THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Sources and Fluxes of Organic Contaminants in Urban Runoff

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ABSTRACT

Urban runoff quality is recognized as one of the most significant pressures on aquatic ecosystems worldwide. Research into pollutants in urban runoff has traditionally focused on nutrients, suspended solids and metals and consequently knowledge of anthropogenic organic pollutants is limited. The aim of this research was to investigate the occurrence and identify the sources of certain selected organic contaminants in urban runoff, and to evaluate tools for predicting the fluxes of these pollutants in urban catchment areas. Alkylphenols and phthalates were selected for further study since they are used in large quantities and emissions of these compounds are likely to end up in urban runoff.

The occurrence of alkylphenols and phthalates was investigated in urban snow, stormwater and sediment. In general, 4-nonylphenol showed high concentrations and detection frequencies compared to most other alkylphenols. Among the phthalates, diisononyl phthalate (DINP) was detected at the highest concentrations in all matrices, followed by diisodecyl phthalate (DIDP) and di(2-ethylhexyl) phthalate (DEHP). Nonylphenol, octylphenol and DEHP were repeatedly detected in stormwater and snow at concentrations exceeding the European water quality standards. This suggests that measures to reduce the discharge of anthropogenic substances to urban areas are necessary to achieve good water status.

Substance flow analysis (SFA) was used to map the sources and quantify the loads of phthalates and nonylphenols in urban catchment areas. The calculated loads of the contaminants were in agreement with measured loads in a studied catchment area and SFA was thus considered efficient for identifying the most important sources of phthalates and nonylphenols. The emission factors used in the calculation of the pollutant loads were also used in a process-based stormwater quality model for predicting nonylphenol and phthalate concentrations in runoff. The model revealed low predictive power; the simulated concentrations were generally one magnitude higher than the measured concentrations. In future studies, it is recommended to link the outcomes from the SFA to a fate model. This integrated model would provide a holistic overview of the sources and sinks of pollutants in urban catchment areas and could be used to evaluate both source control and end-of-pipe mitigation practices.

Keywords: alkylphenols; concentrations in urban matrices; phthalates; sediment; snow; source identification; stormwater; substance flow analysis; urban runoff quality predictions.

LIST OF PAPERS

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I. Björklund K, Strömvall A-M and Malmqvist P-A (2010) Screening of organic contaminants in urban snow. In: van Bochove E, Vanrolleghem PA, Chambers PA, Novotna B and Thériault G, editors. 14th International Conference on Diffuse Pollution and Eutrophication, 12–17 September 2010, Beaupré, Canada. *Selected for publication in Water Science and Technology*.

II. Björklund K, Palm Cousins A, Strömvall A-M and Malmqvist P-A (2009) Phthalates and nonylphenols in urban runoff: Occurrence, distribution and area emission factors. *Science of the Total Environment*, 407(16), 4665–4672.

III. Björklund K (2010) Substance flow analyses of phthalates and nonylphenols in stormwater. *Water Science and Technology*, 62(5), 1154–1160.

IV. Björklund K, Malmqvist P-A and Strömvall A-M (2010) Simulating organic pollutant flows in urban stormwater: Development and evaluation of a model for nonylphenols and phthalates. *Accepted for publication in Water Science and Technology*.

V. Björklund K, Almqvist H, Malmqvist P-A and Strömvall A-M (2008) Best management practices to reduce phthalate and nonylphenol loads in urban runoff. In: *Proceedings of the 11th International Conference on Urban Drainage*, 31 August–5 September 2008, Edinburgh, United Kingdom.

ABBREVIATIONS

AA	Annual average
AP	Alkylphenol
APEO	Alkylphenol ethoxylate
BBP	Benzyl butyl phthalate
BCF	Bioconcentration factor
BFR	Brominated flame retardant
CA	Cluster analysis
CP	Chlorinated paraffin
CSO	Combined sewer overflow
DBP	Dibutyl phthalate
DEHP	Di(2-ethylhexyl) phthalate
DINP	Diisononyl phthalate
DIDP	Diisodecyl phthalate
d.l.	Detection limit
EMC	Event mean concentration
EO	Ethylene oxide
EQS	Environmental quality standard
HWM/LMW	High/low molecular weight
MAC	Maximum allowable concentration
NP	Nonylphenol
NPEO	Nonylphenol ethoxylate
NP/EO	Nonylphenolic compound (nonylphenol and/or ethoxylate)
OP	Octylphenol
OPEO	Octylphenol ethoxylate
PAH	Polycyclic aromatic hydrocarbon
PBDE	Polybrominated diphenyl ether
PCA	Principal component analysis
PFC	Perfluorinated compound
SFA	Substance flow analysis
SMC	Site mean concentration
SQM	Stormwater quality model
WFD	Water framework directive

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1 INTRODUCTION

The greatest threat to urban water quality has historically been pollution from point sources, such as industrial activities and wastewater effluents (Makepeace *et al.* 1995; Novotny 2002). Considerable effort to clean up major point sources has significantly improved the health status of many water bodies. However, many streams are still threatened by the pollutant inflow from nonpoint sources. In urban areas, nonpoint source pollution, or diffuse pollution, is generated by emissions from human activities, such as transportation and construction (Figure 1). Pollutants are transported into sewer systems and receiving waters with rainfall or snowmelt as it travels across land surfaces. The United States Environmental Protection Agency has identified urban runoff as one of the top five sources of water quality impairment in the US (US EPA 2009), and urban runoff quality is recognized as one of the most significant pressures on aquatic ecosystems worldwide (Ellis 1991; Malmqvist and Rundle 2002).

The role of diffuse pollution in deteriorated water quality has been recognized in both the United States Clean Water Act (CWA [1972]) and the European Water Framework Directive (WFD [Directive 2000/60/EC]). When the CWA was introduced in the 1970s, the focus was put on regulating discharges from point sources (Novotny 2002). Polluted surface runoff came into focus in the late 1980s and through the enactment of Section 319 of the CWA, a national program to control nonpoint sources and urban runoff pollution was established (US EPA 2010). The European WFD aims at achieving “good surface water status” by 2015, which will require measures to control and prevent the discharges of pollutants originating from both point and nonpoint sources. Although urban runoff is not explicitly acknowledged in the WFD, mitigation of stormwater pollution is considered critical in tackling diffuse pollution impacts (Ellis *et al.* 2002; Scholes *et al.* 2007). In the strategy for eliminating pollution of surface water, the WFD has set out a list of substances or groups of substances which should be prioritized for action (Annex X to Decision 2455/2001/EC). This list currently contains 33 priority substances which, based on toxicity and occurrence, present a significant risk to or via the aquatic environment. Among these 33 substances, there are five metallic compounds. The remaining 28 compounds are organic pollutants. Research into stormwater pollution has, however, traditionally focused on pollutants other than organic compounds, such as nutrients, suspended solids and metals, which have demonstrated effects on the aquatic environment and for which analysis techniques are well established. Apart from the occurrence of, for example, polycyclic aromatic hydrocarbons (PAHs) and fuel-derived aliphatic and aromatic hydrocarbons, knowledge of anthropogenic organic pollutants in urban runoff is limited. This may be explained by the low level of awareness of their occurrence in goods and products, and thus a low level of awareness of their emission into and occurrence in the environment. In addition, a wide spectrum of properties, including a potential to degrade in the environment and in collected samples, generally renders the sampling and analysis of organic pollutants more time-consuming and costly than for e.g. metals (Wegman *et al.* 1986; de Boer and McGovern 2001). New or improved analytical procedures for many groups of organic contaminants are, however, constantly appearing, which opens the way for the monitoring of these compounds in urban environments.

Mitigation of water pollution is generally conducted through end-of-pipe solutions, which reduce the pollutant loads directly before discharge into receiving waters. However, in the WFD amendment on environmental quality standards (Directive 2008/105/EC), it is clearly stated that “causes of pollution should be identified and emissions should be dealt with at source, in the most economically and environmentally effective manner”. As the term implies, sources of diffuse pollution may be difficult to identify and the management of such contamination is often more complex than for identified point discharges of pollutants. The sources of metals detected in the urban environment have been surveyed thoroughly in recent decades (see e.g. Malmqvist [1983]; Davis *et al.* [2001]; Sörme and Lagerkvist [2002]) but for many organic contaminants, comprehensive source mapping has not yet been carried out. To achieve a non-toxic environment with good water status, it is of great importance to investigate the occurrence of organic contaminants in the environment and to identify the sources of these compounds to make it possible to prevent further discharges into the environment.

1.1 Research hypotheses

This research is based on four hypotheses:

- The first task was to select organic substances relevant to the study of urban runoff contamination. The hypothesis was that alkylphenols and phthalates are relevant to runoff quality since emissions of these chemicals from products and materials are likely to end up in urban runoff with potentially negative effects on aquatic environments (Chapter 3, Papers I and II).
- Given the extensive use of alkylphenols and phthalates in common products and materials in our society, it was hypothesized that these substances occur at detectable levels in urban runoff, which here includes stormwater, snow and urban sediment (Papers I and II).
- Identification of pollutant sources is a prerequisite for abating discharges of contaminants in urban runoff. The hypothesis was that the sources of alkylphenols and phthalates in urban catchment areas can be identified and quantified (Papers III, IV, and V).
- The prediction of contaminant concentrations and loads in runoff is useful for environmental impact assessments and setting up pollution management programs. The hypothesis was that the fluxes of alkylphenols and phthalates in urban runoff can be predicted e.g. by using available data on alkylphenol and phthalate emission from sources, and knowledge of their fate in the environment (Papers III and IV).

2 POLLUTION OF URBAN RUNOFF

Figure 1. *Pollution in urban areas is mainly a result of human activity, including production and construction, transportation, dwelling and commerce.*

2.1 Pollution generation

The type and the concentration of pollutants in runoff vary considerably between sites due to watershed and land use characteristics, such as imperviousness and traffic intensity (Novotny 2002; Butler and Davies 2004). Pollutant concentrations may also vary by several orders of magnitudes between storm events in a single catchment area as a result of wet and dry weather characteristics, such as rainfall amount and intensity, seasonal changes and antecedent dry periods (Brezonik and Stadelmann 2002; Glenn III and Sansalone 2002).

Accumulation and removal of pollutants from impervious surfaces are most often described as a build-up/wash-off process (Barbé *et al.* 1996; Vaze and Chiew 2002; Egodawatta *et al.* 2007, 2009). The build-up phase is generally expressed either as a linear process where the accumulated load is constantly increasing with time since the last wash-off event, or more frequently as an asymptotic process where accumulation is limited due to wind removal and degradation processes. The build-up of pollutants has been shown to result from land use and dry weather conditions. A subsequent rain event may wash off a fraction of the accumulated pollutant load from impervious surfaces. Particulate-bound pollutants generally need higher rain intensities than dissolved pollutants to be mobilized by runoff. It is often assumed that, depending on the size of the catchment area, the initial volumes of runoff contain the highest pollutant levels, a phenomenon known as first flush.

The accumulation and removal of pollutants differ considerably between winter and non-winter conditions. The snowpack may accumulate pollutants during sometimes month-long periods, whereas snowmelt generally occurs during a short time period, which may give rise to concentration peaks of contaminants in surface runoff and in receiving waters (Oberts *et al.* 2000; Westerlund *et al.* 2003; Meyer and Wania 2008). Ions and water-soluble substances elute from the snowpack with early meltwater fractions in a first flush. Compounds with low aqueous solubility may be sorbed to particles and retained in the snowpack until the end of the melt period. Of the particle-bound pollutants, over 90% may remain in the residual sediment after snowmelt (Viklander 1997).

2.2 Major pollutants and sources

An extensive literature review by Eriksson (2002) revealed that approximately 600 specific compounds have been observed in urban runoff and rainwater worldwide. The number of stormwater quality parameters in focus during recent decades, however, is far from being that exhaustive. The most common parameters analyzed in urban runoff have traditionally been oxygen-demanding constituents, nutrients, chloride, pathogens, suspended solids and metals (Table 1). Suspended solids are important carriers of both metals and organic pollutants, and are often used as a universal water quality parameter. Apart from PAHs, the occurrence of organic pollutants in urban runoff has only occasionally been investigated (see e.g. Makepeace *et al.* [1995]; Strömvall *et al.* [2006]; Eriksson *et al.* [2007]).

Traffic is recognized as one of the largest contributors to stormwater pollution and high concentrations of pollutants are frequently found in runoff from parking lots and roads with high traffic intensity (Viklander 1999; Ellis and Revitt 2008a). Metals are leached and emitted from a large number of sources in traffic areas, including abrasion of tires, brakes and road material, and spills of petrol and diesel (Sörme *et al.* 2001; Hjortenkrans 2008). Alkanes, alkenes, PAHs, and other petrol-related compounds are also frequently observed in runoff from traffic areas (Rogge *et al.* 1993; Murakami *et al.* 2005).

In addition to traffic, wet and dry atmospheric deposition on roofs and roads is identified as one of the major sources of stormwater pollution (Davis *et al.* 2001; Van Metre and Mahler 2003). Roof runoff quality is also affected by leaching from the roof material itself and zinc, copper and cadmium have occasionally been found in roof runoff at concentrations exceeding guidelines regarding ambient water quality (Robson *et al.* 2006; Clark *et al.* 2008; Lye 2009). Common building and construction materials have also demonstrated the potential to release pollutants into the environment: impregnated wood may leach As, Cr, Cu, and Pb; Cd, Pb, Zn are released from PVC plastics, and concrete has been shown to leach Cr and Ni (Bergbäck *et al.* 2001; Davis *et al.* 2001; Sörme *et al.* 2001). Other examples of pollutants include nonylphenol and thiocyanate emitted from concrete (Togerö 2006), biocides from facades and roofs (Burkhardt *et al.* 2007), as well as phthalates from PVC roofing (Pastuska *et al.* 1983).

Table 1. *Parameters commonly analyzed in urban runoff, their sources in urban areas and potential effects on receiving waters (Makepeace et al. 1995; Ellis and Hvitved-Jacobsen 1996; Oberts et al. 2000; Burton and Pitt 2002).*

Parameter	Examples of sources	Potential impact on the aquatic environment
Nitrogen, phosphorous	Atmospheric deposition; degradation of organic material; animal and human waste; combined sewer overflows; fertilizers and waste from gardens and parks	Eutrophication: excessive plant growth, which can choke streams and lead to fluctuations in dissolved oxygen levels; increase in algal blooms reduces the amount of light and oxygen in the water
Suspended solids and sediment	Erosion from construction sites, roads, driveways and footpaths; car washing; corrosion of vehicles and building materials; winter road maintenance; organic matter from plants and animals	Increased turbidity; reduced light penetration; interference with fish and aquatic invertebrates; important for transport of other contaminants through water systems
Oxygen-demanding compounds (biochemical and chemical oxygen demand – BOD and COD, respectively)	BOD is a measure of the oxygen used by microorganisms to decompose organic material; COD is based on the chemical decomposition of organic and inorganic contaminants containing oxygen	Low levels of dissolved oxygen or even anoxic conditions in receiving waters
Pathogens (viruses, bacteria, fungi and parasites)	Animal and human feces; naturally occurring in soil and water	May cause disease in plants and animals, including humans; a concern for contact recreation, such as swimming
Ions (of Ca, Cl, Na)	De-icing salts; atmospheric deposition	Potential groundwater contamination
Acids	Atmospheric deposition	Acidification; may corrode and damage road and building material
PAHs	Incomplete combustion of organic material including vehicular emissions, oil combustion, wood burning, waste incineration; lubricating oil; bitumen and asphalt; tire rubber	Some of the PAHs are classified as carcinogenic, mutagenic, and teratogenic
Petroleum hydrocarbons (aliphatic and aromatic hydrocarbons), oil and grease	Spills and leaks of lubricants, petrol and diesel; road runoff; car parks; car washing	Wide range of toxic effects, from less toxic to carcinogenic; may form emulsions and films on water surfaces, which reduces re-aeration and makes it difficult for animals and plants to breathe
Metals (Cd, Cu, Zn and Pb are the most reported metals, although Co, Cr, Fe, Mn, Ni, and platinum group elements have also been frequently detected in runoff)	Tire wear; road wear; lubricants; auto body and engine corrosion; brake linings; corrosion of road furniture and building materials; atmospheric deposition	The speciation determines the toxicity and bioavailability of the metals; many metals have toxic effects on aquatic plants and animals

2.3 Stormwater management

The first sewer systems were built primarily to convey surface runoff and sewage from urban areas to the nearest receiving waters in order to avoid flooding of streets and buildings and to clear the cities of waste and wastewater (Brombach 2002; Novotny 2002; Butler and Davies 2004). The sewers constructed in Europe in the late 19th and the early 20th century were combined conduits for sanitary wastewater and stormwater. When sewage treatment plants were introduced later in the 20th century, relief structures – combined sewer overflows (CSOs) – needed to be installed. The CSOs help avoid flooding of the sewer system and treatment plants by diverting excess water flows of untreated stormwater and wastewater into receiving watercourses. The CSOs often contain high levels of suspended solids, pathogens and nutrients and are a major water pollution concern in cities with combined sewers. To bypass the problems associated with CSOs, separate sewers for surface runoff and wastewater have been constructed. In Sweden's two largest cities, Stockholm and Gothenburg, 30–40% of the total stormwater volume is currently conveyed in combined sewers to treatment plants (Göteborg Vatten 2001; Stockholms Stad 2005). Urban runoff in combined sewers contributes to the pollution of sewage sludge, which obstructs the use of the sludge as a nutrient source on arable land. The remaining 60–70% of the stormwater volume in Stockholm and Gothenburg is discharged directly, through separate sewers, into receiving waters. Mitigation of stormwater in these cities is currently done "only to a small extent" although the importance of improving stormwater quality is gaining ground worldwide (Oberts *et al.* 2000; Ellis *et al.* 2002; Mikkelsen 2004).

Management practices for urban runoff pollution include physical devices, such as ponds and bioretention areas, as well as strategies for source control (Barbosa and Hvitved-Jacobsen 1999; Muthukrishnan *et al.* 2004; Muthanna *et al.* 2007). Source control may include education campaigns, legislative control and voluntary agreements to prevent pollution of urban runoff before it arises. A complete depletion of many pollutant fluxes may, however, not be feasible and additional mitigation practices that reduce the pollutant load at the end of the stormwater pipe are therefore necessary. These end-of-pipe practices are designed to remove pollutants through physical, physicochemical and biological processes, such as settling, filtration and plant uptake (Muthukrishnan *et al.* 2004; Scholes *et al.* 2008). The processes are relevant to a varying degree for different mitigation practices, and efficiency in removing pollutants from the water phase is very much dependent on substance properties. An integrated approach to stormwater management, where different types of management solutions are adopted, is regarded as being more effective in reducing pollution than any single mitigation practice used on its own.

3 SELECTED ORGANIC COMPOUNDS FOR FURTHER RESEARCH

3.1 Selection criteria

Organic compounds have one common feature; they contain carbon. The compounds may have both a natural and anthropogenic origin and cover a broad spectrum of properties (Connell *et al.* 1997). Many anthropogenic organic compounds, produced intentionally or unintentionally, have been shown to be persistent in the environment due to an inherent resistance to degradation through biotic and abiotic processes. Consequently, many organic pollutants may bioaccumulate in biota, biomagnify in food chains and have the potential to affect human and animal health negatively.

Given the large number of organic pollutants used in our society, vigorous sorting out of the most interesting candidates for further research was done. The selection process was based on a literature review, taking the following criteria into consideration:

- Quantities used in Sweden and in the European Union – the use should be widespread in terms of both the application area and the geographical area
- Urban runoff relevance – the chemical should be used in products and materials that are likely to be found in urban outdoor areas, and emissions into water would most likely occur
- Risk of effects on aquatic environments – the chemical should accumulate in the environment, and/or be acutely toxic, and/or show endocrine, carcinogenic, mutagenic or other adverse effects

This study does not claim to identify emerging contaminants, i.e. substances which are more or less unknown to the research community in terms of properties and occurrence in the environment. As the project did not aim at developing or improving analytical procedures for organic pollutants, the availability of techniques for chemical analysis was also an important criterion for selection of the substances for further research. Unintentionally produced pollutants, such as dioxins, were not included, since the focus was on compounds found in commonly used commodities.

3.2 Candidate compounds

The shortlist of compound groups considered for further study included alkylphenols (APs), brominated flame retardants (BFRs), chlorinated paraffins (CPs), perfluorinated compounds (PFCs), tertiary butylphenols and phthalates. These compounds show a variety of adverse environmental effects, are widely used in society and are likely to be present in urban water systems (Table 2). Polybrominated diphenyl ethers (PBDEs, one class of BFRs), short-chain (C_{10}-C_{13}) chlorinated paraffins, di(2-ethylhexyl)-phthalate (DEHP), nonylphenol and octylphenol are identified as priority pollutants in the WFD (Decision 2455/2001/EC). Other international agreements, such as the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) and the Baltic Marine Environment Protection Commission (HELCOM), also include these substances on their list of chemicals for priority action (OSPAR Commission 2007; Helsinki Commission 2008). Furthermore, the OSPAR and HELCOM lists include additional brominated flame retardants (tetrabromobisphenol A and hexabromocyclododecane), an additional phthalate (dibutyl phthalate), a butylphenol (2,4,6-tri-*tert*-butylphenol), and perfluorinated compounds (perfluorooctane sulfonate and perfluorooctanoic acid). Similar to the WFD, the OSPAR and the HELCOM commissions aim to bring the discharges, emissions and losses of the selected priority substances to an end by 2020.

Based on the listed criteria, alkylphenols and phthalates were identified as the most interesting substance groups for further study. Compounds within these groups have attracted attention due to their toxicity (see e.g. Servos [1999]; Heudorf *et al.* [2007]), including endocrine-disrupting effects, and due to their occurrence in aquatic environments worldwide (see e.g. Clark *et al.* [2003]; Soares *et al.* [2008]). Among the APs, nonylphenolic compounds are in focus since they are used in the largest amounts, and there is more background data available for these substances compared to other APs. Among the phthalates, DEHP, DINP, DIDP and DBP are in focus since they are the most used high and low molecular weight (HMW and LMW) phthalates, respectively. Tertiary butylphenols, BFRs, CPs, and PFCs also fulfill the criteria for selection for further study (Table 2), although the advantages of studying alkylphenols and phthalates outrival the other substances. These advantages include availability of analysis techniques, which has been limited for chlorinated paraffins and tertiary butylphenols, and a broader application of the chemicals in both commodities and materials used in outdoor environments, which is less extensive for BFRs and PFCs.

Outcomes from the screening of organic contaminants in urban snow (Chapter 4.2 and Paper I) justify the selection of alkylphenols and phthalates for further study. Alkylphenols and phthalates were frequently detected in urban snow, repeatedly at concentrations exceeding the European environmental quality standards (EQS) for surface waters (Directive 2008/105/EC). Brominated flame retardants, perfluorinated compounds and chlorinated paraffins were detected less frequently in urban snow.

Table 2. *Sources, environmental fate and toxicity of the candidate compound groups.*

Substance group	Examples of compounds	Sources/use	Properties/fate	Accumulation and toxicity	References
Alkylphenols (APs)	4-*tert*-octylphenol (OP); 4-nonylphenol (NP); octylphenol and nonylphenol ethoxylates	Very versatile additives used in paints, detergents, polymers, sealants, rubber, coatings, lubricants etc.	Shorter ethoxylates, 4-NP and 4-*t*-OP partition to suspended material in aquatic systems whereas higher oligomers are more hydrophilic	Shorter ethoxylates, 4-NP and 4-*t*-OP show estrogenic effects in aquatic organisms, mammals and birds; bioaccumulation has been observed	Ying *et al.* (2002); Månsson *et al.* (2008); Soares *et al.* (2008); Björklund (2010)
Brominated flame retardants (BFRs)	Polybrominated diphenyl ethers (PBDE); tetrabromobis-phenol A (TBBPA); hexabromocyclo-dodecane (HBCDD)	Used in textiles, upholstery, cables, building materials, electric and electronic products	Semivolatile; hydrophobic (log K_{ow} 5–10 PBDEs, 4.5 TBBPA, 5.8 HBCDD); persistent	Very toxic to aquatic organisms (pentaBDE, proposed for HBCDD and TBBPA); bioaccumulates (penta- and oktaBDE, TBBPA, HBCDD)	Cousins and Palm (2003); ECB (2001, 2002b, 2006, 2008b)
Chlorinated paraffins (CPs), also called poly-chlorinated alkanes	Technical mixtures; C_{10}–C_{13} short-chain chlorinated paraffins (SCCP); C_{14}–C_{17} medium-chain chlorinated paraffins (MCCP); $\leq C_{18}$ long-chain chlorinated paraffins (LCCP)	Metal-working fluids, plasticizers, paint and varnish, sealants and adhesives, flame-retardants in rubber and other polymeric materials	Non-volatile; lipophilic with log K_{ow} values from 5 (SCCP) to over 12 (LCCP); adsorb strongly to particles and sediment in aquatic systems; persistent	SCCP more toxic than other CPs, suspected carcinogen, very toxic to aquatic organisms; no classification for MCCPs, but "very toxic to aquatic organisms" is suggested; all CPs may bioaccumulate	Bayen *et al.* (2006); Fridén and McLaclan (2007); Feo *et al.* (2009)
Perfluorinated compounds (PFCs)	Perfluorooctane sulfonate (PFOS); perfluorooctane-sulfonamide (PFOSA); perfluorooctanoic acid (PFOA);	Fire-fighting foams, detergents, stain, grease and water repellants for carpets, furniture, paper, textiles etc.	Hydrophobic alkyl chain and -philic anionic functional group (can be very water soluble, difficult to determine K_{ow}); persistent	PFOS chronically toxic, a reproduction toxin, toxic to aquatic organisms; PFOA possibly carcinogenic and disruptive to reproduction; little data on other PFCs	Giesy and Kannan (2002); KemI (2006); Giesy *et al.* (2010)
Phthalates	Dimethyl (DMP); diethyl (DEP); dibutyl (DBP); di(2-ethylhexyl) (DEHP); benzyl butyl (BBP); diisodecyl (DIDP); diisononyl (DINP) phthalate	Plasticizers in PVC, additives in sealants, adhesives, paints and lacquers, shoe and textile wear, toys, paper and packaging, coil coating	Log K_{ow} increases, water solubility and volatility decreases with increasing molecular weight; predominant partitioning to soils, suspended solids and sediments	Acute toxicity demonstrated for the lower phthalates ($<C_6$); BBP, DBP and DEHP show endocrine disrupting effects	Staples *et al.* (1997b); Cousins *et al.* (2003); Björklund (2010)
Tertiary butylphenols	2,6-di-*tert*-butyl-4-methylphenol (BHT); 2,6-di-*tert*-butylphenol (2,6-DTBP); 4-*tert*-butylphenol (4-TBP)	Additives in a large variety of products such as food, cosmetics, pharmaceuticals, rubber, plastics, petroleum products, paint, adhesives, lubricants, asphalt, wood preservatives	BHT not readily biodegradable, partitions to air, soil and sediment; 2,6-DTBP poorly water soluble, not readily biodegradable, partitions into air and soil; 4-TBP biodegradable, partitions to water	The substances show varying toxicity, e.g. highly toxic to aquatic organisms (2,6-DTBP); potentially carcinogenic (4-TBP); bioaccumulate (2,6-DTBP, 4-TBP, BHT)	ECB (2008c); European Commission (2008); OECD (2000, 2002, 2005); Remberger *et al.* (2003)

3.3 Phthalates

3.3.1 Production and application

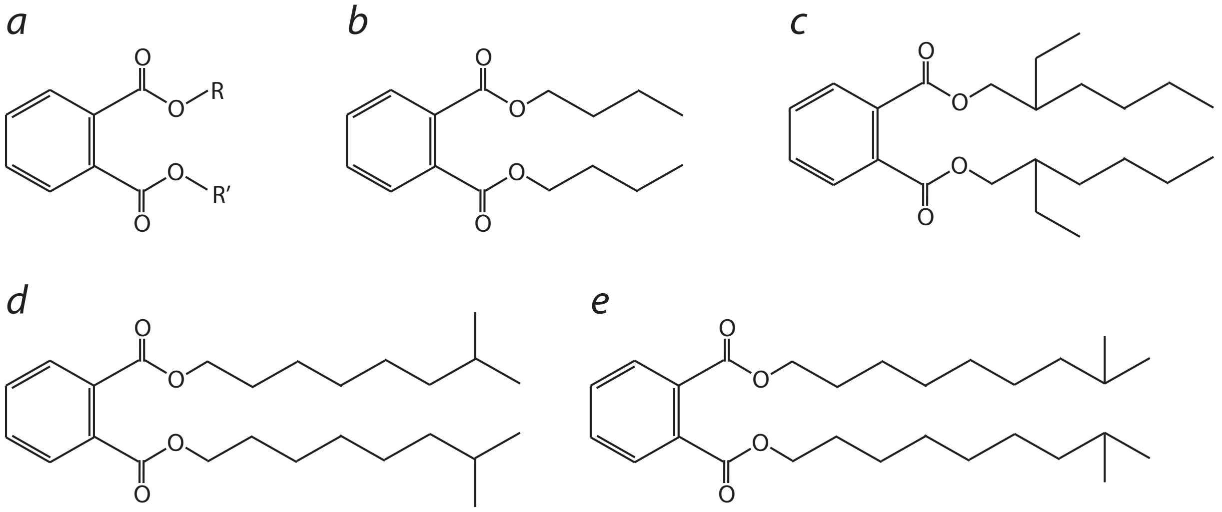


Figure 2. *Structure of a) general phthalate, where R and R' are carbon chains of various character; b) dibutyl phthalate (CAS No 84-74-2); c) di(2-ethylhexyl) phthalate (CAS No 117-81-7); d) diisononyl phthalate (CAS Nos 68515-48-0 and 28553-12-0); and e) diisodecyl phthalate (CAS Nos 68515-49-1 and 26761-40-0).*

Phthalates, or phthalate esters, are produced by reacting phthalic acid with an alcohol. Alcohols from methanol (C_1) up to C_{13} are used for manufacturing most commercially available phthalates (ECPI 2010). The length and the branching of the carbon chain determines the physical and chemical properties of the phthalate esters, and thereby the application area of the compound (KemI 2001). Commercially available phthalates may be mixtures of compounds with a varying chain character, which is often evident from the addition of "iso" in the compound name. Commonly used phthalates (Figure 2) include the LMW dimethyl phthalate (DMP, C_1) and dibutyl phthalate (DBP, C_4), and the HMW di(2-ethylhexyl) phthalate (DEHP, C_8), diisononyl phthalate (DINP, C_9), and diisodecyl phthalate (DIDP, C_{10}) (KemI 2009; ECPI 2010). More than 90% of the total mass of phthalates used in Sweden during the past decade are HMW phthalates. Historically, DEHP has been used in the largest amounts worldwide, but following restrictions on the marketing and use of DEHP (e.g. Directives 2003/36/EC, 2004/93/EC and 2005/84/EC), DINP has increasingly taken over the market (Figure 3).

The primary use of HMW phthalates is as plasticizers whereas LMW phthalates are used as solvents (ECPI 2010). More than 90% of the one million metric tons of phthalates produced annually in Europe are used as plasticizers in PVC, where the content of plasticizers can be up to 50%. Flexible PVC has a very wide application area and can be found in e.g. wires and cables, hoses, flooring, wall covering, cladding and roof membranes, packaging, stationery, footwear, rainwear, coil and fabric coating, car undercoating and interior, upholstery, trims and fittings (Hoffmann 1996; ECB 2003a, b, 2004, 2005, 2008a; ECPI 2010). Benzyl butyl phthalate (BBP) is primarily used in the manufacturing of foamed PVC for flooring, whereas DEHP, DINP and DIDP dominate other applications of flexible PVC. To a small extent,

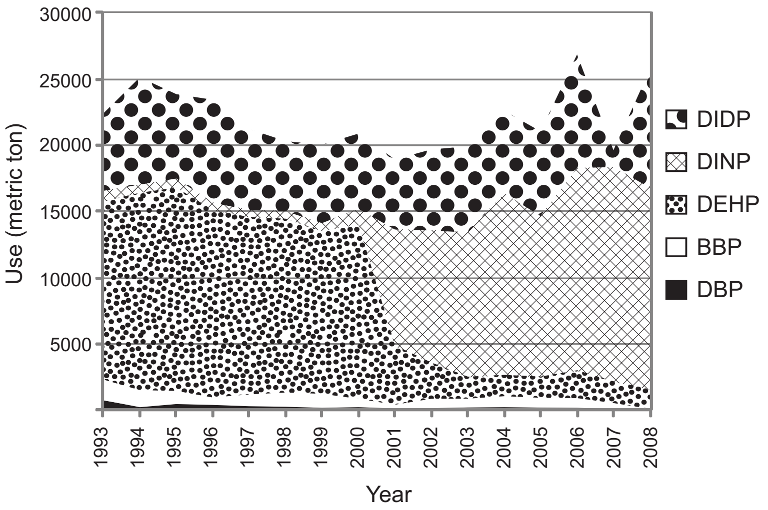


Figure 3. *The use (total quantity in the Products Register, export excluded) of certain phthalates in Sweden during the years 1993 and 2008 (KemI 2010a).*

phthalates are used in non-PVC polymers such as other vinyl resins, cellulose ester plastics and rubbers. Non-polymer applications of phthalates include paints, lacquers and varnishes, adhesives, sealants, lubricants, printing inks, cosmetics, pesticides, fabrics, and coatings for e.g. cars and coils.

3.3.2 Releases into and occurrence in the environment

Phthalates are not chemically bound to the material and may migrate from a product during use and disposal (Cadogan *et al.* 1993). The extensive use of phthalates is reflected in their ubiquitous occurrence in environmental media worldwide, including the atmosphere and precipitation (Teil *et al.* 2006; Xie *et al.* 2007); surface water and sediment (Fromme *et al.* 2002; Peijnenburg and Struijs 2006); soil (Vikelsøe *et al.* 1999; Xu *et al.* 2008); and biota (Mackintosh *et al.* 2004; Huang *et al.* 2008). Wastewater represents a significant source of these compounds in the environment and phthalates have frequently been observed in landfill leachates, treatment plant influent and effluent water, sludge and receiving waters (Marttinen *et al.* 2003; Roslev *et al.* 2007; Beauchesne *et al.* 2008). The occurrence of phthalates in urban runoff has occasionally been reported (see e.g. Makepeace *et al.* [1995]; Clara *et al.* [2010]). Data on the currently most used phthalates, DINP and DIDP, are very infrequent for both urban runoff and other environmental matrices (see Chapter 4).

3.3.3 Properties and environmental fate

In general, the vapor pressure decreases and the water solubility and log K_{ow} values increase with an increasing carbon chain length of the phthalate (Staples *et al.* 1997b; Cousins *et al.* 2003). The phthalates show large variations in water solubility; from almost 5 g/l for DMP, to 10^{-11} g/l for C_{13} phthalates. The log K_{ow} values range from 4.3 for DBP to 9.5 for DIDP and only DMP and diethyl phthalate (DEP) show log $K_{ow}<3$. Fate modeling of phthalates has shown that DMP and DEP will partition to water in a soil-air-water-sediment system, whereas higher phthalates to 96–100% sorb to soil or sediment (Cousins *et al*. 2003).

Microbial degradation is believed to be the dominant breakdown process for phthalates in both aquatic and terrestrial systems (Peterson and Staples 2003). Degradation begins by ester hydrolysis forming the monoester, which can undergo further degradation to phthalic acid and alcohol. However, complete degradation of phthalates may not always be achieved. The metabolic by-products 2-ethylhexanol, 2-ethylhexanal and 2-ethylhexanoic acid have been shown to be more stable and more toxic than the parent phthalate ester (Horn *et al.* 2004; Nalli *et al.* 2006). Biodegradation half-lives tend to increase with increasing alkyl chain length. Studies by Cartwright *et al.* (2000) and Yuan *et al.* (2002) showed that LMW phthalates were rapidly degraded in soil and aerobic sediments and were not expected to persist in the environment. The HMW phthalates, however, were poorly degraded due to lower bioavailability. Phthalates are also degraded under aerobic conditions, but at a lower rate than in aerobic environments (Staples *et al.* 1997b; Yuan *et al.* 2002; Peterson and Staples 2003).

3.3.4 Toxicity

The high log K_{ow}s of phthalates indicate a potential for bioaccumulation. The LMW phthalates, however, are readily degraded into monoesters and the partition of HMW phthalates to sediment and soil leads to low bioavailability (Gobas *et al.* 2003; ECB 2004, 2005, 2008a). Biomagnification of phthalates in aquatic and terrestrial food chains has been shown to be limited, mainly due to biodegradation, which increases with the trophic level.

Toxicity tests show that $<C_6$ phthalates are acutely and chronically toxic to algae, aquatic invertebrates, and fish at concentrations below their water solubility (Adams *et al.* 1995; Staples *et al.* 1997a; Bradlee and Thomas 2003). Toxicity increases with increasing alkyl chain length of the LMW phthalate whereas $>C_6$ phthalates show neither acute nor chronic toxicity to aquatic organisms at concentrations below their solubility limit (Staples *et al.* 1997a; ECB 2003a, 2008a). This lack of toxicity is suggested to be a result of the substances' low water solubility and their degradation in aquatic organisms. However, the HMW phthalates have shown carcinogenic, reproductive and developmental toxicity effects such as prenatal mortality, malformed fetuses, decreased sperm production, testicular damage, and incomplete formation of secondary sex organs in laboratory animals (Gill *et al.* 2001; David and Gans 2003; ECB 2004, 2005, 2008a). The metabolites monobutyl, monobenzyl and mono-(2-ethylhexyl) phthalate may cause testicular changes in rats and it is suggested that the monoesters play an important part in the toxicity expressed by phthalates.

The endocrine effects of phthalates are often discussed, as studies demonstrate equivocal findings (Harris and Sumpter 2001; ECB 2004, 2005, 2008a). It has been shown that DBP and BBP may reduce the binding of natural estrogen to the receptor in rainbow trout, and that DEHP can influence sexual differentiation and interfere with endocrine functions. The most potent endocrine disruptor is BBP, which is still several magnitudes less potent than the natural 17β-estradiol. Rather than acting as an estrogen-active disruptor, phthalates are suspected to cause antiandrogenic activity. In particular the monoester metabolites have been shown to inhibit the binding of natural androgen to its receptor (Harris and Sumpter 2001).

DEHP, DBP and BBP are classified as being toxic to reproduction and DBP and BBP are also classified as being very toxic to aquatic life (European Commission 2008). No other phthalates are currently classified. Toxicity tests have shown that DIDP and DINP may lead to e.g. organ weight changes, skeletal and soft tissue variations in fetuses, and lower mean offspring bodyweights in laboratory animals (ECB 2003a, b), and Grey *et al.* (2000) showed that DINP displayed antiandrogenic activity in rats. It has been concluded, however, that the substances are neither genotoxic nor have adverse effects on fertility. Toxicity studies of DINP and DIDP are far fewer than for most other phthalates and Oehlmann *et al.* (2008) concluded that there is a general lack of exposure data for these compounds, and that more studies are needed to evaluate their risk in the environment.

3.4 Alkylphenols

3.4.1 Production and application

Alkylphenols consist of a phenol with one or more attached alkyl chains, which vary in length and degree of branching (Figure 4). The most commonly used APs in industrial applications are nonylphenol (NP) and octylphenol (OP). The commercially available NP is predominantly the *para*-substituted 4-nonylphenol (4-NP) with a varied and undefined degree of branching of the alkyl chain (ECB 2002a). The tertiary 4-*t*-octylphenol (4-*t*-OP) is the only OP isomer currently available commercially in Europe (DEFRA 2008). The estimated use of NPs in the EU was close to 80 000 metric tons in 1997 (ECB 2002a). Due to voluntary agreements and legal restrictions during the 1990s and the 2000s (e.g. Regulations 793/93, 689/2008, and Directive 2003/53/EC), the use of NPs in the EU has decreased. However, there are no restrictions on the import of goods including NPs from outside Europe. Both NP and OP are identified as priority hazardous substances in the WFD, which implies that emissions, discharges and losses of these pollutants into water must cease. Despite the directive, there are no current restrictions on the use of OPs within the EU and in 2002, around 23 000 metric tons were used (DEFRA 2008; European Commission 2008).

Alkylphenols are used in the production of alkylphenol ethoxylates (APEOs), which is one of the most used surfactant groups worldwide. The number of polar ethoxylate units (EO), which determines the physical and chemical character of the substance, may range from one to one hundred (Figure 4). In the EU, approximately 60% of the NPs are used to produce nonylphenol ethoxylates (NPEOs), whereas only 2% of the OPs are used in the production of octylphenol ethoxylates (OPEOs) (ECB 2002a; DEFRA 2008). The application areas of

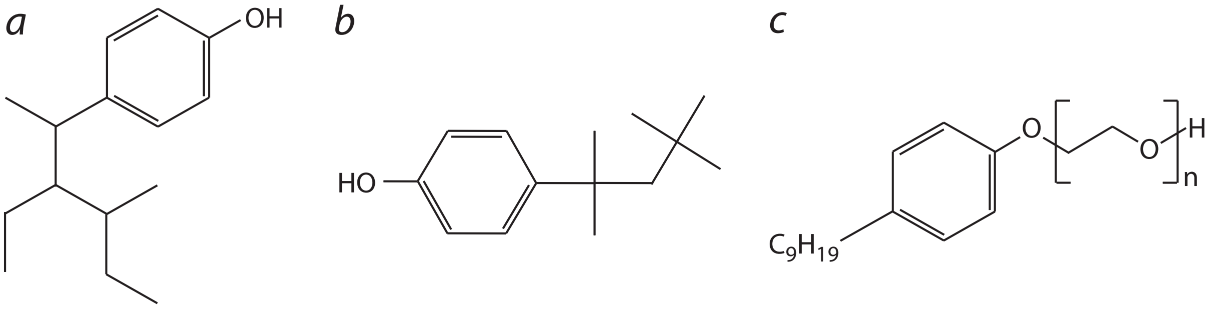


Figure 4. *Structure of a) branched nonylphenol (CAS No 84852-15-3); b) tertiary octylphenol (CAS No 140-66-9); and c) nonylphenol ethoxylate (CAS Nos 26027-38-3, 37205-87-1, 68412-54-4, 9016-46-9 etc.), where n is the number of ethoxylate units.*

NPEOs are not far from being universal; lubrication, dyeing, pulp and paper manufacturing, plastics manufacturing, textiles, pesticides, cleaning products, detergents, personal care products, paints, lacquers, varnishes, resins, adhesives, concrete, dust control etc. (CEPA 1999; ECB 2002a; Andersson 2006). Cleaning agents were formerly the major application for NPEOs, but due to regulations other areas are taking over. A substance flow analysis of APs in Stockholm showed that the largest uses were paint and varnish, sealants, building materials, adhesives, additives in concrete, cleaning agents, plastic materials and textiles (Andersson 2006). In addition to their role as raw material for NPEOs, approximately 40% of the NPs are used in the production of phenol/formaldehyde resins, polymers, epoxy resins, plastics stabilizers, tri(4-nonylphenyl) phosphate (an antioxidant used in the stabilization of natural and synthetic rubbers), vinyl polymers, polyolefins and styrenics (OSPAR Commission 2001; ECB 2002a; Andersson 2006). The major use (98%) of OP in the EU is as an intermediate in the production of phenolic resins, used mostly in the manufacturing of tire rubber (Brooke *et al.* 2005; DEFRA 2008). Secondary uses of the resins are in varnishes, printing inks and paints. Octylphenol ethoxylates are mainly used for emulsion polymerization, and to a smaller extent in textile and leather auxiliaries, pesticides and water-based paints.

3.4.2 Releases into and occurrence in the environment

Alkylphenolic compounds are released into the environment during the production, use and waste management of products containing the chemicals (ECB 2002a; DEFRA 2008). The main transportation routes of APs and APEOs into the environment are via industrial and domestic wastewater flows (Thiele *et al.* 1997; Soares *et al.* 2008). Consequently, surface waters and sediments are the main compartments to which the releases are addressed. Reviews of observed concentrations of APs and APEOs in wastewater, surface water and sediment can be found in e.g. Thiele *et al*. (1997); Ying *et al*. (2002); and Soares *et al*. (2008). Observations of APs in urban runoff have occasionally been reported (e.g. Kjølholt *et al.* [1997]; Karlsson [2006]; Rule *et al.* [2006]) but no comprehensive review of occurrence and levels in runoff can be made.

3.4.3 Properties and environmental fate

The branching and length of the alkyl group define the physicochemical properties of alkylphenols. 4-nonylphenol and 4-*t*-octylphenol show low solubility in water; reported values range between 3 and 10 mg/l for NP and around 20 mg/l for OP (Ahel and Giger 1993a; ECB 2002a; Brooke *et al.* 2005). The APEOs show both hydrophobic and hydrophilic properties; compounds with <5 EO units are described as water-insoluble, whereas the oligomers with >5 EO units are water-soluble (Ahel and Giger 1993a; Thiele *et al.* 1997). The octanol-water partition coefficients (log K_{ow}) are 4.12 and 4.48 for OP and NP, respectively (Ahel and Giger 1993b). Lower lipophilicity has been found for the ethoxylates, whose log K_{ow} values decrease with an increasing number of EO units. The environmental properties of alkylphenols suggest that the substances are likely to be associated with organic matter and adsorbed to sediments if released into the aquatic environment.

Alkylphenol ethoxylates are degraded through a stepwise loss of ethoxy groups, forming shorter ethoxylate homologs, ethoxycarboxylates, and ultimately alkylphenols in the environment (Thiele *et al.* 1997; Jonkers *et al.* 2005). Fate studies of APs in wastewater treatment plants show that the higher APEO oligomers generally are degraded through the treatment processes, while the metabolic products, which are more or less resistant to further microbial degradation, are adsorbed to the sludge or discharged via effluent water (Ahel *et al.* 1994; Loyo-Rosales *et al.* 2007a; Céspedes *et al.* 2008). Alkylphenols tend to accumulate in sediments of natural waters, where they are likely to persist (Shang *et al.* 1999; Ferguson *et al.* 2001). Biodegradation by means of microorganisms may, however, take place and degradation in sediment samples has been shown under both aerobic and anaerobic conditions (Isobe *et al.* 2001; Chang *et al.* 2004; Yuan *et al.* 2004).

3.4.4 Toxicity

The lipophilic character of nonylphenol, octylphenol and lower ethoxylates implies that these substances bioaccumulate in aquatic organisms (Thiele *et al.* 1997; Servos 1999; ECB 2002a). The bioconcentration factor (BCF) for APs differs considerably between species and studies; BCFs between 10 and 3 000 have been reported for mussels and <1–741 for fish.

Toxicity tests reveal that NPs and OPs are acutely and chronically toxic to e.g. crustaceans, algae, fish and mussels (Thiele *et al.* 1997; Servos 1999; ECB 2002a). Observed effects include significant reductions in growth, photosynthetic activity, and reproduction. Reported no effect concentrations of NP and OP start at 6 µg/l for rainbow trout. The ethoxylates show increasing toxicity with decreasing EO chain length and are generally toxic at concentrations which are at least one magnitude higher than for NP and OP. Alkylphenols have attracted considerable attention because of their endocrine disrupting effects. The substances compete with the hormones for binding to the receptor and appear to express several estrogenic and antiandrogenic responses in organisms, such as synthesis of a female-specific protein (vitellogenin) in male fish, effects on the growth of testes, disrupted smoltification, and intersex in fish (White *et al.* 1994; Jobling *et al.* 1996; Pedersen *et al.* 1999; Servos 1999; Soares *et al.* 2008). The estrogenic potency is suggested to be higher for OP than for NP. Nonylphenol is classified as being very toxic to aquatic life with long-lasting effects and is suspected of damaging fertility, whereas other APs are not classified (European Commission 2008). Despite the observed toxicity of OP, research on the use, negative effects and environmental occurrence of APs has focused mainly on NP.

4 DETERMINATION OF PHTHALATE AND ALKYLPHENOL CONCENTRATIONS IN URBAN RUNOFF

Pollutants in stormwater are generally reported as event mean concentrations (EMC) or as loads, which is the mass of pollutants in runoff (Charbeneau and Barrett 1998; Kayhanian and Stenstrom 2005). The EMC is defined as the total pollutant load divided by the total runoff volume discharged during an event. The EMC is usually determined through chemical analysis of flow-weighted composite samples of runoff, which reveal no information on temporal variability of contaminant concentrations. The EMC is used in most stormwater monitoring programs and is considered appropriate for evaluating the effects of stormwater on receiving waters. For pollutants that exhibit cumulative rather than acute effects in aquatic environments, it may be relevant to consider event or annual loads (Marsalek 1990; Vaze and Chiew 2003). To estimate annual loads, site mean concentrations (SMCs) are occasionally used. The SMC is determined by dividing the total pollutant mass by the total runoff volume of all measured events or as the arithmetic average of all EMCs observed at a monitoring site (Taebi and Droste 2004; Mourad *et al.* 2005a). Pollutant concentrations are, however, highly variable and it has been shown that estimations of SMCs can be biased, which will influence the estimated load significantly. The load is often expressed as a unit area load (e.g. [kg/ha×year]), which can be used to determine the contribution of different areas and land uses to the total pollution (Ellis and Revitt 2008b).

In cold regions, up to 50% of the annual precipitation can be stored in the snowpack, and 60% of the annual load of certain pollutants may be produced during the winter season (Oberts *et al.* 2000). Snow is most often grab-sampled and the pollutant levels are reported as concentrations in the thawed snow, whereas snowmelt may be sampled in a similar way to stormwater runoff in the field and concentrations are reported as EMCs (see e.g. Westerlund and Viklander [2006]; Engelhard *et al.* [2007]).

Many metallic and organic compounds tend to sorb onto particles and partition studies of pollutants show that both the water and the particulate phase are important for their transport into the stormwater system (Sansalone and Buchberger 1997; Meyer *et al.* 2006). High molecular weight phthalates tend to partition to particles in water (Cousins *et al.* 2003). This behavior has been predicted in a fugacity modeling of the fate of alkylphenols and phthalates in a stormwater sedimentation system (Paper II). Alkylphenols and LMW phthalates, such as DBP, also partition onto particles but not to the same degree as HMW phthalates (Ahel and Giger 1993b; Cousins *et al.* 2003).

4.1 Analysis and sampling strategy

Given the environmental fate of alkylphenols and phthalates, the occurrence of these compounds was investigated in both water and sediment. As land use has been shown to substantially influence runoff quality (see Chapter 2), stormwater and sediment from urban areas of different character were sampled (Table 3).

In addition to target analyses of alkylphenols and phthalates, screening analyses of organic compounds were performed (Paper I). The aim of the screening study was to make an inventory of the most frequently occurring organic contaminants in runoff. The hypothesis was that alkylphenols and phthalates are among the most relevant substance groups – in terms of occurrence frequency and environmental concentrations compared to quality standards – for studies of organic substances in urban runoff. Snow and road dust were expected to be appropriate matrices for the screening study since these matrices may accumulate pollutants over long periods of time. The screening comprised both target and non-target analyses of organic pollutants. A non-target screening of substances without *a priori* conception of the contamination content may identify source-specific tracer compounds and reveal new priority pollutants at high concentrations. Non-target screenings have successfully been accomplished for e.g. river water (Dsikowitzky *et al.* 2004) and landfill leachates (Eggen *et al.* 2010). In addition to alkylphenols and phthalates, the target analyses included the candidate substance groups for further studies presented in Chapter 3 (BFRs, CPs and PFCs), except for the tertiary butylphenols, for which commercial analyses were not available. The PAHs were included for comparison with other studies of snow.

Flow-weighted composite samples of stormwater (Gårda, Kärra, Skarpnäck, Nybohov) were collected using automated samplers (Figure 5). Stormwater sediment (Gårda) was sampled using a metal core sampler, and road sediment (Gårda, Kärra, Järnbrott) was collected from a delimited area of the roadside using soft brushes of natural bristle and a metal shovel (Figure 5). Surficial roadside snow (Gårda, Kärra, Järnbrott) and vertical segments of snow from deposits (Heden, Vallhamra, Gårda, Delsjön) were collected in glass bottles and stainless steel containers.

Table 3. *Sites for sampling of stormwater, snow, stormwater sediment and road sediment.*

Area	Area character	Matrix (*n*)	Paper No
Gårda (Gothenburg)	Motorway, AADT[a] ~ 85 000; sedimentation facility for road runoff	Stormwater (5); stormwater sediment (4); roadside snow (2); snow deposit (1); road sediment (1)	Papers I and II
Kärra (Gothenburg)	Suburban residential AADT ~ 500	Stormwater (1); roadside snow (2); road sediment (1)	Paper I
Järnbrott (Gothenburg)	Major road AADT ~ 60 000	Roadside snow (2); road sediment (2)	Paper I
Skarpnäck (Stockholm)	Suburban residential AADT ~ 2000	Stormwater (5)	Paper II
Nybohov (Stockholm)	Urban residential AADT ~ 1000	Stormwater (3)	Paper II
Heden (Gothenburg)	Centrally located open space	Snow deposit (1)	Paper I
Vallhamra (Gothenburg)	Suburban parking area	Snow deposit (1)	Paper I
Delsjön (Gothenburg)	Urban background, open-air recreation area	Snow (1)	Paper I

[a] Annual average daily traffic. Reported as the number of vehicles including motorcycles, cars and trucks.

Figure 5. *From left to right: automatic sampler used for flow-weighted stormwater sampling (photo from ISCO); core sampler used for sediments in Gårda; snow sampling in Järnbrott; and road dust collection in Gårda.*

Analyses of APs, BFRs, CPs, PFCs, PAHs and phthalates in stormwater, snow and sediment were performed by commercial laboratories (see Papers I and II for details of the analytical procedures). All analyses, except phthalates in sediment from Gårda and in stormwater, and CPs in snow, are accredited by Swedac (The Swedish Board for Accreditation and Conformity Assessment).

4.2 Screening of organic contaminants in snow (Paper I)

In the non-target screening of contaminants in snow, the identification of the most abundant substances was obstructed by the large number of peaks and the occurrence of an unresolved complex mixture (UCM) in the chromatograms. It should be noted that the non-target screening of road dust showed similar results (not reported). This implies that the snow and the road dust samples contained a multitude of different compounds, presumably of anthropogenic origin, and that these matrices may act as effective passive samplers of organic contaminants in urban environments. However, to successfully identify and quantify specific pollutants in a non-target screening of urban snow and dust, further fractionation and clean-up steps are necessary.

All analyzed compounds were found at detectable concentrations in the target screening of urban snow (Figure 6, more details in Figure 2 in Paper I). The HMW phthalates DEHP, DIDP and DINP, NPs and OPs were detected more frequently than BFRs, CPs and PFCs. Nonylphenol, octylphenol, DEHP, PAHs, and PBDEs were repeatedly found in concentrations exceeding the European environmental quality standards (EQS) for priority substances, expressed as annual average (AA) and maximum allowable concentration (MAC) in surface water (Directive 2008/105/EC). The screening confirmed that APs and phthalates are relevant to studies of organic substances in urban runoff.

The analytical detection limits (d.l.) of CPs were 0.20–5.0 µg/l (the higher value in one sample with large matrix effects), whereas reported concentrations found in natural waters are in the nanogram-per-liter range (Bayen *et al.* 2006; Feo *et al.* 2009). For the flame retardants HBCDD and TBBPA, the detection limits (up to 0.10 µg/l) were also presumably too high

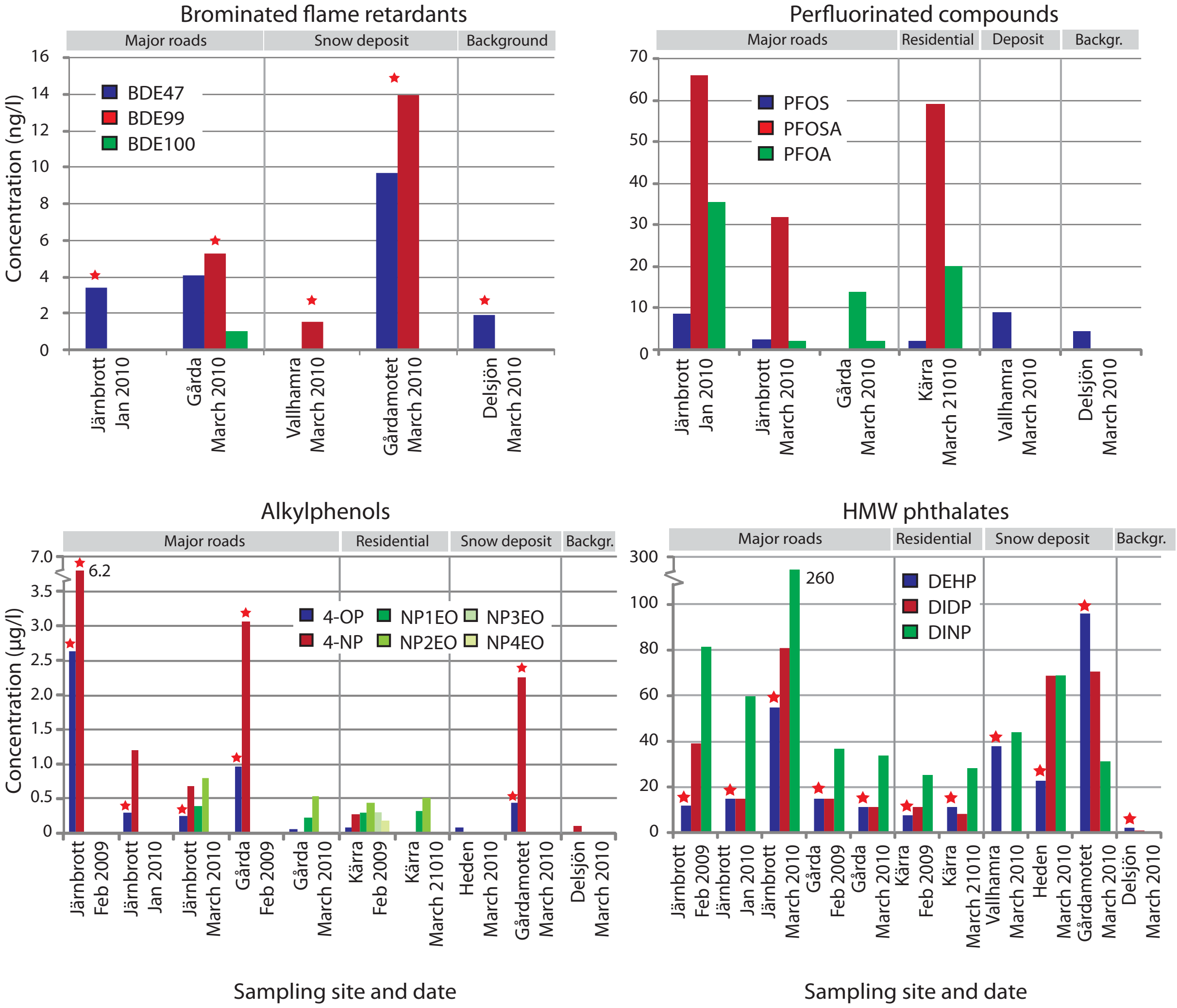


Figure 6. *Detected concentrations of brominated flame retardants (top left), perfluorinated compounds (top right), alkylphenols (bottom left) and HMW phthalates (bottom right) in snow. Concentrations exceeding the European environmental quality standards are marked with a red star.*

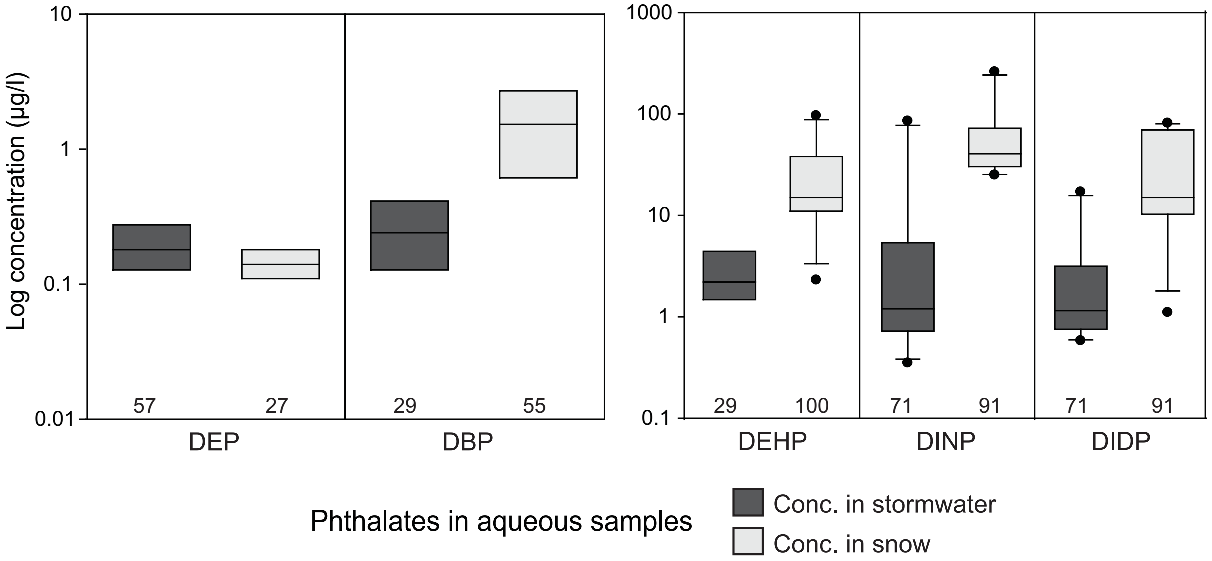
compared to expected environmental concentrations (Remberger *et al.* 2002; Law *et al.* 2008), and the substances were below the d.l. in all snow samples. Elevated detection limits – occasionally one magnitude higher for APs, BFRs, CPs and phthalates – were seen in several samples. According to the analyzing laboratories, this was due to strong matrix effects. The sampled snow contained high levels of suspended solids and an oily film was commonly observed in the thawed samples, which is likely to have caused the elevated detection limits.

4.3 Phthalate and alkylphenol concentrations in stormwater, snow and sediment

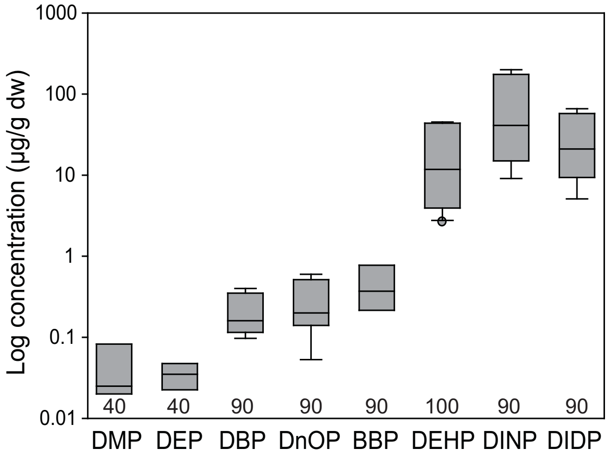
The concentrations of phthalates and alkylphenols measured in stormwater, snow and sediment are shown as box-and-whisker plots, indicating the detected minimum and maximum concentrations, the lower, median and upper quartile, and possible outliers. See also Papers I and II for measurement data.

4.3.1 Phthalates

The HMW phthalates DEHP, DINP and DIDP were generally detected at concentrations at least one magnitude higher than the LMW phthalates DEP and DBP in stormwater, snow and sediment (Figure 7). For aqueous samples (snow and stormwater, including non-detects), the range and the median concentration for DEHP were <d.l.–96 and 2.3 µg/l, respectively. The corresponding concentrations for DINP were <d.l.–260 and 5.0 µg/l, respectively, and for DIDP <d.l.–81 and 1.5 µg/l, respectively. Other phthalates detected in aqueous samples were DMP (detected in three stormwater samples at 0.13–0.23 µg/l; <d.l. in all snow samples); DnOP (detected in one stormwater sample at 0.16 µg/l; one snow sample at 1.2 µg/l); and BBP (detected in one stormwater sample at 0.15 µg/l; three snow samples at 0.19–0.88 µg/l). The HMW phthalates were detected more frequently than the LMW phthalates in all three matrices, with the exception of DEHP in stormwater (Figure 7). The d.l. for DEHP in stormwater was 1 µg/l, compared to 0.1 µg/l for all other phthalates, which may explain the lower detection frequency for DEHP. The median of the detected concentration of DEHP in stormwater is higher than for DINP and DIDP, but this may be explained by the small DEHP data set. In all three matrices, DINP were found in the highest concentrations.



Phthalates in aqueous samples



Phthalates in sediment samples

Figure 7. *Detected concentrations of phthalates in stormwater (n = 14), snow (n = 9) and sediment (n = 10) sampled in Gothenburg and Stockholm. The number below the box denotes the detection frequency, expressed as a percentage.*

Table 4. *Concentration ranges (medians) [µg/l] of selected phthalates in stormwater and snow from Gothenburg and Stockholm, and reported levels from other studies.*

Matrix	DBP	DEHP	DINP	DIDP	Reference
Urban snow	<1.0–3.9 (0.29)	2.3–96 (15)	<1.0–260 (37)	<dl–81 (15)	Paper I
Stormwater	<0.1–0.45 (<0.1)	<1–5.0 (<1)	<0.1–85 (0.87)	<0.1–17 (1.0)	Paper II
Stormwater	<dl[a]–0.27 (0.10)	0.45–24 (3.9)	0.22–23 (7.4)	<dl –9.9 (<dl)	Clara *et al.* (2010)
Stormwater	<dl–1.6 (1.1)	1.3–30 (17)			Boutrup and Plesner (2001)
Stormwater	1.3[b]	32[b]			Kjølholt *et al.* (1997)
Stormwater	0.5–11	7–39			Makepeace *et al.* (1995)
Stormwater		15–61 (30)			Zgheib *et al.* (2011)
Influent/ effluent ww	3–9; <dl–4	32–122; 2–8			Marttinen *et al.* (2003)
Influent/ effluent ww[c]	15–24 (20)[b]; 1.8–2.7 (2.4)[b]	53–84 (72)[b]; 2.1–9.9 (4.9)[b]			Roslev *et al.* (2007)
Influent/ effluent ww	<dl–8.7 (0.76); <dl–2.4 (0.34)	3.4–34 (18); 0.08–6.6 (0.50)			Clara *et al.* (2010)

[a] <dl = below the detection limit; [b] Mean concentrations; [c] Wastewater

The European environmental quality standard (Directive 2008/105/EC) for DEHP in surface water (both AA and MAC 1.3 µg/l, no standards for other phthalates) was exceeded in all snow samples, including the background sample from Delsjön, and in all four stormwater samples where DEHP was detected. The Canadian freshwater quality guidelines for the protection of aquatic life (CCME 2007) were not exceeded for DBP (16 µg/l) in any aqueous samples, whilst the CCME guideline for DEHP (19 µg/l) was exceeded in four snow samples.

Concentrations of DEHP in stormwater from Gothenburg and Stockholm are comparably lower than concentrations found in other studies of urban runoff (Table 4). Historically, DEHP has been used in large quantities worldwide, and it has often been detected in aquatic environments at high concentrations compared to other phthalates (Marttinen *et al.* 2003; Vethaak *et al.* 2005; Huang *et al.* 2008). The comparably low concentrations of DEHP and the high concentrations of DINP found in the current study are most likely a result of the consumption pattern of phthalates in Sweden (Figure 3). A screening of phthalates in the Swedish environment (Palm Cousins *et al.* 2007) showed that DEHP, DINP and DIDP occurred at comparable concentrations in urban lake sediments (Table 5). The authors concluded that the phthalate distribution in the sediments corresponded to the phthalate usage pattern five years prior to sampling. Similar results were found when the phthalate distribution in sediments from the Gårda facility was compared with Swedish consumption statistics for phthalates (Paper II). Among the LMW phthalates, DBP is often detected at the highest concentrations (Vethaak *et al.* 2005; Zeng *et al.* 2008). The DBP concentrations in stormwater from Gothenburg and Stockholm are generally lower than concentrations found in other studies (Table 4). Dibutyl phthalate has been the most used LMW phthalate, although its production shows a clear decreasing trend (KemI 2010).

Table 5. *Concentration ranges (medians) [µg/g dw] of selected phthalates in road dust and sediment from Gothenburg, and reported levels from studies of sediment and sludge.*

Matrix	DBP	DEHP	DINP	DIDP	Reference
Road dust	<0.10–0.16 (0.12)	2.8–14 (7.6)	<5.0–41 (15)	<5.0–21 (9.4)	
Sediment	0.30–0.40 (0.35)	25–48 (47)	87–200 (180)	31–66 (58)	Paper II
Lake sediment		0.02–37 (2.7)			Sternbeck *et al.* (2003)
Urban lake sediment		1.2–2.8 (1.9)	2.0–3.2 (2.0)	1.2–3.4 (1.5)	Palm Cousins *et al.* (2007)
Primary / secondary sludge	0.65 / 0.16	61 / 3.5			Fauser *et al.* (2003)
Sewage sludge	<dl[a]–4	91–200			Marttinen *et al.* (2003)
Sewage sludge		36–80 (46)	38–65 (51)	15–51 (21)	Palm Cousins *et al.* (2007)
Dewatered sludge	1.0–1.4 (1.2)[b]	61–78 (67)[b]			Roslev *et al.* (2007)
Sewage sludge	0.27–1.2 (0.64)	20–29 (26)			Clara *et al.* (2010)

[a] <dl = below the detection limit; [b] Mean concentrations

Current studies by Clara *et al.* (2010) show DBP, DEHP, DIDP and DINP concentrations in runoff in Austria which are in the same range as concentrations found in stormwater from Gothenburg and Stockholm (Table 4). The median and maximum levels of DIDP and DINP in snow are, however, generally one order of magnitude higher than concentrations reported by Clara *et al.* (2010). Other studies of phthalates in urban snow have not been found, although concentrations of PAHs found in the screening of snow are generally within the range of other snow studies (Paper I). Reported levels of DBP and DEHP in wastewater are comparable to the concentrations found in stormwater and snow in Gothenburg and Stockholm (Table 4).

The DBP concentrations found in road dust and sediment in Gothenburg are comparable to levels found in lake sediment and sewage sludge worldwide (Table 5). Urban lake sediments from Stockholm (Palm Cousins *et al.* 2007) show DEHP, DIDP and DINP concentrations that are one magnitude lower than most reported concentrations in sediment and road dust from Gothenburg (Table 5). However, DEHP concentrations found in another sediment study from Stockholm (Sternbeck *et al.* 2003) are of the same magnitude as those detected in Gothenburg. Sediments from a stormwater pond located in Järnbrott, studied by Strömvall *et al.* (2006), showed a DEHP concentration of 23 µg/g dw ($n = 1$), and in a study of stormwater sediments in Stockholm, the maximum DEHP concentration analyzed was 98 µg/g dw (Wahlberg and Wistrand 2006). These studies indicate that the Gårda catchment does not exhibit extreme DEHP concentrations in sediments.

Sewage treatment plants represent a significant source of plasticizers in the environment. Results from the current study indicate that urban runoff may be equally important – in terms of concentrations – as sewage effluents as a source of phthalates in the aquatic environment (Table 4). In addition, reported concentrations in sewage sludge are comparable to the concentrations found in urban sediments in Gothenburg (Table 5).

4.3.2 Alkylphenols

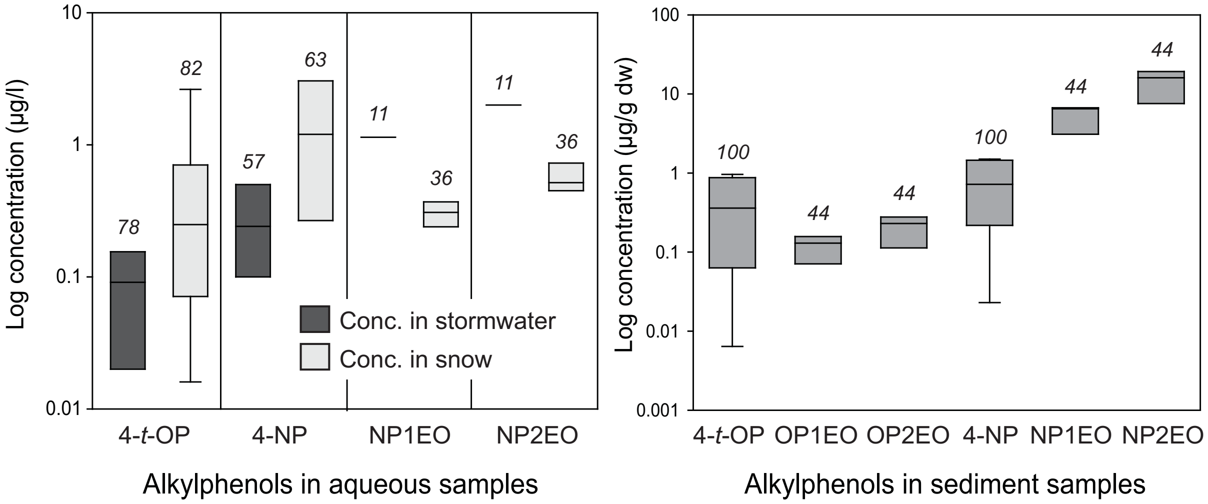


Figure 8. *Detected concentrations of alkylphenols in stormwater (n = 14 for 4-NP, n = 9 for other compounds), snow (n = 11) and sediment (n = 9) sampled in Gothenburg and Stockholm. The number above the box denotes the detection frequency, expressed as a percentage.*

In water, snow and sediment, 4-*t*-octylphenol, 4-nonylphenol and ethoxylates including up to six EO units were determined. 4-nonylphenol was generally found in higher concentrations than 4-*t*-octylphenol in all matrices (Figure 8). The most frequently detected AP in all matrices was 4-*t*-OP, followed by 4-NP, NP1EO, NP2EO, OP1EO and OP2EO, the latter two being detected in only one aqueous sample. The NPEOs were detected at concentrations that occasionally exceeded and occasionally were below the 4-NP concentrations. Nonylphenol triethoxylate was detected in one stormwater sample from Gårda (at 0.053 µg/l) but ethoxylates with four or more EO units were not detected in any samples.

The European environmental quality standard (Directive 2008/105/EC) for OP in surface water (AA and MAC 0.1 µg/l) was exceeded in two stormwater samples, both from Gårda, and in five snow samples. The AA and the MAC for NP (0.3 and 2.0 µg/l, respectively) were exceeded in three and none of the stormwater samples and in five and three of the snow samples, respectively. The Canadian freshwater quality guidelines for the protection of aquatic life (CCME 2007) for NP and its ethoxylates (1.0 µg/l) was exceeded in three stormwater and five snow samples.

Nonylphenols are used in larger amounts than OPs, and the trend of higher NP than OP concentrations has been observed in environmental matrices worldwide (Bennie *et al.* 1997; Mayer *et al.* 2007; Céspedes *et al.* 2008). The insignificant use of OPEOs compared to the parent compound OP (Brooke *et al.* 2005) may explain the low occurrence of OPEOs in all samples. Nonylphenol ethoxylates are used in large quantities in a variety of applications, and it is somewhat surprising that the NPEOs are not detected frequently in either of the sampled matrices. This may be a result of degradation into shorter ethoxylates and nonylphenol or inadequate analyses. As discussed in Paper II, NPEOs containing between six and twelve EO units are commercially the most significant ethoxylates (ECB 2002a). The water solubility of the APEOs increases with the number of EO groups; ethoxylates with EO>5 are considered

Table 6. *Concentration ranges (medians) of alkylphenols in aqueous samples [µg/l], road dust and sediment [µg/g dw] from Gothenburg and Stockholm, and reported levels in sediment and sludge. More references can be found in e.g. Soares et al. (2008).*

Matrix	**4-*t*-OP**	**OP1EO**	**OP2EO**	**4-NP**	**NP1EO**	**NP2EO**	**Reference**
Urban snow	<dl–2.6 (0.08)	<dl	<dl	<dl–6.2 (0.27)	<dl–0.38 (<dl)	<dl–0.79 (<dl)	Paper I
Stormwater	<dl–0.35 (0.03)	<dl–0.05 (<dl)	<dl–0.08 (<dl)	<dl–1.2 (0.10)	<dl–1.1 (<dl)	<dl–2.0 (<dl)	Paper II
Road dust	0.01–0.43 (0.11)	<dl	<dl	0.02–0.79 (0.39)	<dl	<dl	
Sediment	0.36–0.96 (0.88)	0.06–0.16 (0.13)	0.09–0.28 (0.23)	0.72–1.5 (1.5)	2.0–6.7 (6.5)	5.1–20 (16)	Paper II
Lake sediment	<dl[a]–0.14			0.07–5.3			Sternbeck *et al.* (2003)
Pond sediment	0.16	0.05	0.01	3.1	5.3	1.5	Strömvall *et al.* (2006)
Primary/secondary sludge				12/0.19	39/1.3		Fauser *et al.* (2003)
Sewage sludge	1.9–9.0			20–190	60–90[b]		Céspedes *et al.* (2008)
Sewage sludge	7.5			170	140		Petrovic *et al.* (2008)

[a] <dl = below the detection limit; [b] Sum-concentration of NP1EO and NP2EO.

water-soluble whereas the lower APEO oligomers are hydrophobic and partition to particulate matter (Ahel and Giger 1993b). This means that the analyses of NPEOs (including NP1EO–NP6EO) in water do not succeed in detecting the most commercially significant, and the most hydrophilic, ethoxylates. A study by Shang *et al.* (1999) revealed that the most frequently reported NP, NP1EO and NP2EO made up less than half of the sum-concentrations of total nonylphenolic compounds in marine sediments. The NP3EO–NP20EO made up the remaining half, which suggests that the total NPEO concentration is often underestimated by a factor of 2. However, Ferguson *et al.* (2001) found that NP4–15EOs made up only 8.5% of the total measured NPEO concentration in marine sediments. The predominant occurrence of NP and shorter NPEOs was suggested to be a result of degradation of long-chain NPEOs prior to deposition in the marine environment. This suggests that the analyses of nonylphenolic compounds in stormwater, snow and sediment only succeed in detecting an unknown portion of the total concentration of nonylphenolic compounds. The inclusion of NPEOs with more than six EO units in the analysis is desirable, especially for the aqueous samples. Studies on the analysis of long-chain ethoxylates are beginning to appear (Loyo-Rosales *et al.* 2007a; Loyo-Rosales *et al.* 2007b; Céspedes *et al.* 2008). Most current reports, however, include ethoxylates with one and two EOs, and analysis of NPEOs with more than six EOs are at present not offered by many commercial laboratories.

Kjølholt *et al.* (1997) and Boutrup and Plesner (2001) have reported NP levels in stormwater from Denmark (sum of NP, NP1EO and NP2EO, mean concentration 5.7 and 3.3 µg/l, respectively) that are in the same range as concentrations found in snow, and in one stormwater sample from Gårda (Table 6). In the study by Boutrup and Plesner (2001), 4-*t*-OP and NPEOs with three to fifteen EO units were below the d.l. in all samples (n = 3). More recent studies from Denmark (Miljøstyrelsen 2006) show 4-NP concentrations in stormwater that are in the same range (<d.l.–0.4 µg/l, mean 0.2 µg/l, n = 9) as found in Stockholm and

Gothenburg (Table 6). Studies by Zgheib *et al*. (2011) showed NP and 4-*t*-OP concentrations in stormwater from the Paris area ranging between 1.6–9.2 and 0.11–0.26 µg/l, respectively. No studies of APs in urban snow have been found. Sediment from a stormwater pond in Gothenburg (*n* = 1, Strömvall *et al.* [2006]) and from lakes around Stockholm (Sternbeck *et al.* 2003) show AP concentrations that are comparable to the levels found in urban sediments (Table 6). In summary, concentrations of APs detected in Gothenburg and Stockholm are comparable to levels found in other studies of runoff. However, the levels of APs found in aqueous samples are comparably lower than most reported concentrations found in sewage water (Fauser *et al.* 2003; Céspedes *et al.* 2008; Soares *et al.* 2008). Similarly, higher AP concentrations have been observed in sewage sludge compared to stormwater sediment and road dust from Gothenburg (Table 6). Sewage treatment plants have been identified as a major source of APs in the aquatic environment and studies have reported elevated levels of APs in sediments close to treatment plant effluents (Ferguson *et al.* 2001; Soares *et al.* 2008).

4.3.3 General trends in the data

Variations in pollutant concentrations between samples

Stormwater EMCs and snow concentrations of 4-*t*-OP, 4-NP and the HMW phthalates DEHP, DIDP and DINP vary by up to two orders of magnitude in samples from the same site. This trend has also been observed for e.g. metals and nutrients in stormwater and snow (Butler and Davies 2004; Herbert *et al.* 2006; Kayhanian *et al.* 2007) and is suggested to be due to varying wet and dry weather factors and land use characteristics. Studies have demonstrated the difficulty of predicting stormwater quality in relation to weather characteristics (Egodawatta *et al.* 2007; Kayhanian *et al.* 2007) and in the current study there was no correlation between pollutant concentrations and e.g. rain level and intensity, and antecedent dry period. The quality of urban snow depends on factors such as traffic load, snow-handling practices and time of the year (Reinosdotter and Viklander 2005). Consequently, pollutant concentrations from different years or sites may not be comparable due to different climatic conditions, snow-handling activities and factors such as changes in traffic intensity. In addition, the generation of pollutants in roadside snow and snow deposits is very different and not directly comparable.

The size of the data set does not allow testing for significant differences in pollutant concentrations between sites. However, the data indicate a trend with higher phthalate and alkylphenol concentrations in stormwater and sediment from Gårda than from the other sites. The detection frequencies are also higher in samples from this area. In addition, higher concentrations of DEHP, DIDP and DINP were found in road dust and stormwater sediments from Gårda than in urban lake sediments in Stockholm (Palm Cousins *et al.* 2007). Studies have shown that traffic intensity is often correlated positively with pollutant concentrations in urban runoff (see e.g. Glenn III and Sansalone [2002]; Opher and Friedler [2010]) and a substance flow analysis has shown that traffic is an important source of alkylphenols and phthalates in the urban environment (Chapter 5, Paper III). It is thus suggested that the high traffic intensity in Gårda caused the elevated alkylphenol and phthalate levels in this area.

Pollutant concentrations in different matrices

In this study, the pollutant concentrations in snow are generally higher than in stormwater (Figure 7 and 8); a trend regularly observed in studies of urban runoff quality (Oberts *et al.* 2000; Westerlund *et al.* 2003). The residence time of the snow pack can be up to several months, during which the snow may act as storage for pollutants. During non-winter periods, the pollutant accumulation time may be shorter between washoff events which generally leads to smaller event loads. Additionally, cold periods give rise to increased emission of certain pollutants due to heating, cold starting of engines, and increased tire and road wear resulting from of studded tires and the use of road salt and sand (Oberts *et al.* 2000). This increase in wear and tear particles may lead to higher loads of phthalates and alkylphenols during winter periods although this hypothesis has not been verified.

The road snow samples were collected from the top layer of the snow banks in close proximity to the road. This is assumed to represent a worst-case scenario since this snow is highly exposed to traffic-related emissions. Reinosdotter *et al.* (2006) found that approximately 50% of the total amounts of PAHs were found in the snowpack within one meter from the road. Higher molecular weight PAHs tend to partition to particles, which are deposited not far from the roadway. The same behavior is expected for other substances with similar properties, e.g. phthalates, NP and OP. Additionally, degradation of alkylphenols and phthalates in the snowpack is suggested to be limited due to the negligible photolysis of these substances and reduced biodegradation at low temperatures. Consequently, the elevated levels of phthalates and alkylphenols found in urban snow compared to levels in stormwater are most likely due to a longer pollution accumulation time in the snow pack, an increase in pollutant emissions during cold periods, limited degradation, and the direct exposure of the roadside snow to traffic-related emissions.

4.3.4 Phthalate and alkylphenol loads

Pollutant loads were estimated using phthalate and nonylphenol concentrations in sediment from the Gårda treatment facility, the sediment mass, and the removal efficiency of PAHs and suspended solids in the facility, measured by Pettersson *et al.* (2005). Surface runoff from the Gårda catchment area either passes this tank system or, in case the tanks are full, is discharged directly to the receiving water through an overflow pipe. Both these flows can be measured and sampled, which facilitates the estimation of pollutant mass balances in the catchment area.

The estimated annual unit area loads for the Gårda catchment area vary from less than a gram per impervious ha for the LMW phthalates, to over a hundred grams for NP2EO and up to over a kilogram for DINP (Figure 9, more details in Paper II). The annual fluxes in the catchment area are approximately 4.4 kilograms of total phthalates, 430 g of nonylphenolic compounds and 23 g of octylphenolic compounds.

The loads are efficient for illustrating the fluxes of pollutants in an urban catchment. The load of pollutants in Gårda is expected to be higher than in the other urban areas studied, as the maximum concentrations of several of the compounds were detected in Gårda. Although a comparison of loads from Gårda and from the residential areas studied would have been interesting, there was no convenient way of calculating loads from the residential areas. The

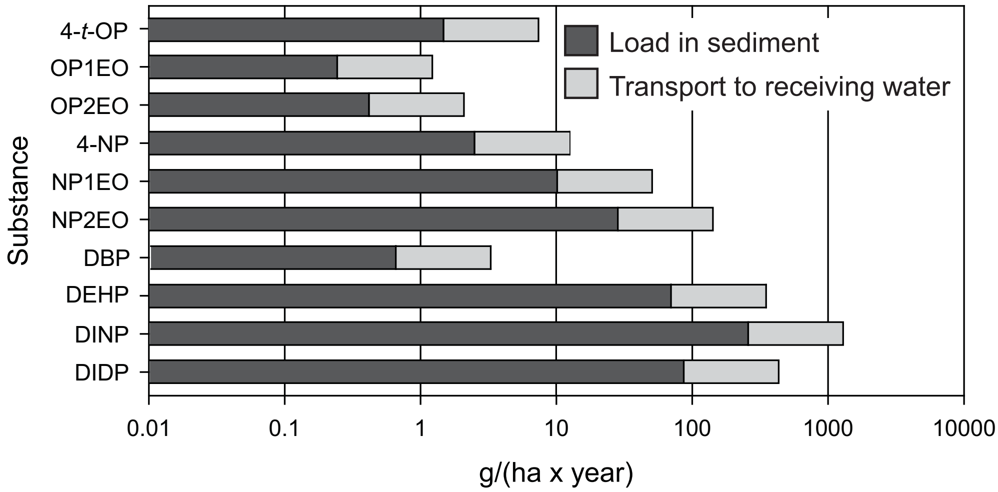


Figure 9. *Estimated annual loads (expressed as g per impervious ha) in the Gårda catchment area. The load transported to receiving waters is assumed to be 80% for all substances.*

use of EMC or SMC for load calculations was regarded as being too uncertain because of the small number of sampled events. It may, however, be possible to use measurements of road dust to estimate loads. If a mass per surface unit (e.g. [mg/m^2]) can be determined, this could be multiplied by the area to obtain a load that represents the entire road or catchment area.

4.4 Quality assessment of water, snow and sediment data

Estimation of the magnitude and identification of the factors influencing uncertainties are necessary when water and sediment quality data are to be used for environmental assessment, management purposes and modeling (Harmel *et al.* 2006; Harmel *et al.* 2009). Sample handling and laboratory analysis are commonly in focus in quality assessment and control studies. However, each step in the acquisition of quality data – flow measurements, sample collection, sample storage and handling, and analysis – may contribute to the cumulative uncertainty in data. Uncertainty budgets for influencing factors are effective in identifying the major contributions to the overall uncertainty of collected water and sediment quality data. Uncertainty budgets for flow measurements, sampling, storage, analysis and data processing have been reported by, for example, Harmel *et al*. (2006; 2009) and McCarthy *et al*. (2008). Since uncertainty data were not available for all individual sources of uncertainties, such as flow measurements, sample collection and storage, no uncertainty budget has been set up for the current study. However, the factors influencing data accuracy are discussed below.

4.4.1 Sampling

Pollutant concentrations in stormwater differ between sites and events; a sampling campaign of runoff should therefore consider both spatial and temporal variabilities in pollutant fluxes (Ahyerre *et al.* 1998). In this study, stormwater was sampled during spring and autumn in 2006 from three urban sites, and snow was collected during two winter seasons. Sediment is accumulated over longer time periods, and the temporal variability of sediment quality is assumed to be less pronounced than for stormwater. In total, 14 stormwater, 11 snow and 10 sediment samples were collected. The analyses of alkylphenols and phthalates are more costly than, for example, metal analyses and this is an important limiting factor in organic contaminant monitoring campaigns.

Flow-weighted sampling is considered to be the most appropriate technique for determining EMCs and loads in stormwater, as it represents the entire storm event (Harmel *et al.* 2003; Ma *et al.* 2009). Grab samples represent an instantaneous concentration within a storm event and time-weighted sampling may underestimate loads in case pollutant peaks are not sampled. Passive samplers can be used for monitoring of long-term trends of contaminants and for identifying pollutant sources in water (Allan *et al.* 2006). The technique is based on the principle of a concentration gradient; the compounds move from high concentrations (the water phase) to low concentrations (the sampling device). The passive samplers provide time-averaged concentrations and have successfully been used for both metals (Blom *et al.* 2002) and organic compounds (Allan *et al.* 2009), but are still not frequently used for stormwater monitoring.

Flow-weighted sampling is performed using automated samplers. For these samplers, a minimum flow threshold at which sample collection begins and a flow interval for each subsample need to be set. Studies have shown that a high flow threshold introduces large errors (Harmel *et al.* 2003). On the other hand, a low threshold increases the number of samples collected, which may exceed the sampler capability during larger storm events. The sampling programs used for collecting stormwater in Gothenburg and Stockholm were based on previous campaigns (see e.g. Ahlman [2006]) and were shown to capture a majority of the rain events at the sites.

Uncertainty budgets presented by Harmel *et al.* (2009) and McCarthy *et al.* (2008) showed that flow measurements gave rise to a substantial part of the total uncertainties in stormwater quality data. Uncertainties in flows depend on the measuring equipment and the flow magnitude and vary considerably between studies. In Gothenburg and Stockholm, water flows have been measured based on area/velocity flow conversions. The velocity is measured using the Doppler effect; a frequency shift is recorded when an ultrasonic signal is reflected by suspended particles or gas bubbles in motion in the water phase (Teledyne Isco Inc. 2007). The number of particles in the water can affect the uncertainty of the velocity measurement as too few or too many particles may interfere with the acoustic signal (Yorke and Oberg 2002). Incorrect water level readings due to disturbed flows or water levels below the minimum level measurement range also influence the flow accuracy but can be avoided through careful placement of the meter (Teledyne Isco Inc. 2007; Blake and Packman 2008). Unsteady flows, most likely due to incorrect recording of water levels, were observed in Kärra whilst measurements from the other sites showed steady flows. To evaluate the accuracy of measured flows and volumes, these were compared with calculated runoff volumes using the rational method (Butler and Davies 2004). All sites showed reasonable measured water volumes, except some events in the Gårda area where the flows were overestimated. This may be due to incorrectly calibrated and registered water levels and velocities, and underestimated baseflows. The collection of subsamples, however, was evenly distributed according to the flow and it was concluded that the samples from Gårda were collected proportionally to the flow.

Since 4-NP, 4-*t*-OP, lower APEOs and most phthalates are lipophilic and tend to partition to particulate matter, it is important that field sampling and analysis include both water and particles. Measurements of suspended solids generally show larger uncertainties than dissolved constituents, which are better mixed in the stormwater flow (McCarthy *et al.* 2008). Studies show that automatic samplers are not able to consistently collect larger particles and bedload material (Burton and Pitt 2002; Li *et al.* 2005; Gulliver *et al.* 2010), and typically give rise to sampling uncertainties of around 20–25% for solids concentrations. Sampling of smaller and more turbulent flows, e.g. at outfalls, and simultaneous sampling of the water column and the bedload, may reduce the uncertainties in solids concentrations.

Sampling of sediments is assumed to include fewer errors than the flow-weighted water sampling as the grab samples of sediment were collected manually (low equipment failure). Three sediment core samples were collected from each chamber in the Gårda sedimentation facility and these were mixed thoroughly before being placed in the sample containers. The road sediment was collected from a delimited stretch of the road. An effort was made to collect both large and fine particles in the road dust. The very fine particles, however, are difficult to collect since the particles may either stay attached to the road surface or swirl up during sample collection. Roadside snow used in the screening of organic contaminants was grab-sampled from the surficial layers of the snow pack, in direct proximity to the roads. Grab sampling of snow requires little equipment and preparation, which means low sampling costs. The grab samples represent the instantaneous pollution situation at that specific sampling spot and provide no information on the vertical or horizontal pollution distribution in the snow pack.

4.4.2 Sample storage and handling

Sample handling and storage are crucial steps for accurate determination of water and sediment constituents (McCarthy *et al.* 2008; Harmel *et al.* 2009). Samples for analyses of organic substances must be placed dark and cold to avoid photolysis and biodegradation and care must be taken to avoid contamination of the sampling equipment. Phthalate analysis is notorious for contamination problems since the plasticizers are used in a number of materials found in laboratories (Fankhauser-Noti and Grob 2007; Reid *et al.* 2007). No materials or products known to contain, or suspected of containing, alkylphenols or phthalates were used during sampling and sample treatment. Teflon tubing was used in the automatic water samplers, and water, snow and sediment samples were collected in glass bottles or stainless steel containers that had been thoroughly washed. The samples were kept cold and in the dark and were analyzed as soon as possible.

4.4.3 Analysis

Since both nonylphenolic compounds and phthalates tend to partition to particles in water, the analyzing laboratories were instructed explicitly to include the particles in the analyses of aqueous samples. An inter-laboratory comparison, performed by Wahlberg and Wistrand (2006), showed that reported 4-NP and DEHP concentrations vary up to 40 and 160 times, respectively, for the same sample analyzed at different laboratories. This may be explained in part by the difficulty receiving homogeneous samples, in terms of particles, for the different laboratories. It may also be due to inclusion or exclusion of particles during sample extraction. If only dissolved contaminants are analyzed in stormwater, reported concentrations of alkylphenols and phthalates may underestimate the total concentrations in the stormwater compartment. However, the inclusion of particles in sample extraction and analysis may lead to an increase in matrix effects, which affect detection capability, repeatability or accuracy. Wastewater samples are known for showing substantial matrix effects and elevated detection limits were reported for all substance groups in the snow deposit samples. The high detection limits of the compounds studied, compared to expected levels in the environment, lead to many non-detects. In addition, the fluctuating detection levels may give rise to faulty summary statistics, such as median and correlation, and consequently render sample comparison difficult. This has previously been discussed by Coquery *et al.* (2005), who concluded that analysis of unfiltered water samples containing solids will provide low representativeness of the contamination in the sample and poor comparability between data from different laboratories. There is also a large risk of underestimating pollutant concentrations, especially for hydrophobic substances, in samples with high concentrations of solids. The solution to this problem could be to filter the sample and analyze the water and the solid phase separately, as presented by Zgheib *et al*. (2011). To obtain sufficient solid material would most likely require large water volumes, which in turn will affect the sampling program for the automated stormwater sampling.

The analyzing laboratories involved in the current study are accredited for all analyses used, except chlorinated paraffins in snow and phthalates in stormwater. For the accredited analyses, control programs need to be followed to accept the result data and the uncertainties of the measurements are reported. For organic contaminants in stormwater, snow and sediment, the reported expanded uncertainties are between 10 and 30%. The lowest uncertainties are reported for PAHs in snow, and the highest for APs in water. It should be noted that the analyzing laboratories did not report uncertainties for all analyses.

4.5 Choice of matrix to study

This study presents the occurrence of alkylphenols and phthalates in three different urban matrices, all relevant to the quality of receiving waters. Each of these matrices presents advantages and disadvantages when it comes to sampling, analysis and relevance in the assessment of water quality and effects (Table 7). The purpose of the study and the use of the outcomes of the study are crucial for determining which matrix is the most relevant to study.

Table 7. *Summary of the major advantages and disadvantages of sampling and analysis of different matrices relevant to the current study.*

	Advantages	**Disadvantages**
Automated flow-weighted sampling of stormwater and snowmelt	+ Collected samples represent the entire hydrograph. Recommended for stormwater sampling as it introduces smaller errors than grab and time-weighted sampling. + Can be used directly for determining EMCs. As environmental quality standards and toxic effects data are based on concentrations, the EMC can be used for assessing the quality and impact of runoff on aquatic ecosystems. + Data on intra-event variations in water quality can be achieved through separate analysis of subsamples. May be used, for example, for the design of end-of-pipe management facilities, which are often based on the assumption that a first flush occurs.	– Requires installation and maintenance of sampling equipment. Equipment failure and malfunction may occur. – Calibration and verification of flow thresholds, flow measurements, water levels etc. are crucial for minimizing sampling uncertainties. – Larger errors have been observed for measurements of suspended solids than for dissolved constituents. Will introduce errors in the quantification of pollutants attached to particles.
Grab sampling of snow	+ Minimum preparation and equipment required, which means low cost and low equipment failure. + Snow acts as a passive sampler during winter and may be used for studying pollutant generation over a long time period. + High pollutant loads can be expected in the snow pack, especially in "older" snow. Snow may therefore be useful for monitoring the occurrence of contaminants expected to be found in low concentrations. This can be advantageous in qualitative studies of pollutants, such as screening studies.	– Inconsistency in collection between sites and events. – The nature of snow is very heterogeneous and concentrations of pollutants may vary considerably over relatively small horizontal and vertical scales. – Instantaneous reflection of the pollutant fluxes in the snow pack. Regular and continuous sampling of snow during the entire snow period is necessary to obtain reliable results on the pollutant situation if used for quantification rather than screening.
Sediment sampling	+ See grab sampling of snow. + Convenient for calculating pollutant loads, as in Gårda. Road dust may be used for estimating the load from an entire road or catchment area.	– Water-soluble substances are not included. – Not as relevant as water quality for assessing the effects on receiving waters.

5 IDENTIFICATION AND QUANTIFICATION OF SOURCES

Identification and quantification of sources of pollutants in runoff is crucial when choosing and applying the most efficient management practices to reduce pollution of urban waterways. Efforts have been made on different scales, from identification of land uses which substantially contribute to pollutant loads in receiving waters (Mitchell 2005; Park *et al.* 2009), to quantification of specific sources in urban catchments (Davis *et al.* 2001; Hjortenkrans *et al.* 2007). The land-use approach is more a tool for predicting pollutant loads (discussed more in Chapter 6) than for locating and quantifying specific sources. Land use-derived loads may be useful for planning end-of-pipe management practices, whereas identification of specific sources is essential for upstream control.

For many pollutants in runoff, such as metals and PAHs, the majority of sources have been identified. Consequently, direct measurement of the compounds in products, such as metals in tire rubber (Davis *et al.* 2001) and PAHs in used oil (Wang *et al.* 2000), can be carried out to quantify the contribution from a specific source to a total pollutant load. Alternatively, the pollutant content in runoff from various surface materials can be analyzed (Davis *et al.* 2001; Persson and Kucera 2001). However, as it is generally difficult to monitor the actual sources, source identification and quantification are commonly based on monitoring of environmental levels of pollutants. One approach is to use marker compounds to indicate emissions from specific sources, such as PAH signatures and ratios for pyro- and petrogenic sources (Larsen and Baker 2003; Jeanneau *et al.* 2008a) and anthropogenic molecular markers for sewage inputs (Dsikowitzky *et al.* 2004; Jeanneau *et al.* 2008b). Moreover, statistical tools for determining relationships between pollutants have frequently been used for source identification of, for example, metals and PAHs. These tools may include correlation matrices (Yongming *et al.* 2006; Helmreich *et al.* 2010) and multivariate methods such as principal component analysis (Harrison *et al.* 2003; Yongming *et al.* 2006) and cluster analysis (Tokalıoğlu and Kartal 2006; Yongming *et al.* 2006).

Sources of alkylphenols and phthalates in urban areas have previously not been mapped thoroughly and direct measurements of the substances in goods were therefore not considered feasible. Although the HMW phthalates could be used as marker compounds for PVC, this would not provide any information on specific sources or source apportionment in urban areas. To identify sources and quantify fluxes of alkylphenols and phthalates in urban runoff, a substance flow analysis (SFA) was considered to be the most appropriate approach.

5.1 Substance flow analysis

The aim of substance flow analysis is to provide quantitative information on important flows of a substance in a delimited system during a specified time period (van der Voet *et al.* 1995; Brunner and Rechberger 2004). The SFA can be used to quantify past, present and future flows and to identify sources. This can be useful information for setting priorities in emission control and assessing the effectiveness of such control strategies. Substance flow analysis has proved useful in describing sources and fluxes of, for example, metals in Stockholm (Sörme *et al.* 2001), solid waste and wastewater (Hansen and Lassen 2002). The SFA procedure is based primarily on three parts: definition of system boundaries in time and space, modeling of stocks and flows, and interpretation of results (van der Voet *et al.* 1995; Hansen and Lassen 2002; Brunner and Rechberger 2004). The modeling part is often performed through bookkeeping. The bookkeeping provides an overview of flows and stocks and can help identify missing flows through the application of the mass balance principle; the amount coming into a node or the entire system must be equal to the amount going out. If the mass flows are not balanced, the data need to be re-evaluated and the discrepancies identified and explained. Performing an SFA is an iterative process where new knowledge and data are added to improve the model until a satisfactory result is achieved.

The aim of the SFA in this study was to account for the fluxes of nonylphenolic compounds (NP/EOs, i.e. both 4-nonylphenol and ethoxylates of different chain lengths) and selected phthalates in an urban catchment area (Paper III) and to use this information in the development of a computer model for predicting pollutant loads in stormwater (see Chapter 6, Papers IV and V). Although the SFA methodology is acknowledged to be a labor-intensive process (e.g. Lassen and Hansen [2000]; Cui *et al.* [2010]) it can provide an extensive overview of all relevant sources and flows which many other approaches, such as use of marker compounds or statistical tools, are unable to do.

5.1.1 Procedure

For the bookkeeping part, the Gårda catchment area was chosen as a study site since the loads of phthalates and alkylphenols had been monitored there (Paper II). The system boundaries of the SFA are presented in Paper III. The general SFA method, which consists of an account of inflows, stocks and outflows, had to be modified when used for a stormwater catchment area. Traffic and building materials are considered to be static sources and the only inflow into Gårda is from atmospheric deposition. The inflows and stocks are therefore presented together as pollutant sources. Sources were mapped using statistical data on import, export, products and application areas; material safety data sheets; scientific publications; governmental and non-governmental reports; and information from manufacturers and trade organizations (Table 8). The flows were calculated by multiplying the occurrence of the source (m^2 for materials, vehicle km for mobile sources) in the system being studied (Gårda catchment area) with calculated emission factors (Table 1 in Paper III). The occurrence of sources in the catchment area was mapped through ocular inspection and using GIS tools. The emission factors describe the atmospheric deposition and the substance emission rate from products and materials. The factors were calculated using statistical information from the Swedish Chemicals Agency (KemI 1992–2006), information on the chemical content in goods, and outcomes from leaching studies (Table 8). Examples of calculations of emission factors are presented in Paper III.

Table 8. *Sources of phthalates and nonylphenolic compounds in urban outdoor environments, including the most important references used to calculate the emission factors. More details are found in Björklund et al. (2007).*

Source	Phthalates	NP/EOs
Atmospheric deposition Wet and dry fallout of substances in air	Thurén and Larsson (1990); Thomsen and Carlsen (1998); Vikelsøe *et al.* (1999; 2001); Teil *et al.* (2006)	Vikelsøe *et al.* (1999; 2001)
Roofing and cladding Coated and painted metal sheets	ECB Risk Assessments; Pastuska *et al.* (1988); OECD (2004)	Berens (1997); Saito *et al.* (2004); Andersson (2006); personal communication with experts from the polymer industry
Flexible PVC Plasticized PVC, e.g. hoses and tarpaulins	See roofing and cladding	See roofing and cladding
Other plastics Unplasticized plastics, e.g. hard PVC and polystyrene	Not relevant	See roofing and cladding
Sealant For joining facades, putty for windows etc.	ECB Risk Assessments; Nilson *et al.* (2004); personal communication with representatives from the Swedish trade organization	Nilson *et al.* (2004); Andersson (2006); personal communication with representatives from the Swedish trade organization
Concrete Air-entraining agents	Not relevant	Togerö (2006); labeling of merchandise, personal communication with representatives from the Swedish Concrete Trade Organization
Vehicles and tires Oil and chemical spillage from vehicles, vehicle components, car care products, tire wear	ECB Risk Assessments; Miljø- og Energiministeriet (1999); Johansson and Zimerson (2000); Nielsen *et al.* (2000); Gustafsson (2003); Thale *et al.* (2004); SIKA (2006)	Ahlbom and Duus (1994); Johansson and Zimerson (2000); Nielsen *et al.* (2000); Gustafsson (2003); Thale *et al.* (2004); Edeskär (2006); SIKA (2006); personal communication with the public research community, tire producers and trade organizations
Parking spaces Oil and chemical spillage from vehicles	Ahlbom and Duus (1994); Vikelsøe *et al.* (1998); Larm and Holmgren (1999); Nielsen *et al.* (2000)	See phthalates
Other human activity Heterogeneous category including e.g. shoe wear, toys and bicycle wear	ECB Risk Assessments; Almqvist and Hanaeus (2006)	See phthalates

5.1.2 Sources and fluxes of phthalates and nonylphenolic compounds

According to the calculated loads, vehicles and painted or coated roofing material were the major sources of the HMW phthalates in Gårda, while atmospheric deposition, sealants and human activity were all minor sources contributing only a few percent to phthalate emissions to stormwater (Figure 10 and Paper III). These results are in agreement with phthalate source estimations presented by Tukker *et al.* (1996), and in the European Chemicals Bureau (ECB) risk assessments. The loads of phthalates in stormwater modeled through SFA are similar to the measured loads in the Gårda catchment area (Paper II), which suggests that the most important phthalate flows in the area have been identified in the SFA. As the use of DBP and DEHP is declining while DINP use is increasing, the emission factors need to be updated to

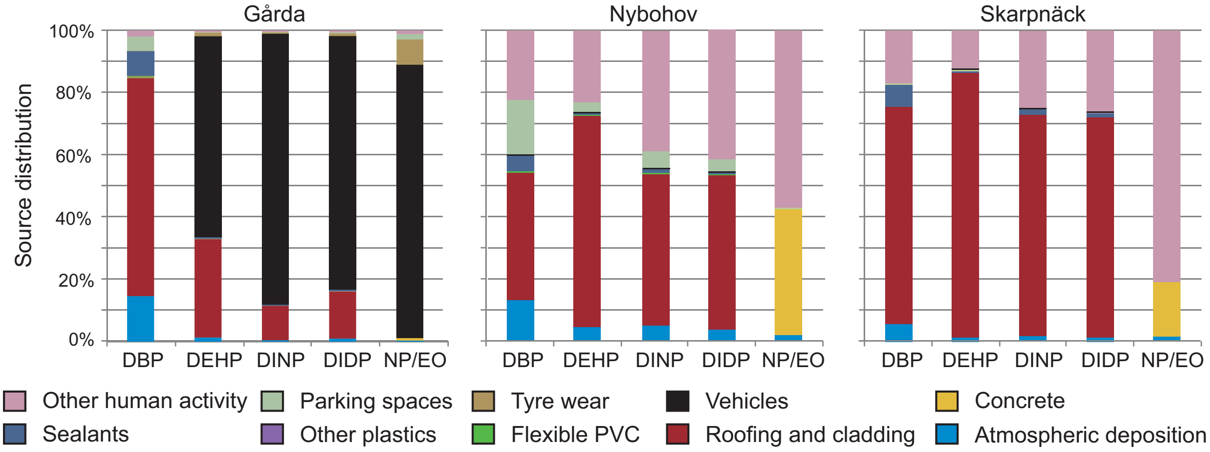


Figure 10. *Estimated source distribution of phthalates and nonylphenolic compounds in the area dominated by traffic (Gårda, left) and in the residential areas of Nybohov (middle) and Skarpnäck (right).*

reflect correctly the current stock of phthalates in goods in urban catchments. Vehicles and concrete were estimated to be the most important sources of nonylphenolic compounds in Gårda (Figure 10 and Paper III). As NP/EOs are found in low concentrations in a large number of goods, the evaluation of contributing sources is complex. The fluxes of NP/EOs correspond, however, to results for NP/EO sources in Danish stormwater, presented by Kjølholt *et al*. (2007).

The high traffic density in Gårda explains the large contribution of phthalates and NP/EOs from vehicles. When the emission factors are used to calculate loads in the residential areas of Nybohov and Skarpnäck, roofing material and concrete are identified as the most important sources of phthalates and NP/EOs, respectively (Figure 10). In addition, the category "other human activity" becomes relevant, explained by the larger number of people residing in these areas compared to Gårda. Loads of phthalates and NP/EOs have not been measured (only concentrations in stormwater) in Nybohov and Skarpnäck, hence a cross-check of calculated loads for these areas was not feasible.

The emission factors used in the SFA have also been used in the development of a stormwater quality computer model for predicting loads and identifying sources of phthalates and NP/EOs (Chapter 6, Papers IV and V). The distribution of sources in Gårda and Nybohov presented in Paper V is different from the results in Figure 10 and Paper III. This is due to the iterative nature of the SFA; in the execution of the analysis, new data and knowledge appeared and were used to recalculate the emission factors. Since the flows presented in Paper III have been cross-checked with measured loads, the source distribution in this study is considered to be more accurate than the distribution presented in Paper V. The outcomes of Paper V, however, are still relevant, as the aim of this study was to evaluate the efficiency of a hypothetical control program to reduce phthalate and nonylphenol loads. Paper V illustrates the usefulness of SFA and the developed model. The origin of pollutants is mapped and this information can serve as guidance for selecting relevant control options to reduce pollutant loads in an urban catchment area. For Gårda, it is evident that reducing traffic would be more efficient than material management to abate phthalate and NP/EO loads in stormwater, and

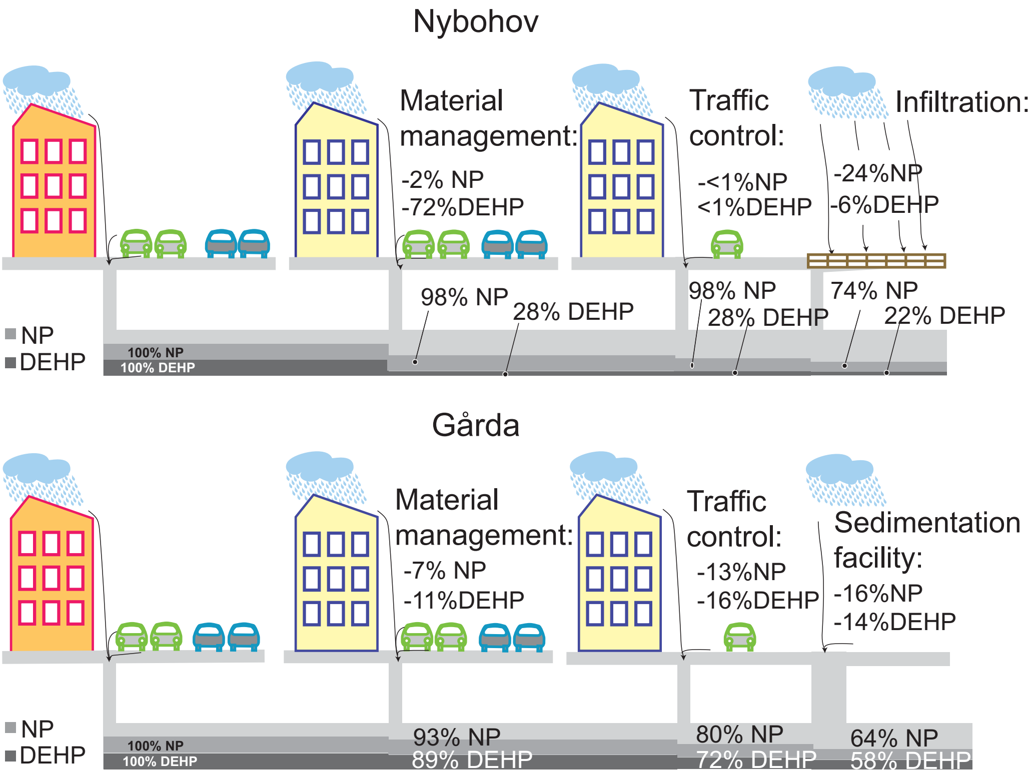


Figure 11. *Simulated reduction of DEHP and NP loads after implementation of different control measures in Nybohov (residential area) and Gårda (high density traffic site). Illustrated in the sewers are the stormwater loads: 100% represents the initial load of pollutants when no measures are applied, the following percentages represent the remaining load after implementing control measures.*

vice versa for the residential areas. The effect of these control options can be simulated using the SFA or the computer model by simply reducing the occurrence of, for example, concrete and vehicles and recalculating the loads. However, as the simulations in the stormwater quality model are based on the outcomes of the SFA, the computer model does not contribute any additional information on sources and effects of control options. Figure 11 illustrates the reduction in loads after implementation of traffic control, building material management and end-of-pipe solutions (more details are found in Paper V).

In the SFA of Gårda, partition to different environmental compartments was estimated roughly using data from the ECB risk assessments. To obtain further information on final sinks of the pollutants, the SFA could be coupled to a fate model, which is discussed in more detail in Chapter 6.

5.1.3 Uncertainties

All data input in an SFA are subject to uncertainty and assessment of data reliability is a necessary part of the work. The assessment can include balancing flows and using different sources of information to confirm, for example, chemical use and content in goods (Lassen and Hansen 2000). The quantity of a flow or stock may be represented by probability distributions and the uncertainty indicated by intervals, the size of which directly reflects the level of uncertainty (see e.g. Eriksson *et al.* [2008]; Månsson *et al.* [2008]). This can be achieved if several sources of information are available, which is often not the case in an SFA

(Sörme and Lagerkvist 2002; Eriksson *et al.* 2008). The best estimate and the uncertainty then need to be determined through expert judgments.

The fluxes of phthalates and NP/EOs determined for Gårda should be regarded as indications rather than as true values. The uncertainty of the fluxes depends on the quality of data on source occurrence in the catchment area (m^2, vehicle km) and the calculated emission factors. When available, two or more references were used for each step in the calculation of emission factors. The intervals of calculated factors generally extended over one order of magnitude, except for the NP/EO factors which occasionally extended over three orders of magnitude. An iterative process was then used to find the best estimate; the factors were modified within the range of calculated values until the SFA outputs were in agreement with observed loads in Gårda (Table 1 in Paper III). For the HMW phthalates and NP/EOs, the highest calculated value of the emission factors generally produced the best estimates compared to measured loads. Had measured loads been available to Nybohov and Skarpnäck, these could have been compared with calculated loads to obtain additional information on the emission factor uncertainties. Since the emission factors have been calibrated for Gårda, it means that emissions from sources not found in large amounts there, such as sealants and "other human activity", are more or less neglected in the calibration. The emission factors for "other human activity" are based on annual loads per person found in wastewater. Hence, the emission factors concerning this source are considered to be more uncertain than emission factors based on source-specific calculations, such as phthalate leaching from flexible PVC.

Most literature found on nonylphenolic compounds does not distinguish between nonylphenol and ethoxylates with different chain lengths. Consequently, it was difficult to separate NP and NPEOs into different flows and all nonylphenolic compounds are accounted for as one flow. This approach will introduce errors in the flow calculations since NP and NPEOs are different when it comes to use and environmental fate, which must be taken into account when interpreting the results of the SFA. The modeled flows of NP/EOs are comparable to the measured loads, but it should be noted that the measured loads only take shorter NPEOs into account. However, as these loads are in agreement, it is suggested that the most important flows of NP/EOs have been identified using the SFA methodology. In general, the calculated load of NP/EOs is considered to be less reliable than the phthalate load because of less data on use and leaching of NP/EOs.

The review of sources and emission data for the compounds studied revealed that there is a lack of available information on the chemical content in goods and emissions into outdoor environments. Moreover, information on sources and use may be contradictory. As an example, NP/EOs have been detected in leachate from scrap tires (Thale *et al.* 2004; Edeskär 2006), whereas the industry representing AP manufacturers claims that NP/EOs have not been used for this purpose. In such cases, evaluation of the reliability of the information is a matter of judgment by the researcher, which adds to the overall uncertainty of the study. Furthermore, information may be protected due to confidentiality; statistics of chemical use generally include a reporting limit (e.g. amounts <100 kg are not included in the Swedish product register); and the import of goods produced outside the EU is not well mapped. This may lead to underestimations of the use of a chemical, or that sources of chemicals remain unknown. Lack of data on chemical content, inaccessible information, and use of data from single references are frequently occurring problems for persons performing SFA (see e.g. Eriksson *et al.* [2008]; Månsson *et al.* [2008]) and this is an important restriction on the applicability of SFA for many pollutants.

5.2 Statistical tools

Since statistical tools have frequently been used to identify sources of metals and PAHs in runoff, it was suggested that this approach be used as a complement to SFA for alkylphenols and phthalates. Pearson's and Spearman's correlations are simple measures of dependence between two variables. Pearson's correlation represents a linear relationship between two variables and requires normally distributed data (McDonald 2009). Spearman's rank correlation works by converting each variable into ranks, and is used when the data do not meet the assumptions about normality and linearity. Principal component analysis (PCA) and cluster analysis (CA) are among the most common multivariate statistical methods used in environmental studies. The PCA can be used to reveal relationships in complex and large datasets by reducing data dimensionality (Hair *et al.* 1998). The dataset is transformed into a new set of variables – principal components (PCs) – that account for most of the variance in the original data. The first principal component explains as much of the variance in the data as possible, and each succeeding component accounts for as much of the remaining variance as possible. The results of a PCA are usually reported as scores and loadings. Each object (e.g. water sample) has a score on each PC and each variable (e.g. water quality parameter) is characterized by a loading on each PC (Herngren *et al.* 2010). In source identification, constituents with high loadings on a PC have been suggested as originating from the same source (e.g. Karar and Gupta [2007]; Fang *et al.* [2004]). In cluster analysis, objects are grouped based on their characteristics (Hair *et al.* 1998). The clusters of objects should exhibit high within-cluster homogeneity and high between-cluster heterogeneity. Similarity between clusters is measured by the Euclidean distance, often illustrated in a dendrogram; smaller distances indicate greater similarity and vice versa.

The relationship between variables can only give an indication of common characteristics or origin and prior knowledge of partitioning or sources is often required to draw conclusions regarding the outcomes of a statistical analysis. In PCA for example, a high Zn loading on a PC may indicate emissions from tires (McKenzie *et al.* 2009) and it may be expected that other constituents with high loadings on the same PC have similar origin. Metals have been analyzed in parallel with alkylphenols and phthalates in many of the snow and stormwater samples from Stockholm and Gothenburg. Since sources of metals are more or less established, it was assumed that running PCA or CA with data for both organic contaminants and metals could be effective for source identification of alkylphenols and phthalates. Analysis of the water, snow and sediment quality data show that there is a relationship between variables, but it is not clear whether this is due to a true relationship or merely to the fact that the samples were collected from the same site or at the same point in time. In other words, it cannot be determined if the relationship is due to similar sources, or factors such as rain height, antecedent dry period and temperature. In addition, the large volume of data below the detection limit, and detection limits which vary between samples, decreases the size of the dataset and further reduces the quality of a statistical analysis. The bottom line is that neither PCA nor CA can be used successfully for the monitoring data.

Instead, a Spearman rank test was performed to find relationships between the constituents in urban runoff. In the sediment samples (n = 9), there was a strong correlation ($0.773 \leq \rho \leq 0.996$; significant at the 0.05 level, two-tailed) between 4-*t*-OP, 4-NP, DBP, DEHP, DIDP and DINP. Only BBP showed insignificant and low correlation with the other substances. For the snow and stormwater samples, strong correlations were seen between 4-*t*-OP–4-NP; 4-NP–DIDP; 4-NP–DINP; and between all HMW phthalates (Table 9). Strong correlation between two variables is either due to the variables influencing each other, or to a common background variable (or several) that affects both variables. For the sediment samples, the affecting variable could be a common source, or partitioning to particles (log K_{ow}>3 for all substances). The deviating results for BBP, however, could not be explained by different sources or properties. The high correlations between HMW phthalates in sediment and water may be due to similar use patterns and properties. Conversely, the low correlations between HMW phthalates and DBP may be explained by DBP being used mainly for non-polymer applications, and being less hydrophobic than the HMW phthalates.

It was in general difficult to interpret the correlations between metals and organic contaminants as there were few significant data and few trends could be seen (Table 9). The correlations with metals were believed to be similar for all HMW phthalates due to similar origin and properties, but only Zn showed consistent results for the phthalates. Significant correlations with phthalates could be seen for Cu and Zn, which are believed to be emitted mainly from brake and tire wear, i.e. traffic sources (Davis *et al.* 2001; McKenzie *et al.* 2009). The strong correlation between Ni and 4-NP may be due to common sources as Ni may leach from concrete or reach the environment through tire and pavement wear (Sörme *et al.* 2001; Bergbäck *et al.* 2001).

Table 9. *Spearman rank correlation coefficients and (n) for variables in aqueous samples.*

	4-*t*-OP	**4-NP**	**DBP**	**DEHP**	**DINP**	**DIDP**
4-*t*-OP	1	0.750* (*9*)	0.433 (*9*)	0.329 (*11*)	0.495 (*14*)	0.584* (*14*)
4-NP		1	0.643 (*7*)	0.426 (*10*)	0.619** (*13*)	0.700** (*14*)
DBP			1	0.359 (*8*)	0.370 (*10*)	0.565 (*10*)
DEHP				1	0.597* (*14*)	0.884** (*14*)
DINP					1	0.881** (*18*)
DIDP						1
Cd	0.611 (*9*)	0.086 (*6*)	0.055 (*5*)	-0.510 (*9*)	0.055 (*11*)	0.123 (*11*)
Cu	0.385 (*9*)	0.657 (*6*)	0.297 (*5*)	0.678* (*9*)	0.297 (*11*)	0.773** (*11*)
Cr	0.410 (*9*)	0.657 (*6*)	0.297 (*5*)	0.669* (*9*)	0.297 (*11*)	0.773** (*11*)
Ni	0.368 (*9*)	0.829* (*6*)	-0.127 (*5*)	0.418 (*9*)	-0.127 (*11*)	0.555 (*11*)
Zn	0.728* (*9*)	0.657 (*6*)	0.745* (*5*)	0.611 (*9*)	0.745* (*11*)	0.809** (*11*)

* Correlation significant at the 0.05 level and ** at the 0.01 level (two-tailed test).

6 PREDICTION OF CONCENTRATIONS AND LOADS IN RUNOFF

Stormwater monitoring programs require considerable resources in terms of personnel, equipment and capital for sampling and analysis (Driver and Tasker 1990; De Keyser *et al.* 2010b). Consequently, prediction of stormwater quality using mathematical tools has attracted interest. Stormwater quality models (SQMs) can be used to estimate the pollution situation where monitoring has not been executed or to plan future scenarios such as land use changes and application of mitigation practices. The most common SQM approaches include regression, land use and process-based models (Zoppou 2001; May and Muttucumaru 2009). The SQMs may also be a combination of these approaches.

6.1 Commonly used modeling approaches

6.1.1 Regression models

Regression models are based on the assumption that stormwater quality can be explained by changes in physical features, land use and climatic characteristics that control the pollution processes (Driver and Tasker 1990; Irish *et al.* 1998). Monitoring data are used to establish mathematical relationships (nonlinear, simple linear, multiple linear etc.) between dependent variables, i.e. loads or EMCs of stormwater constituents, and explanatory variables. Rain intensity and depth, runoff volume, drainage area, antecedent dry period and traffic intensity have commonly been identified as explanatory variables. Their importance for different constituents varies, however, and strong correlations between explanatory variables and stormwater quality are occasionally not found (Brezonik and Stadelmann 2002; Kayhanian *et al.* 2007). In addition, Dembélé *et al.* (2010) showed that calibration of regression models is very sensitive to the data used and is therefore a more or less random process. The regression models are established from monitoring data that reflect certain spatial conditions. Hence, new models need to be developed if these conditions are changed, and regression models are often criticized for showing poor predictions when applied to unmonitored sites (Irish *et al.* 1998; Zoppou 2001).

6.1.2 Land use approaches

Land use models – also referred to as standard or constant concentration models – are generally based on estimations of EMCs expected for a specific type of land use (Mitchell 2005; Ellis and Revitt 2008a). The EMCs are multiplied by the estimated runoff volume to derive annual loads for a catchment area. This information can be used to find pollutant "hotspots" where mitigation measures should be prioritized, and to predict the impact of land use changes on runoff quality. The drawbacks of the method include different definitions of land use types and ascribed EMCs, which may vary considerably between studies (Park *et al.* 2009). Typical EMCs are generally found through statistical analysis of EMC databases. As an example, Mitchell (2005) derived general land use EMCs using data from 678 monitored catchments around the world. Larm (2000), on the other hand, based the EMCs on long-term monitoring of flow-weighted stormwater samples for setting standard EMCs in the StormTac model. The estimations of land use-specific EMCs are more or less geographically limited and should not be used in areas where the urban structure and climatic conditions are different from the sites where the monitoring data have been collected (Larm 2000; Mitchell 2005).

6.1.3 Process-based models

Process-based models are constructed on more or less conceptual ideas of how the rainfall-runoff process, pollutant accumulation and transport of water and pollutants function (Zoppou 2001; Elliott and Trowsdale 2007; Obropta and Kardos 2007). The models vary in complexity; from simplified conceptual equations which explain the underlying processes, to physically based models where the model parameters have a direct physical meaning. The process-based SQMs generally simulate the build-up of pollutants on the catchment surface and the subsequent wash-off during rain events. Commonly used freeware and commercially available SQMs, such as the US EPA Storm Water Management Model (SWMM) and DHI's MOUSE-TRAP, use build-up and wash-off equations to simulate stormwater quality. The different models typically include their interpretation of the build-up and wash-off processes, which may be represented by linear, exponential or power functions. The build-up function is generally based on the number of dry days, decay or wind removal and a build-up coefficient (Barbé *et al.* 1996; Butcher 2003; Egodawatta *et al.* 2009). The wash-off is generally explained by the initial pollutant load, rain intensity, runoff volume, and a wash-off coefficient. Even though build-up and wash-off functions are commonly used, there is still a lack of knowledge concerning these processes (Zoppou 2001; May and Muttucumaru 2009). In addition, the build-up and wash-off coefficients need to be calibrated since they vary with pollutant type and storm, which limit the applicability of the models (Chen and Adams 2006; Egodawatta *et al.* 2007).

6.2 A model for phthalates and nonylphenols

6.2.1 Model development

The intended use of the model should determine the required model type and the degree of its complexity (Bertrand-Krajewski 2007; Obropta and Kardos 2007). As a rule, the least complex model that fulfills the modeling objectives should be used. The aim of this study was to develop a model that is able to predict nonylphenol and phthalate concentrations and loads in runoff. The model should be a user-friendly management tool that requires little input data. The outputs should provide information on substance flows from different sources and be useful in assessing mitigation of stormwater pollution. The small number of field data available for alkylphenols and phthalates prevents the development of both a land use and a regression model. Moreover, these modeling approaches cannot help identify specific sources of pollutants or assess source control strategies. A process-based model was thus seen as the best alternative to fulfilling the modeling objectives.

Process-based models that simplify the functions involved in the generation of stormwater pollution are often preferred for management purposes, whereas the more complex, physically based models are useful as research tools (Ahyerre *et al.* 1998). In this study, the framework of SEWSYS was used (Papers IV and V). SEWSYS is a dynamic model for simulating substance flows and identifying pollutant sources in urban catchment areas (Ahlman 2006). The model has proved to be a useful tool for evaluating fluxes of metals in stormwater, and the open source approach facilitates the future development and adaptation of the model.

In SEWSYS, the generation of stormwater is controlled by rainfall on impervious areas, initial loss and the runoff coefficient (see Ahlman and Svensson [2002] and Ahlman [2006] for details). The accumulated pollutant load is determined by deposition and removal rates, and the wash-off is controlled by the accumulated amount, washout factors and rainfall intensity. The model calculates a pollutant load for each specific source, for example atmospheric deposition, traffic and roofs, by means of emission factors, which are generally expressed in [µg/m^2 year] for emissions from materials and [µg/km] for emissions from vehicles. These factors were established in the SFA of nonylphenolic compounds and phthalates (Chapter 5, Paper III). The required model inputs include catchment area data, such as total area, roof area and traffic loads, and precipitation data. The model produces total stormwater volumes and pollutant loads, which can be combined to express EMCs. The loads can be evaluated separately for each source to illustrate the contribution from different sources.

Calibration of the model was performed using monitored data on rainfall and runoff volumes and EMCs collected from Gårda, Nybohov and Skarpnäck (Chapter 4). Using an iterative process, the model parameters were modified within a range of reported values until the outputs best fitted the measured data. The water quality was calibrated by adjusting the emission factors for each source and the reduction factor, which accounts for pollutant losses during transport from source to sewer.

6.2.2 Performance of the SEWSYS model for phthalates and nonylphenols

The graphical display of observed vs simulated data (Figure 2 in Paper IV) shows that the simulated EMCs of both DINP (other phthalates were not evaluated) and NP/EOs generally are overestimated. Furthermore, the coefficient of determination (R^2, Table 2 in Paper IV) shows that ≤3% of the variation in the observed data can be explained by the model. Since the simulated water volumes agree with measured volumes, the simulated loads appear to be the major source of error in the EMCs. The simulated source distribution was, however, in agreement with outcomes from the SFA (Papers III and V). This suggests that SEWSYS can be used to identify sources and evaluate control options although the predictive power is not satisfactory when simulating EMCs.

Calibration of SEWSYS for metals showed that 75% of the variation in the copper data was accounted for by the model (Ahlman 2006). Opher *et al.* (2009) reported coefficients of the same magnitude ($0.77 \leq R^2 \leq 0.95$) for a calibrated data-driven model whereas Kayhanian *et al.* (2003) showed lower R^2’s (0.20–0.50) for a multiple linear regression model for metal concentrations in runoff water. Both Ahlman (2006) and Opher *et al.* (2009), however, show considerably lower R^2’s (0.22 and 0.32–0.56, respectively) when evaluating additional validation data sets. Models which simulate the emission and transport of organic contaminants in runoff are rarely found in the literature. One exception is the dynamic source-and-flux model developed in the SCOREPP project (2010). SCOREPP is a comprehensive project which involves identification of WFD priority pollutant sources, quantification of fluxes, determination of sinks and evaluation of source control options by means of an integrated urban and river scale fate model. The urban model operates by using emission strings based on a pollutant's expected release pattern from a specific source (De Keyser *et al.* 2010a). Release factors for priority pollutants from sources could only be established for 17% of the emission scenarios and due to the lack of field measurements the model has not yet been validated.

6.2.3 Uncertainties in modeling

The uncertainties in SQMs and in the evaluation of such models typically originate from several sources including i) uncertainties in water quality monitoring data used to evaluate the model outputs; ii) uncertainties in the model structure, i.e. the imperfect description of real-world processes; iii) uncertainties related to parameter value; and iv) uncertainties in the input data used for the simulations (Ahyerre *et al.* 1998; Freni *et al.* 2008). This is also the case for the model used for NP/EOs and phthalates. The emission factors calculated in the SFA and used in SEWSYS could be a reason for the low predictive power of the computer model. However, in the SFA it was shown that calculated and measured loads were in agreement and it was concluded that the emission factors were adequate for use in the SEWSYS model. The major factors that impede the development of a reliable and useful model for NP/EOs and phthalates include (more details in Paper IV):

- Uncertainties in chemical analyses of NP/EOs and phthalates in stormwater (see Chapter 4), which prevent accurate calibration and verification of the model.
- Lack of knowledge concerning the build-up and wash-off processes. Moreover, these processes have not been calibrated for NP/EOs and phthalates.
- Lack of knowledge concerning other pollutant generation and removal processes, such as sediment deposition and erosion, pollutant evaporation and degradation.
- Ocular inspection of sources in catchment areas, which may give rise to uncertainties in both material identification and surface occurrence.

The high temporal and spatial variations in stormwater quality generally render the prediction of pollutant concentrations and loads difficult (Goonetilleke *et al.* 2005; Freni *et al.* 2009; Dotto *et al.* 2010). The processes governing pollutant build-up, wash-off and transport are not fully understood and process-based models have been criticized for being rough approximations of a complex system (Freni *et al.* 2009; May and Muttucumaru 2009). Many authors therefore recommend the use of less complex models, such as data-driven models or even simpler methods based on a few equations (Chandler 1994; Francey *et al.* 2005; 2009; Opher *et al.* 2009). Ahyerre *et al.* (2005) compared the outcomes of three process-based SQMs (FLUPOL, used by used by the Seine-Normandie Water Agency, InfoWorks CS and MOUSE-TRAP) with a simple constant concentration approach. It was shown that the constant concentration method gave the same or even higher accuracy of simulated suspended solids mass than the three process-based SQMs. The authors concluded, however, that the pollutographs produced by the process-based models can be useful in the planning of stormwater mitigation practices. Vaze and Chiew (2003) compared regression models with a model based on pollutant build-up and wash-off functions, and concluded that both the regression and the process-based models predicted pollutant loads satisfactorily. The authors suggest that if only loads are required, and not EMCs, regression models should be used since they are simpler to build and require less data than the process-based models. As evident from these studies, the different model approaches have inherent strengths and weaknesses that limit their application. Process-based models can generate information that land use and regression models cannot, but are generally more time-consuming to construct and require large field data sets for calibration before they can be operational. Field data are in most cases limited, which affects the evaluation of the model (Ahyerre *et al.* 1998; Vaze and Chiew 2003). Mourad *et al.* (2005b) showed that the calibration of two constant concentration models and a model based on build-up/wash-off functions was very sensitive to variability in data. The use of few observations for calibration might lead to a good fit but poor prediction of additional data. In conclusion, the quantity and quality of experimental data is a major limitation for calibration and verification, and thus also the applicability, of stormwater-quality models.

6.3 Alternative modeling strategies

The prediction capacity of SEWSYS for NP/EO and phthalate EMCs could be improved by further studies of the build-up, wash-off and pollutant transport processes. However, the SFA helps fulfill the objectives of the study to some extent; it can identify sources of nonylphenols and phthalates in urban areas and predict their loads in runoff, but it cannot predict pollutant concentrations. This may be solved by coupling the SFA to a fate model. Fate models simulate the behavior of substances in different environmental media and can be used to identify pollutant sinks (Mackay *et al.* 1996; Wania *et al.* 2006). A variety of environmental fate models have been developed and evaluated for organic pollutants and many of them are based on the fugacity concept, i.e. the tendency of a substance to "escape" from a compartment (Mackay 2001). The fugacity capacity is calculated using the substances' physical and chemical properties, such as Henry's law constant and solubilities. There are several successful examples of the application of fugacity models, such as the QWASI (quantitative water-air-sediment interaction) model applied for DEHP in rivers (Warren *et al.* 2007); Cousins and Mackay (2003) simulated phthalate fate in a generalized industrially developed region; Zhang *et al.* (2011) modeled alkylphenols in the Jialu River, China; and Huang *et al.* (2007) investigated nonylphenol fate in aquatic microcosms. The fugacity approach was also used to determine the fate of nonylphenols and phthalates in the stormwater sedimentation facility in Gårda (Paper II).

To predict the fate and sinks of alkylphenols and phthalates in urban areas, several processes need to be included (Figure 12). First, the model must be able to determine the fate of the fluxes from each source (estimated using the SFA) to each sink. For example, the fluxes of DEHP from roofs can be directed into the atmosphere, water or soil, or be degraded. Secondly, the fate of the pollutants in the water compartment must be modeled. This could generate more knowledge of the pollutant transport and removal processes not accounted for in the SEWSYS model, such as sediment deposition and erosion, pollutant evaporation and degradation. In the current model, these processes are represented by a reduction factor, which is a rough estimate of all loss processes during transport from source to sink.

Furthermore, the removal of alkylphenols and phthalates in stormwater treatment systems could be predicted. This approach was investigated in Paper II, and it was concluded that fugacity-based tools may be used for investigating pollutant fate in stormwater treatment systems. Coupling this type of model to the outcomes of the SFA would imply that the efficiency of both source control options (material management, traffic reduction etc.) and end-of-pipe solutions (ponds, swales, wetlands etc.) could be evaluated.

Models which integrate simulations of pollutant emissions and multimedia fate are beginning to appear in the literature. De Keyser *et al*. (2010b) have merged a model for urban water systems (wastewater, stormwater and receiving waters) and a multimedia fate model to a common simulation platform. The model consists of different unit models for each part of the water system and calculates fate processes by using well-known substance properties. The model was tested for DEHP in a combined sewer system and a stormwater treatment pond, but no monitored data were available to validate the model outcomes. The authors concluded that this type of modeling provides a holistic overview of the environmental status, but the lack of data on pollutant emissions causes large uncertainties in the model outputs. Cui *et al*. (2010) developed a coupled source-transport-storage model for predicting the response in aquatic levels of copper to changes of its use in the urban area. The sources of copper were identified through an SFA similar to the approach used for nonylphenols and phthalates. A portion of the stormwater and its pollution, determined by the land use, is directed to a lake, where the transfer of copper between compartments is modeled using process-based transfer rates. Tests of the model indicated that sediment levels were satisfactorily predicted whereas the copper content in water was overestimated. The authors concluded that the major weakness of the model is the requirement of extensive site-specific data for modeling copper fluxes from sources.

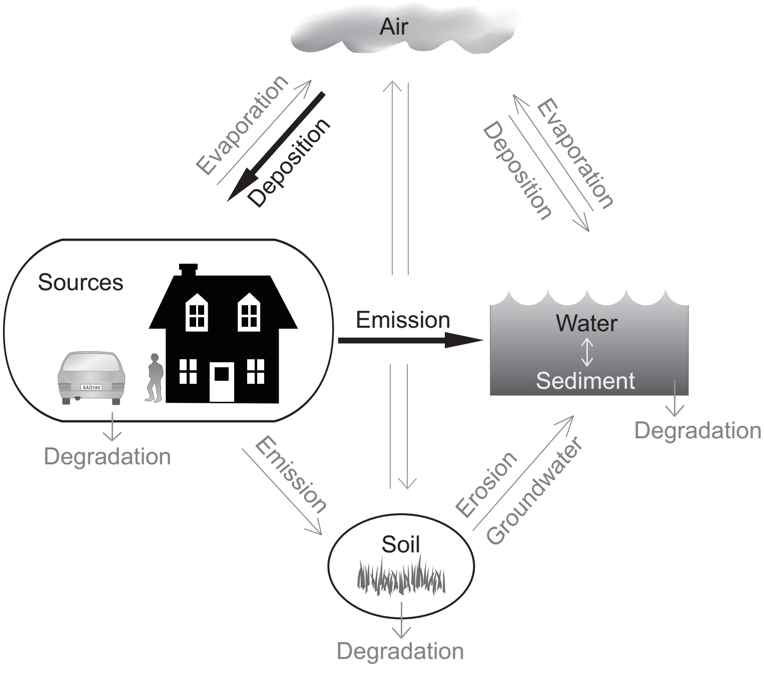


Figure 12. *Conceptual model of the fluxes of pollutants in urban areas. The developed stormwater quality model simulates atmospheric deposition to urban surfaces and emissions from sources to the stormwater compartment (black arrows). Other relevant fluxes (grey arrows) could be determined by means of a fate model.*

7 CONCLUSIONS

This research was based on four hypotheses:

- Hypothesis 1: Alkylphenols and phthalates are relevant to runoff quality since emissions of these chemicals from products and materials are likely to end up in urban runoff with potentially negative effects on aquatic environments.

Alkylphenols and phthalates have attracted attention due to their toxicity, which includes both acute and endocrine-disrupting effects. These compounds are used in large quantities within the European Union, although the consumption of certain substances, such as nonylphenolic compounds and DEHP, are on the decrease. These substance groups are used in a wide range of products found in society.

In this study, a screening of organic compounds in urban snow showed that alkylphenols and phthalates were frequently detected, whereas the other candidate compounds considered for further study – brominated flame retardants, perfluorinated compounds and chlorinated paraffins – were detected less frequently. This justifies the selection of alkylphenols and phthalates for further study.

Other organic compounds relevant to the study of runoff quality could be identified, for example, among the priority pollutants of the WFD, OSPAR and HELCOM conventions. In addition to these international agreements, many environmental protection agencies, research groups and non-governmental organizations have come up with their own lists of priority pollutants which may be relevant to pollution of urban waters. However, for studies of organic compounds in runoff, criteria besides potential occurrence and environmental impact need to be addressed. Two important aspects are the cost and the quality of analysis – accredited methods and laboratories may be lacking and detection limits are often high compared to levels found in the environment.

- Hypothesis 2: Alkylphenols and phthalates occur at detectable levels in urban runoff, which here includes stormwater, snow and urban sediment.

Among the alkylphenols, 4-*t*-OP and 4-NP were detected most frequently in all three matrices. In general, 4-nonylphenol showed high concentrations and detection frequencies compared to most other alkylphenols. This may be due to the fact that nonylphenols are used in higher amounts than octylphenols, and that nonylphenol ethoxylates are degraded into nonylphenol in the environment. Concentrations of alkylphenols in snow, stormwater and sediment from Gothenburg and Stockholm are generally of the same order of magnitude as levels found in other studies of runoff. However, reported concentrations found in sewage water and sludge are higher than detected concentrations in stormwater and urban sediment.

Among the phthalates, DEHP has been used in the largest amounts worldwide and has often been detected in aquatic environments at high concentrations compared to other phthalates. However, the current study showed that DINP was found at the highest concentrations in all investigated matrices. This is most likely a result of the current consumption pattern of phthalates in Sweden. In general, detected concentrations of DBP and DEHP in stormwater and sediment are comparable to results from other studies of urban runoff, lake sediment, sewage effluents and sludge. Although DINP and DIDP are currently the most used phthalates, and also the phthalates found at the highest concentrations in this study, there are very few studies of DIDP and DINP for comparison.

The European surface water quality standards and the Canadian freshwater quality guidelines for DEHP, NP and OP were exceeded in several stormwater and snow samples. Among the other compounds included in the target screening of urban snow, PAHs and PBDEs were also detected in concentrations exceeding the European standards for water quality. The water quality standards and guidelines apply to surface waters, and stormwater and snowmelt will most likely be diluted when it reaches the receiving water. However, the infringements of the guidelines imply that negative effects on aquatic life from these anthropogenic stressors cannot be excluded. This suggests that measures to reduce the discharge of anthropogenic substances to urban areas are necessary to achieve good water status.

- Hypothesis 3: Sources of alkylphenols and phthalates in urban catchment areas can be identified and quantified.

Regression models and standard value models, such as land use approaches, may be useful for planning end-of-pipe management practices for stormwater, whereas identification of sources is essential for implementing upstream control. In this study, SFA was used to map the sources and quantify the loads of phthalates and nonylphenolic compounds in urban catchment areas. The outcomes of the SFA showed that the calculated loads of the contaminants were comparable to measured loads in the area studied and SFA was thus considered efficient for identifying the most important sources of phthalates and nonylphenols. The emission factors used for estimating substance flows are not area-dependent and can be used for flow calculations in catchment areas varying in character. The weakness of the SFA is that it is labor intensive. In addition, there is a general lack of needed input data, such as information concerning sources, chemical content and emission rates.

- Hypothesis 4: The fluxes of alkylphenols and phthalates in urban runoff can be predicted.

To predict nonylphenol and phthalate concentrations in runoff, a process-based model was developed. The model showed low predictive power; the simulated EMCs were generally one magnitude higher than the measured concentrations. This may be due to errors and uncertainties in the model structure, input data and field data used to calibrate the model.

The predictive capacity of the process-based model for nonylphenol and phthalate EMCs could be improved by further studies of build-up, wash-off and pollutant transport processes. An alternative is to use the outcomes from the SFA. The SFA helped identify sources of nonylphenols and phthalates in urban areas and predict their loads in runoff, although it cannot be used directly to predict pollutant concentrations. Further studies may solve this problem by linking the SFA to a fate model. A fate model could help simulate the fate of pollutant fluxes from each source to each sink, including the fate of pollutants in the water compartment and removal of pollutants in stormwater treatment systems. Linking the outcomes from an SFA to a fate model could be beneficial in evaluating both source control and end-of-pipe mitigation practices to reduce the pollutant loads from urban areas.

This study has highlighted the occurrence of alkylphenols and phthalates in urban matrices. There are indications that other organic compounds, for example perfluorinated compounds and brominated flame retardants to name a few, may pose a threat to the quality of urban runoff and receiving waters. The SFA approach presented in this study, using factors that express the emission rate of a specific substance from a specific source, could serve as a model for source and flux studies of other organic contaminants in urban catchment areas. In addition, the outcomes of this study can be used as a guide when planning effective source control strategies to reduce discharges of alkylphenols and phthalates into the environment. The modeling of source control effects shows that additional end-of-pipe mitigation practices are necessary to effectively reduce pollutant loads into receiving waters. However, more research is needed to evaluate the removal performance of end-of-pipe facilities for organic contaminants in urban runoff.

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