrappings. Other uses include vacuum pump oil and dielectric fluids in capacitors. Because phthalates can emerge from these products, they have become nearly ubiquitous environmental pollutants (Kleinsasser, et al, 2000; Francis, 1993).

Environmental Fate: Phthalates are readily taken up via all exposure routes and are quickly distributed throughout the organism. Due to the persistence in the environment,

phthalates are also commonly found in groundwater, rivers and drinking water (Harris et al, 1997). A major human exposure to phthalates is believed to be from foods which have absorbed the chemical from their packaging, or from manufacturing processes. Many of the bags used in hospitals are made of PVC and leach phthalate plasticisers. Phthalate values can be found in foods like crisps, chocolate bars, baby milk and cheese (Warhust, 1999). Some exposure occurs from leaching of the compound from containers used in the food and medical industries. This is of particular concern to patients exposed to large amounts of blood or blood products. DEHP, in particular, is extracted from the containers by the blood and is converted to mono(2-ethylhexyl)phthalate by a plasma enzyme (Francis, 1993).

These compounds undergo $\geq$ 50 % ultimate degradation within 28 days in standardised aerobic biodegradation tests with sewage sludge inocula. Biodegradation is expected to be the dominant loss mechanism in surface water, soils and sediments. However, hydrolytic degradation is of no importance under environmental conditions. DIBP is readily degradable under aerobic conditions, but degradation apparently stops at concentrations in an order of magnitude of 20-100ng/l. A transport with leachate into groundwater is expected through complex formation, e.g. with humic acids (RSC, 1999).

DEHP is an environmental contaminant and has been detected in ground water, surface water, drinking water, air, soil, plants, fish and animals. It is rapidly absorbed from the gastrointestinal tract primarily as mono(2-ethylhexyl)phthalate. In the environment, *DEHP* undergoes biodegradation in water and soil, and is predicted to react with hydroxyl radicals in the atmosphere. It is estimated to have a half-life of about 12 hours in the air, 10 to 20 days in the soil, and days to weeks in water. Volatilization of *DEHP* from contaminated water does not contribute significantly to its removal. The half-life of the molecule due to evaporation alone from bodies of water has been estimated to be as long as 15 years. It has been found to bind to organic acids in the soil and water resulting in an increase in its solubility and its mobility in the environment. It also adsorbs to both freshwater and marine sediments where it may serve as a long-term sink. Experiments have shown that fish do not extensively bioaccumulate *DEHP* (Harris, et al, 1997).

Effects: Phthalates are probable human carcinogens, on the basis of an increased incidence of liver tumors in rats and mice. Animal studies have indicated that the primary target organs are the liver and kidneys. Oral exposure has also been shown to result in decreased sperm count in rats (Francis, 1993).

These compounds have negative reproductive effects in rats and mice. High testosterone and maternal death may be observed. Aquatic toxicity, especially to invertebrates and fish, has also been observed in some studies. Phthalates are fat soluble, so tend to concentrate in materials such as butter, margarine and cheese. In addition, they are likely to accumulate in body fat (RSC, 1999).

Many toys contain phthalate plasticizers, and research has shown that these plasticisers can leach out of the toys into the mouths of the children chewing them. These extensively used chemicals have a detrimental influence on the reproductive systems of humans and

wildlife. DIBP, in particular, has estrogenic activity. Although the shorter chain phthalates, such as DIBP and dibutyl phthalate (DBP) are used in small quantities by industry they are more estrogenically active than longer chain phthalates which are used in larger quantities by industry (Harris, et al, 1997). DBP's endocrine (estrogenic) activity has also been demonstrated in vitro and in some cases in vivo (Leisewitz and Schwarz, 1998).

In a study by Kleinsasser et al (2000) genotoxicity was observed for DEHP, DIBP and DBP in mucosal cells of head and neck cancer patients, with more genotoxicity pronounced for DIBP. Possible promoting influences in a human breast cancer cell line and hepatocarcinogenesis in an animal model have been reported. Minor but regularly occurring breaks in DNA strands due to phthalates have been observed in human mucosal cells taken from the upper aerodigestive tract in otherwise healthy individuals (Kleinsasser, et al, 2000).

11.2 Butylated hydroxytoluene

Identification of sources: BHT is used as an antioxidant, a stabiliser in petroleum, rubber and plastic, and as a widely used food additive. It is also used as an antiskinning agent in paints and inks. There is thus widespread human exposure to this compound (RSC, 1999).

Environmental Fate: BHT is metabolised rapidly in soil. It can also undergo photodegradation in water. Measured data on the bioaccumulation potential of BHT are available only for the aquatic environment. Accordingly it is unlikely that a considerable amount would accumulate via the food chain. When heated to decomposition this compound emits irritating fumes (RSC, 1999).

Effects: There is no adequate data for BHT carcinogenity to humans, but there is sufficient evidence that BHT is carcinogenic in animals. The results of carcinogenity testing in rats are contradictory; in some studies carcinogenity has been observed while in others no indication has been reported. It is very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. Irritation to mucous membranes and upper respiratory tract has been reported in humans and in rabbits. Epigastric cramping, nausea, vomiting and generalised weakness, unconsciousness, skin sensitisation and confusion are some effects of BHT in humans. Adverse effects to kidneys, lungs, heart and blood were reported in rodents (RSC, 1999).

It is harmful if swallowed, inhaled or absorbed through skin. Depending on the intensity and duration of exposure, effects may vary from mild irritation to severe destruction of tissue. Prolonged contact can cause damage to the eyes, nausea, dizziness and headache. Laboratory experiments have shown mutagenic effects. BHT induces impairment of blood clotting in animals and liver tumours in rats. Toxic effects to the lungs have only been observed (NTP, 2000).

11.3 Naphthalene

Identification of sources: used in the manufacture of dyes, synthetic resins, celluloid, lamp-black, smokeless powder, hydronaphthalenes, moth repellants and insecticides. Most abundant single constituent of coal tar/dry coal tar contains about 1% naphthalene. It occurs in crude oil, from which it may be recovered directly as white flakes; it can also be isolated from cracked petroleum, coke-oven emissions, or from high-temperature carbonisation of bituminous coal. Naphthalene is used as raw material and chemical intermediate in the chemical, plastics, and dye industries. Other sources include urban air pollution and cigarette smoke. Small amounts of naphthalene are released to the aqueous environment as a result of discharges from coal tar production and distillation processes (RSC, 1999).

Environmental Fate: Naphthalene can be biodegraded in soil. Naphthalene is rapidly and efficiently converted into CO_2 in the presence TiO_2 under simulated solar light. So it can be removed abiotically (RSC, 1999). Microbial degradation to CO_2 in seawater at 12 °C in the dark after 24hour incubation was observed. Degradation rate was 0.1 µg/l/day and turnover time was 500 days. In the atmosphere, naphthalene undergoes a number of degradation processes including reaction with photochemically produced hydroxyl radicals. In natural waters and soils, volatilization and biodegradation are major removal processes. Naphthalene has a short half-life and is not thought to bioaccumulate over time.

Effects: It has moderate toxicity to invertebrates and fish. The compound may be taken up through the skin, may affect the central nervous system and form mathaeglobin in the blood. Naphthalene may cause anaemia, nausea, headache, sweating, cramp, high body temperature, kidney and liver injuries. It is very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment.
It has caused cancer in female mice in one study. No evidence of carcinogenity for male mice, but some evidence in female mice. Mild skin irritation. In humans it can cause headaches, nausea, vomiting, diarrhoea, acute haemolytic anaemia, coma and convulsions (RSC, 1999).

Comments

As mentioned before, not all the compounds which were identified in the first screening were observed again in the second one. This means that the analysis could have been more accurate if the screening was repeated immediately, not after a long period, since there is a danger of compounds reacting with each other, evaporating, or breaking down into metabolites.
There are contradictory studies concerning carcinogenity of phthalates to humans, indicating the importance of further studies to verify this. As illustrated in table 4 almost all of the identified compounds: naphthalene, DEHP, DIPB, DBP and BHT are not significantly persistent. Studies show that they can degrade readily if there is enough oxygen. It is surprising that these compounds could be detected form stormwater and groundwater if they are easy to break down. In the sediments found in stormwater ponds,

there is usually not enough oxygen, meaning that degradation of these compounds in the ponds is slow. Carcinogenic and estrogenic effect of these compounds is a contradictory issue. Some studies show that they have these effects and in some studies the effects are not observed. This shows that a repetitive study of these compounds can help in identifying their actual effects in the environment.

<div align="right">Chapter 12</div>

Case Three - Brief Investigation of sediment health in the river Viskan

Project Performance Date: 1999-2000
Project Name: Determination of Sediment Health in Viskan
Location: Västra Götaland
Key Contaminants: Naphthalene, diethyhexyl phthalate, nonylphenol, dibutylphthalate
Technical Team: Länsstyrelsen in Västra Götaland and Golder Grundteknik
Evaluation of Data and Ecotox. Assessment: Thabisa

Project Summary

The sedimentation area and the occurrence of inorganic and organic pollutants in the catchment area of the river Viskan were investigated. Sediment samples were taken from 14 different locations, including the lakes Tolken, Oresjö, Djupasjön, Guttasjön, St Halsjön, Kinnasten, Dran, Kalvhult, Askloster, and Marsjön until Viskan's outlet into Kattegatt. Toxicity tests, physical characterisation and analysis of approximately 200 compounds or groups of compounds were done (HydroQual, 2000).

Surface (0-10 cm) sediment samples were the most analysed and deeper level (10-114cm) sediments were also analysed in some locations. The results from this and other investigations indicated that the levels of pollutants entering river Viskan have been reduced to a high extent since the wastewater treatment plant was amplified with a step of chemical treatment in 1977, except for brominated flame-retardants and phthalates.

Results

Low or slightly enhanced concentrations of pollutants were observed in the sediment samples upstream the city of Borås (in the lakes Tolken, Marsjön and Öresjön). Significantly high concentrations were observed in sediments of the lakes Djupasjön and Guttasjön situated downstream the city of Borås. In these lakes high concentrations (ten times higher than other locations) of pollutants such as heavy metals, some pesticides, oils, chlorides, hydrocarbons, plasticisers, phenols, dioxins and furans were found. In the lake Djupasjön the highest concentrations were observed in deeper level sediments, and the surface layers contained lower concentrations. This indicated that the effects of pollution from Borås have decreased during the recent years.
In lake Guttasjön high pollutant concentrations were observed in surface sediments and probably depend on the slow sedimentation rate in this lake. The polluters of the sediment in these two lakes were suspected to be situated close to Borås.

Detected levels of brominated flame-retardants were only in samples taken downstream the city of Kinna. The highest concentrations were detected in soil samples taken close to the lake Veselången, an area that has flooded several times. These concentrations were

<div align="center">61</div>

high and in the same range as the concentrations found in sludge samples from the largest wastewater treatment plants in Sweden. The reason for absence of brominated flame-retardants upstream the city of Kinna could be attributed to the fact that the use of these compounds has only been reported in the textile industries in the city of Skene. In the lake Marsjön, upstream Borås, high concentrations of phthalates were detected in surface sediments. The sources were not identified, but could be one or some of the plastic producers upstream the lake. Downstream Kinna, no high levels of pollutants were observed, except for the high concentrations of brominated flame-retardants. These data were confirmed by the investigation of the bottom fauna, which was performed in this study.

Table 5. Concentrations of selected organic pollutants identified in the sediment of lakes in the Viskan catchment area (HydroQual, 2000)

Concentrations of compounds (μg/g)	Djupasjön	Guttasjön	Veslången	Åskloster	Marsjön
Nonylphenols	250 - 2600	160 - 619	< 0.1	< 0.1	< 0.1
Naphthalene	0.12 - 0.72	0.44-0.47	0.008	0.009	0.008
Diethylhexyl phthalate	27 - 100	9.1 - 33	0.7	1.1	11
Dibutyl phthalate	< 0.35	< 0.35	< 0.07	< 0.07	1.2

Risk Assessment

The environmental effects and sources of the various compounds detected in this study are similar to those discussed in case study 2. Due to the large number of different organic compounds that were identified in the sediments of the lake Guttasjön, the ecotoxicological effects on the aquatic life are probably rather extensive. But, the extent of the ecotoxicological effects is not easy to assess with the results from this investigation. This is because a wide range of pollutants was detected, so it is difficult to assess the risk associated with synergistic actions of the all compounds. More careful assessments have to be done in the future.

Nevertheless, toxicity tests that were made in the investigation indicate distinct adverse effects on the organisms. The high concentrations of pollutants in the sediments of the lakes Guttasjön and Djupasjön can pose a high risk if for any reason, constructions and change in the water level could cause release of the pollutants from the sediments.

The two lakes should be protected as high-risk pollution areas. The risks associated with the high concentrations in the lake Marsjön are hard to evaluate since many organic pollutants were detected in that site.

Sediment Health Quotient

Sediment Health Quotient (SHQ) is an approach for assessing the health and ecological potential of sediments. The quotient is based on a physical, chemical, and biological characterisation and rating of sediment conditions. The approach is flexible, permits comparisons amongst sediments with widely different properties and contaminant levels, and it can be adapted to site-specific conditions. The level of impairment is ranked relative to what is defined as a non-toxic, or a healthy state and condition of the sediment.

In this approach sediment health is defined in terms of abiotic properties, such as sediment pore water pH, electrical conductivity (salts), particle size distribution (sand, silt, clay), pore water ammonium, total organic carbon (TOC), colour and odour. Most of these parameters are gross measures of the physical and chemical environment. Organisms must respond to changes in the quality of their environment in order to survive and the physiological tolerances of most living things are also well defined. So, frequent and large exceedances of their physiological limits can be stressful and ultimately lethal. Two biotic components are essential in SHQ. The first biotic component is an assessment of indigenous microbial, invertebrate and plant populations (what is present in the sample). The microbes are planted out onto a nutrient agar and allowed to grow. The second biotic component involves measurement of two types of responses. The first response involves community processes and the second is the response of the individual organisms exposed to the sample and sample extracts. The test battery is composed of organisms representative of the major trophic levels and could include microbes, plants, invertebrates, vertebrates and others depending on information needs.

The level of effort required to interpret the findings is determined by the overall sediment quotient, followed by the pattern in trophic level ratings, and then by effects on individual species. Tests are performed on the sediments as received (solid phase) and on the pore water or aqueous extract. All the test results are normalised on a scale from 1 to 5. Higher values are assigned to lower responses or no effect (non/toxic condition). A lower value is assigned to sediments or extracts that are toxic. The following approach is recommended for interpreting the results based on the overall sediment health quotient.

- SHQ of 4 to 5: healthy sediment with high ecological potential
- SHQ of 2 to 3: slight but significant impairment
- SHQ of 1: impaired with low ecological potential

These ratings are then carried forward to a trophic level assessment, then finally an overall sediment health quotient. A sediment health quotient for the sample is the average of the trophic level scores.

A full guide of the conditions, methods, and criteria for Sediment Health Quotient assessment is explained fully in the Golder Grundteknik KB report (HydroQual, 2000). The rationale and development of the quotient are documented in the report with sample handling, assessment methods, and quality assurance practices. The guide was written for

freshwater sediments, but the same approach can be used for marine sediments, but with different test species.

Comments

Measurement techniques used for the project were not explained fully in the report, so it is not easy to determine if they are sustainable or not. SHQ test is an interesting method for evaluating the extent of contamination of sediments. Although this was done briefly in this study, it is a promising tool for toxicology assessments of pollutants in sediments. It can be used as an extensive part of risk assessments, because it involves a thorough investigation of the immediate living environment of many aquatic organisms.
SHQ tests were designed to provide a measure of the biological health and condition of sediment. The results must be interpreted in light of other test results and sample information.
As a basis for an ecotoxicological risk assessment, a more extensive investigation of the river Viskan is needed. Furthermore, if the community of Borås wants to use the lake Marsjön as a drinking water supply, more investigations are necessary.

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Chapter 13
Discussion

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The model has proven applicable for solving real life problems associated with organic pollutants in urban areas after it was applied to case studies. Sustainable measurement techniques, risk assessment and partition have been applied in the case studies successfully and are very important steps of the methodology. All these investigations can be used as basis for decision-making.

It is hard to develop a conventional methodology; different researchers have different ways of approaching problems. Moreover, environmental cases can be unique thereby requiring different approaches for solving pollution problems. However, in situations where there is limited knowledge the model can be used as a starting point for giving general ideas of handling pollution problems.

In this model indicators for environmental pollution are seen as an important tool in environmental monitoring. Pollution indicators (at least biomarkers) can actually be used for almost every step of the model, for screening, diagnosis and risk assessment (see table 1, chapter 1). Indicators are therefore an important step of the methodology. Measurement techniques are cornerstones of sustainable engineering systems. All the steps of the model involve measurements, starting form identification of the problem to the measurement of whether sustainability has been achieved or not.

Due to time constraints indicators for sustainability could not be considered. They are also an important part of the methodology since they can be used for assuring that the whole model leads to sustainability. It is therefore important in the future to improve the methodology by including sustainable development indicators.

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Chapter 14
Concluding Recommendations

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Analysis of organic pollutants, especially POPs is a complicated field, which involves a lot of uncertainties. A combination of measurement models, laboratory and field experiments is the best option that can be used by engineers and scientists to understand the behaviour of organic pollutants in the environment. Because of their persistence, organic compounds pose a great danger to the environment; therefore they should be treated urgently before great damage of the environment affects future generations.

A shift is recommended from detailed studies on the more traditional POPs i.e. PCBs, PAHs to metabolites and newer classes of POPs (e.g. NPE metabolites) which maybe more dangerous or enhancing the toxicity of the traditional POPs. Investigation of organic stormwater pollutants is still in its infancy and is of special importance because of its adverse effects on the environment, which are usually undermined.

Risk assessments, pollution and sustainability indicators, and environmental impact assessments are cornerstones of a sustainable analysis of organic pollutants. Recently developed analytical methods for analysis of organic pollutants are promising, and may lead to a sustainable future. The key developments in the area of organic pollution include improvement in the source inventories in pathways and exposure analyses, so that reliable, quantitative assessments can be undertaken.

In environmental monitoring it is important to prioritise pollutants based on their effects in the environment. This is because when measurements are made, compounds which are moderately toxic can be present at higher concentrations than the very toxic ones. It is, therefore, always good to base the choice of 'priority pollutants' on the severity of toxicity of the compounds. Moreover, some pollutants may be carcinogenic to humans and some might be fatal to aquatic organisms. It is important to decide which of these compounds deserve immediate attention. Therefore, for further studies it is recommended to include prioritisation of pollutants in risk assessment.

The methodology proposed in this study can be used as a basis for decision-making. Developing and agreeing legislation can take many years. A faster alternative could be voluntary action by industry to quickly reduce exposure.

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Databases

RSC Royal Society of Chemistry
BUA Bergatergremium fuer umweltrelevante Alstoffe
BPS Basis for Product safety data sheet