Legacy and emerging pollutants in pristine and polluted boreal catchments

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Abstract

Persistent organic pollutants (POPs) are bioaccumulative chemicals that are ubiquitously and globally distributed in the environment. Several species of POPs have been studied extensively and are continuously being monitored in various environmental matrices for decades. However, with the increasing amounts of chemicals produced and made commercially available, potential emerging POPs are receiving more attention. Per- and polyfluoroalkyl substances (PFASs) and polycyclic aromatic compounds (PACs) are two groups of emerging substances that are currently of great concern due to their potential toxicity and high mobility in terrestrial and aquatic ecosystems. The overall objective of this thesis was to improve our understanding on the impact of various pollution sources, environmental pathways, transport and fate of both legacy and emerging PFASs and PACs in pristine and polluted boreal catchments.

In Paper I, population density was found to be significantly correlated with PFAS levels in rivers. Ten rivers with distinctly higher ΣPFAS concentrations and with a common compositional profile (higher fraction of perfluoroalkane sulfonic acids) were identified, suggesting a major impact from a similar kind of point source(s) in these rivers. Significant positive relationships between several PFASs and dissolved organic carbon were detected in river and sea water, indicating chemical binding and co-transport in aquatic ecosystems. The findings in Paper II show that levels and compositional profiles of PFASs in river water were highly impacted by point sources and hydrological conditions. Seasonal trends of PFASs were impacted by river flow probably caused by mobilization of PFASs from contaminated soil and groundwater. In Paper III, fluxes of PACs in atmospheric deposition showed that they were higher during the cold season, both for PAHs and PAH-derivatives. The deposited PACs were found to be largely retained in the terrestrial environment of the boreal forest catchment or lost by other processes with <2% of the total deposited amount of ΣPACs exported via the outlet of the headwater on average over a year. During spring flood, the concentrations of PACs were found to be significantly higher than levels during the preceding snow-covered and snow-free seasons (Paper IV). Besides seasonal changes, landscape type (forest or mire) was found to have an impact on terrestrial export of PACs, with higher levels of PACs in a mire stream than in stream water in a forested sub-catchment.

Keywords: boreal catchments, diffuse source, PACs, PFASs, point source, POPs, seasonal changes, water, emerging pollutants, micropollutants

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Klassiska och nya föroreningar i opåverkade och förorenade boreala avrinningsområden

Sammanfattning

Persistenta organiska föroreningar (POPs) är bioackumulerande ämnen som är allmänt utbredda i den globala miljön. Många POPs har undersökts och övervakats kontinuerligt i olika miljömatriser i decennier, men på grund av det stora antalet kemikalier som har tillverkats och är i användning får nu potentiella nya POPs, så kallade ‘emerging POPs’, allt mer uppmärksamhet. Två grupper av nya POPs är per- och polyfluorerade alkylsubstanser (PFAS) respektive polycykliska aromatiska föreningar (PAC). Dessa är av stort intresse på grund av sin potentiella toxicitet och höga rörlighet i terrestra och akvatiska ekosystem. Det övergripande målet med den här avhandlingen var att öka vår förståelse av påverkan från olika föroreningskällor och av transportvägar av både klassiska och nya POPs i opåverkade och förorenade boreala avrinningsområden.

I Paper I observerades befolkningstätheten vara signifikant korrelerad med PFAS-halter i vattendrag. Tio vattendrag med tydligt högre PFAS-koncentrationer och ett liknande mönster av PFAS (högre fraktion av perfluorerade alkylsulfonsyror) identifierades, vilket tyder på en stark påverkan av en liknande typ av punktkälla (eller punktkällor) i dessa vattendrag. Signifikanta positiva förhållanden mellan flera PFAS och löst organiskt kol kunde observeras i vattendrag och i havsvatten, vilket indikerar att det finns en kemisk bindning till och samtransport med löst organiskt kol i akvatiska ekosystem. Resultaten i Paper II visade att nivåer och mönster av PFAS i vattendrag påverkas starkt av punktkällor och hydrologiska förhållanden. Årstidstrenderna för PFAS påverkades av vattenflödet, förmodligen som ett resultat av mobilisering av PFAS från förorenad mark och grundvatten. I Paper III visades flödena av PAC i atmosfärisk deposition vara högre under den kalla årstiden, både för PAH:er och PAH-derivat. Deponerade PAC hölls i stor utsträckning kvar i den terrestra miljön eller förlorades genom andra processer än via avrinning i vattendrag, eftersom mindre än 2 % av den totala deponerade mängden PAC exporterades från avrinningsområdet som ett genomsnitt över ett år. Under vårfloden var PAC-koncentrationerna signifikant högre än under de föregående snötäckta och snöfria årstiderna (Paper IV). Förutom årstidsvariationer visade sig landskapstyper (skog eller myr) ha en påverkan på den terrestra exporten av PAC, med högre PAC-nivåer i ett vattendrag som avvattnade ett myrområde än i ett som avvattnade ett skogsområde.

Nyckelord: boreala avrinningsområden, diffusa källor, PACs, PFASs, punktkälla, POPs, årstidsvariationer, vatten, nya föroreningar , mikroföroreningar

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Dedication

Gửi tặng Ba Má. Không có tình yêu thương và chăm sóc của Ba Má, con không thể thành người!

“We are all connected in the great circle of life”
Mufasa – The Lion King (1994)

Contents

List of publications

This thesis is based on the work contained in the following papers:

I Minh A. Nguyen*, Karin Wiberg, Erik Ribeli, Sarah Josefsson, Martyn Futter, Jakob Gustavsson, Lutz Ahrens (2017). Spatial distribution and source tracing of per- and polyfluoroalkyl substances (PFASs) in surface water in Northern Europe. *Environmental Pollution* 220,1438-1446.

II Minh A. Nguyen*, Karin Norström, Karin Wiberg, Jakob Gustavsson, Sarah Josefsson, Lutz Ahrens. Seasonal trends of per- and polyfluoroalkyl substances (PFASs) in riverine surface water affected by fire training sites and wastewater treatment plants (manuscript)

III Minh A. Nguyen*, Lutz Ahrens, Sarah Josefsson, Jakob Gustavsson, Hjalmar Laudon, Karin Wiberg. Seasonal pattern of polycyclic aromatic compounds (PACs) in atmospheric deposition and their potential retention in a boreal catchment (manuscript)

IV Minh A. Nguyen*, Lutz Ahrens, Jakob Gustavsson, Sarah Josefsson, Hjalmar Laudon, Karin Wiberg. The role of spring flood and landscape type in the terrestrial export of polycyclic aromatic compounds (PACs) to stream water (submitted manuscript)

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The contribution of Minh Anh Nguyen to the papers included in this thesis was as follows:

I Planned the study together with co-authors. Shared responsibility for sampling and laboratory analyses. Had main responsibility for data interpretations, writing, and publishing.

II Planned the study together with co-authors. Shared responsibility for sampling and laboratory analyses. Had main responsibility for data interpretations, and writing.

III Planned the study together with co-authors. Had main responsibility for sampling, laboratory analyses, data interpretations, and writing.

IV Planned the study together with co-authors. Had main responsibility for sampling, laboratory analyses, data handling, data analyses, interpretations, writing, and submission.

Abbreviations

AFFF	Aqueous fire-fighting foam
DCM	Dichloromethane
DOC	Dissolved organic carbon
EMEP	European monitoring and evaluation programme
GC-EI-MS/MS	Gas chromatography-electron impact-tandem mass spectrometry
GFF	Glass fiber filter
HLB	Hydrophilic lipophilic balance
IS	Internal standard
K_{ow}	Octanol-water partitioning coefficient
LC-ESI-MS/MS	Liquid chromatography-electrospray ionization-tandem mass-spectrometry
LRAT	Long range atmospheric transport
MDL	Method detection limit
PACs	Polycyclic aromatic compounds
PAHs	Polycyclic aromatic hydrocarbons
PFASs	Per- and polyfluoroalkyl substances
PFCAs	Perfluoroalkyl carboxylic acids
PFSAs	Perfluoroalkane sulfonic acids
POP	Persistent organic pollutant
SPE	Solid phase extraction
SPM	Suspended particulate matter
WAX	Weak anion exchange
WWTP	Waste water treatment plant

1 Introduction

In the European Union, there are more than 100 000 registered chemicals, of which more than 30 000 are in high production and in use in society (Williams *et al.*, 2009; Ahlers *et al.*, 2008; Schwarzenbach *et al.*, 2006). During the production, use and disposal of chemicals/products, they can be emitted and reach the environment (Schwarzenbach *et al.*, 2006). There are also environmental pollutants that have never been in production or use, but are formed unintentionally through various processes. Organic pollutants that are persistent, potentially bioaccumulative and toxic, and capable of long range transport are defined as Persistent Organic Pollutants (POPs) under the Stockholm Convention (2009). Some of these have been studied extensively over decades, for instance polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) (Josefsson *et al.*, 2016; Chiffre *et al.*, 2015; Meyer *et al.*, 2011; Witt, 2002; Franz & Eisenreich, 1998; Wania & Mackay, 1996). These classical POPs have been included in monitoring programs for contaminants in many countries including Sweden for decades.

Besides the classical, legacy POPs, there are emerging pollutants, i.e. chemicals that are not monitored routinely but have potential to spread into the environment and pose risk to ecological and human health (Geissen *et al.*, 2015). Per- and polyfluoroalkyl substances (PFASs) and some polycyclic aromatic compounds (PACs) are examples of two groups of emerging substances that are currently of great concern due to their potential toxicity and high mobility in terrestrial and aquatic ecosystems. Several compounds belonging to these two groups have been listed as being of environmental concern by the NORMAN-Network, in a database comprising more than 900 emerging pollutants and their metabolites as well as other transformation products (NORMAN-Network, 2016). Moreover, one of the PFASs, perfluorooctanesulfonic acid (PFOS) has been listed as a POP under the Stockholm Convention (2009), while perfluorooctanoic acid (PFOA) and perfluorononanoic acid (PFNA) are included in the candidate list of substances of very high concern for authorization by the European chemicals agency (ECHA) since 2013 and 2015, respectively (ECHA, 2015; ECHA, 2013).

1.1 Impact of point and diffuse sources on POP contamination in the aqueous environment

Since approximately 70% of the Earth's surface is covered by water, the aquatic environment has great potential for importing POPs from the terrestrial environment and becoming a sink for those substances (Zeng, 2015). The POPs found in aquatic environments enter these through various pathways, for instance via discharge from point sources, atmospheric deposition, soil surface run-off, and ground water transport (Zeng, 2015). Once released into the aqueous environment, POPs distribute between different matrices (e.g. sediment, biota) and may have an impact on aquatic ecosystem and human health (Houtz *et al.*, 2016; Ahrens *et al.*, 2015; Taniyasu *et al.*, 2015; Guelfo & Higgins, 2013). The concentrations of POPs in the aquatic environment are subjected to change depending on seasonal variations, as has been observed in several studies in e.g., China (Zhu *et al.*, 2015), Germany (Zhao *et al.*, 2015), Italy (Bettinetti *et al.*, 2012), Japan (Minomo *et al.*, 2011), the U.S. (Ko & Baker, 2004), and Sweden (Gago-Ferrero *et al.*, 2017; Josefsson *et al.*, 2016; Ahrens *et al.*, 2015).

1.1.1 Per- and polyfluoroalkyl substances (PFASs)

Per- and polyfluoroalkyl substances are synthetic chemicals of concern due to their extreme persistence and high bioaccumulative potential (Giesy *et al.*, 2010; Martin *et al.*, 2003). They have unique physicochemical properties due to their hydrophobic and hydrophilic characteristics, and they have been used as surfactants in e.g. textiles, carpets, leather, paper products, and fire-fighting foams since the 1950s (Ahrens *et al.*, 2009a; KEMI, 2006). Due to their wide range of applications worldwide, they are ubiquitously present in the environment (Ahrens, 2011; Houde *et al.*, 2006). They are also of great concern due to the risk they pose to environmental and human health (Ulhaq *et al.*, 2013a; Ulhaq *et al.*, 2013b). This has led to a shift in production and application to shorter chained PFASs and PFAS precursors (Ahrens, 2011; Möller *et al.*, 2010; Martin *et al.*, 2003). These shorter chained PFASs are believed to have a shorter half-life in biota than the longer chained PFASs (Danish EPA, 2015).

Per- and polyfluoroalkyl substances are emitted from point sources (Gago-Ferrero *et al.*, 2017; Weber *et al.*, 2017; Ahrens *et al.*, 2015; Herzke *et al.*, 2012; Becker *et al.*, 2008) or derive from diffuse sources, e.g., atmospheric deposition

(Taniyasu *et al.*, 2013; Kim & Kannan, 2007). One important point source of PFASs to surface water and groundwater is PFAS-containing aqueous fire-fighting foam (AFFF) employed in fire-fighting training areas (Banzhaf *et al.*, 2017; Baduel *et al.*, 2015; Kärrman *et al.*, 2011; Moody *et al.*, 2002; Moody & Field, 1999). Another important point sources of PFAS contamination is effluent from wastewater treatment plants (WWTPs) (Banzhaf *et al.*, 2017; Becker *et al.*, 2008; Sinclair & Kannan, 2006; Boulanger *et al.*, 2005).

Three subgroups of PFASs were investigated in this thesis: perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and PFAS precursors. Both PFCAs and PFSAs contain a fully perfluorinated carbon alkyl chain and are characterized by their carboxylic acid group (COOH) and sulfonic acid group (SO_3H), respectively. In addition to PFCAs and PFSAs, there are some PFAS precursors that can undergo various (bio)degradation processes to form persistent final degradation products such as short chained and long chained PFCAs and PFSAs. A summary of the PFASs studied in this thesis and their physical- and chemical properties is provided in Table 1.

Table 1. *Abbreviation, full names, molecular formula, CAS numbers, and octanol-water partitioning coefficients (log K_{ow}) of PFASs included in this thesis.*

Abbrev	**Name**	**Molecular formula**	**CAS No.**	**Log K_{ow}[a]**
PFBA	Perfluorobutanoic acid	$CF_3(CF_2)_2COOH$	375-22-4	2.82
PFPeA	Perfluoropentanoic acid	$CF_3(CF_2)_3COOH$	2706-90-3	3.43
PFHxA	Perfluorohexanoic acid	$CF_3(CF_2)_4COOH$	307-24-4	4.06
PFHpA	Perfluoroheptanoic acid	$CF_3(CF_2)_5COOH$	375-85-9	4.67
PFOA	Perfluorooctanoic acid	$CF_3(CF_2)_6COOH$	335-67-1	5.30
PFNA	Perfluorononanoic acid	$CF_3(CF_2)_7COOH$	375-95-1	5.92
PFDA	Perfluorodecanoic acid	$CF_3(CF_2)_8COOH$	335-76-2	6.50
PFUnDA	Perfluoroundecanoic acid	$CF_3(CF_2)_9COOH$	2058-94-8	7.15
PFDoDA	Perfluorododecanoic acid	$CF_3(CF_2)_{10}COOH$	307-55-1	7.77
PFTriDA	Perfluorotridecanoic acid	$CF_3(CF_2)_{11}COOH$	72629-94-8	8.25
PFTeDA	Perfluorotetradecanoic acid	$CF_3(CF_2)_{12}COOH$	376-06-7	8.90
PFHxDA	Perfluorohexadecanoic acid	$CF_3(CF_2)_{14}COOH$	67905-19-5	N/A[b]
PFOcDA	Perfluorooctadecanoic acid	$CF_3(CF_2)_{16}COOH$	16517-11-6	N/A[b]
PFBS	Perfluorobutanesulfonic acid	$CF_3(CF_2)_3SO_3H$	375-73-5	3.90
PFHxS	Perfluorohexanesulfonic acid	$CF_3(CF_2)_5SO_3H$	355-46-4	5.17
PFOS	Perfluorooctanesulfonic acid	$CF_3(CF_2)_7SO_3H$	1763-23-1	6.43
PFDS	Perfluorodecanesulfonic acid	$CF_3(CF_2)_9SO_3H$	335-77-3	7.66
6:2 FTSA	6:2 fluorotelomer sulfonic acid	$F(CF_2)_6CH_2CH_2SO_3H$	27619-97-2	4.44
FOSA	Perfluorooctanesulfonamide	$CF_3(CF_2)_7SO_2NH_2$	754-91-6	5.62
MeFOSA	*N*-methyl perfluorooctane sulfonamide	$CF_3(CF_2)_7SO_2NH(CH_3)$	31506-32-8	6.07
EtFOSA	*N*-ethylperfluoro-1-octanesulfonamide	$CF_3(CF_2)_7SO_2NHC_2H_5$	4151-50-2	6.71
MeFOSE	*N*-methyl perfluoro-octanesulfonamidoethanol	$CF_3(CF_2)_7SO_2N(CH3)C_2H_4OH$	24448-09-7	6.00

EtFOSE	*N*-ethyl perfluorooctanesulfonamidoethanol	$CF_3(CF_2)_7SO_2N(C_2H_5)C_2H_4OH$	1691-99-2	6.52
FOSAA	Perfluoro-1-octanesulfonamidoacetic acid	$CF_3(CF_2)_7SO_2NHCOOH$	2806-24-8	N/A[b]
Me-FOSAA	*N*-methyl perfluorooctanesulfonamidoacetic acid	$CF_3(CF_2)_7SO_2N(CH_3)CH_2\text{-}COOH$	2355-31-9	N/A[b]
Et-FOSAA	*N*-ethylperfluoro-1-octanesulfonamidoacetic acid	$CF_3(CF_2)_7SO_2N(C_2H_5)COOH$	2991-50-6	N/A[b]

[a](Wang et al., 2011); [b] N/A = not available.

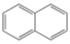
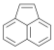
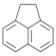
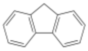
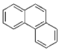
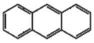
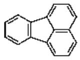
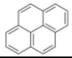
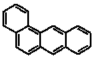
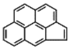
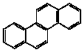
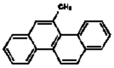
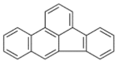
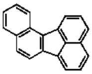
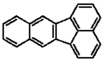
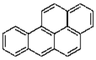
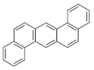
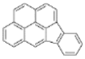
1.1.2 Polycyclic aromatic hydrocarbons (PACs)

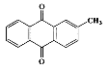
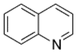
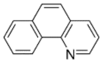
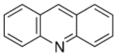
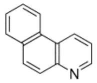
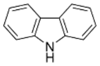
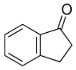
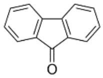
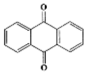
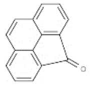
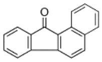
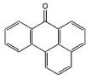
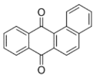
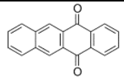
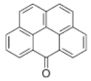
The group of PACs includes PAHs and their derivatives such as oxygenated PAHs (oPAHs), nitrated PAHs (nPAHs) and methylated PAHs (mPAHs). PAHs are a group of legacy persistent organic pollutants (POPs) that have been studied extensively (Chiffre *et al.*, 2015; Friedman *et al.*, 2014; Meyer *et al.*, 2011; Witt, 2002; Franz & Eisenreich, 1998; Wania & Mackay, 1996), PAH-derivatives are emerging pollutants, which have not yet been well studied.

Polycyclic aromatic hydrocarbons contain two or more fused aromatic rings. They are components of coal, petroleum and related products like the pesticide creosote, but can also be formed unintentionally through incomplete combustion of organic materials such as fossil fuels and domestic waste (Srogi, 2007). Although PAHs have low bioaccumulation potential in biota, they are still a concern due to their potential to cause harm to organisms, by e.g., induction of cytochrome P450 metabolic enzymes (Jung *et al.*, 2012; Rose *et al.*, 2012), which can cause mutagenic and carcinogenic effects.

Polycyclic aromatic hydrocarbon-derivatives may also be formed in the same processes as PAHs or by various transformation reactions of PAHs (e.g. chemical oxidation, photo-oxidation, biological transformation by enzymes or microorganisms) (Walgraeve *et al.*, 2010; Lundstedt *et al.*, 2007). These PAH-derivatives are of increasing concern due to their higher polarity (Chibwe *et al.*, 2015; Lundstedt *et al.*, 2007) and therefore higher mobility in comparison with their PAH counterparts in the terrestrial and aquatic environment. Furthermore, oPAHs and nPAHs have been reported to be potentially more harmful than their corresponding PAHs (Chibwe *et al.*, 2015; Lemieux *et al.*, 2008; Lundstedt *et al.*, 2007; Pašková *et al.*, 2006; WHO, 2003; Bleeker *et al.*, 2002). A summary of the PACs studied in this thesis and their physical- and chemical properties is provided in Table 2.

Table 2. *Abbreviation, full names, CAS numbers, structures, octanol-water partitioning coefficients (log K_{ow}), and type of PACs included in this thesis.*

Abbrev	**Name**	**Structure**[a]	**CAS No.**	**Log K_{ow}**[b]	**Type**
NPH	naphthalene		91-20-3	3.3	PAH
ACY	acenaphthylene		208-96-8	4.1	PAH
ACE	acenaphthene		83-32-9	3.9	PAH
FLR	fluorene		86-73-7	4.2	PAH
PHE	phenanthrene		85-01-8	4.6	PAH
ANT	anthracene		120-12-7	4.5	PAH
FLN	fluoranthene		206-44-0	5.2	PAH
PYR	pyrene		129-00-0	5.2	PAH
B[*a*]A	benz[a]anthracene		56-55-3	5.7	PAH
CP[*c,d*]P	cyclopenta[c,d]pyrene		27208-37-3	5.7	PAH
CHR	chrysene		218-01-9	5.8	PAH
MCHR	5-methylchrysene		3697-24-3	6.1	PAH
B[*b*]FA	benzo[*b*]fluoranthene		205-99-2	6.4	PAH
B[*j*]FA	benzo[*j*]fluoranthene		207-08-9	6.4	PAH
B[*k*]FA	benzo[*k*]fluoranthene		205-82-3	6.4	PAH
B[*a*]P	benzo[*a*]pyrene		50-32-8	6.2	PAH
DB[*a,h*]A	dibenzo[*a,h*]anthracene		53-70-3	6.5	PAH
I[1,2,3-*c,d*]P	indeno[1,2,3-*c,d*]pyrene		193-39-5	6.7	PAH
B[*g,h,i*]P	benzo[*g,h,i*]perylene		191-24-2	6.8	PAH

Abbrev	Name	Structure[a]	CAS No.	Log K_{ow}[b]	Type
M[9,10]D	2-methylanthracene-9,10-dione		84-54-8	3.9	mPAH
QNL	quinoline		91-22-5	2.0	nPAH
B[*h*]Q	benzo[*h*]quinoline		230-27-3	3.4	nPAH
ACR	acridine		260-94-6	3.4	nPAH
B[*f*]Q	benzo[*f*]quinoline		S770310	3.4	nPAH
CBZ	carbazole		86-74-8	3.3	nPAH
IDN	1-indanone		83-33-0	2.1	oPAH
9FLR	9-fluorenone		486-25-9	3.6	oPAH
A[9,10]D	anthracene-9,10-dione		84-65-1	3.4	oPAH
4[*DEF*]P	4H-cyclopenta[*def*]phenanthrenone		5737-13-3	4.1	oPAH
B[*a*]F	benzo[*a*]fluorenone		479-79-8	4.7	oPAH
B[*de*]A	7H-benz[*de*]anthracen-7-one		82-05-3	4.8	oPAH
B[*a*]D	benzo[*a*]anthracene-7,12-dione		2498-66-0	4.4	oPAH
N[5,12]D	naphthacene-5,12-dione		1090-13-7	4.5	oPAH
B[*cd*]P	6H-benzo[*cd*]pyren-6-one		3074-00-8	5.3	oPAH

[a] *Figures from www.sigmaaldrich.com;* [b] *Calculated using EPI SUITE 4.1*

1.2 Spatial distribution of POPs in the aquatic environment

Persistent organic pollutants are well known to be ubiquitously distributed in the environment including both densely populated and remote areas (Shatalov *et al.*, 2004; WHO, 2003; Environment-Ontario, 1992). In Sweden, POPs have been found to be present in aquatic systems including rivers and sea water (Gago-Ferrero *et al.*, 2017; Josefsson *et al.*, 2016; Ahrens *et al.*, 2015; Filipovic & Berger, 2014; Filipovic *et al.*, 2013; Bergknut *et al.*, 2011; Josefsson *et al.*, 2011), sediment (Ahrens *et al.*, 2015; Assefa *et al.*, 2014; Sundqvist *et al.*, 2009), biota (Ahrens *et al.*, 2015; Nordén *et al.*, 2013), and the human body (Gyllenhammar *et al.*, 2015; Borg *et al.*, 2013; Glynn *et al.*, 2012). Positive correlations between population densities and concentrations of POPs in water have been observed in studies in Italy (Pistocchi & Loos, 2009), Canada (Scott *et al.*, 2009), and Sweden (Filipovic & Berger, 2014), indicating that urban areas are the main sources for POPs. Subsequently, POPs can be further transported over long distances via water (Sundqvist *et al.*, 2009; Witt, 2002) or in the atmosphere (Filipovic *et al.*, 2013). Therefore, it is important to identify the sources of POPs and improve knowledge of their transport and distribution in the aquatic environment.

1.3 Atmospheric deposition and snow melt as sources of POPs contamination in pristine boreal environments

Persistent organic pollutants undergo long range atmospheric transport (LRAT) via the gas phase or as aerosols, and they partition between those two phases, depending on temperature, vapor pressure and the physicochemical properties of the compound (Brun *et al.*, 2004). The levels of POPs in the atmosphere vary depending on several factors, such as source strength, climate and hydrological conditions. For instance, PAH levels can be high during the winter season due to the increased demand in society for energy for heating and transport (Brun *et al.*, 2004). The net LRAT of POPs is mainly from mid-latitudes towards colder latitudes in the northern and southern hemispheres (Wania & Mackay, 1996).

Boreal forests, which cover large areas of the northern hemisphere, play a key role in trapping airborne POPs due to the cold climate, forest filter effect and presence of soils rich in organic carbon (Su *et al.*, 2007). Deposition of POPs on the Earth's surface occurs through dry and wet deposition (Bidleman, 1988). Snowfall efficiently scavenges airborne POPs during winter (Bergknut *et al.*, 2010; Herbert *et al.*, 2004; Franz & Eisenreich, 1998). Once deposited, the fate of POPs in the terrestrial and aquatic environment is determined by various processes, e.g., retention in soils and sediments and (re-)volatilization. Many of these processes depend on seasonal changes, such as variations in temperature and hydrological conditions (Bergknut *et al.*, 2011; Bergknut *et al.*, 2010). Snowpack can cover 50% of the land mass in the northern hemisphere and accumulate POPs over the winter season (Robinson *et al.*, 1993). The snowpack can then be a major source of POP contamination of the aquatic environment during the spring melt season. Several studies have observed relatively high concentrations of POPs in both urban and rural rivers during snow-melt (Meyer *et al.*, 2011; Ko & Baker, 2004; Quémerais *et al.*, 1994; Simmleit & Herrmann, 1987). Moreover, the melting of snowpack enriched with PAHs has been shown to impact boreal stream water quality in a wetland dominated boreal catchment in Canada (Birks *et al.*, 2017). Landscape types (e.g. forests and mires) can also have a large influence on hydrology and biogeochemical dynamics (Peralta-Tapia *et al.*, 2014; Ågren *et al.*, 2007; Mattsson *et al.*, 2005; Laudon *et al.*, 2004), which in turn affects the export of POPs from the terrestrial environment to streams and lakes in boreal areas (Josefsson *et al.*, 2016).

2 Overall aim of the thesis and objectives of included papers

The overall aim of this thesis was to improve understanding of PFASs and PACs in pristine and polluted boreal catchments, including the impact of various sources of contamination, environmental pathways as well as transport and fate. Specific objectives are described below (Papers I-IV).

Paper I
The aim of this study was to evaluate the impact of point and diffuse sources on the spatial distribution of PFASs in Swedish rivers and their recipient seas.

Paper II
The aim of this study was to assess the impact of point sources on the occurrence and seasonal variation of PFASs in river water.

Paper III
The aim of this study was to increase knowledge on seasonal changes of PACs in atmospheric deposition at a pristine catchment in northern Sweden.

Paper IV
The aim of this study was to better understand the impact of seasonal changes and landscape types as well as the impact of point sources on PACs in streams and rivers of a boreal catchment.

3 Methods

3.1 Sampling

In order to achieve the aims of this thesis, different types of samples were collected from various sampling locations, including atmospheric deposition and surface water (dissolved and particulate phases). The sampling locations, matrices, sampling methods and target analytes used in Papers I to IV are given in Table 3. Field blanks and replicates were also collected for quality control of analytical procedures (for details, Papers I-IV).

Table 3. *Sampled matrices, methods, locations, and target analytes included in each paper of this thesis*

Matrices	**Sampling methods**	**Sampling location**	**Target analytes**	**Paper**
Surface water	Grab samples	Baltic Sea, Kattegat, and rivers in Sweden (mainly river mouths)	PFASs	Paper I
Surface water	Grab samples	Stockholm Arlanda Airport and Fyris River, Uppsala, Sweden	PFASs	Paper II
Bulk atmospheric depostition	Passive deposition samplers	Vindeln, Sweden	PACs	Paper III
Surface water	Grab samples and high-volume active samplers	Streams/rivers within the Vindeln and Umeå river catchment, Sweden	PACs	Paper IV

Paper I: Surface water samples were collected along the Swedish coast, close to the mouth of the rivers that contribute most water discharge to the recipient seas (the Baltic Sea and Kattegat). In addition, four upstream river sites were included, three of them which were also used as sampling sites in Paper IV. The sampling of rivers was conducted in October 2013 at the mouth of 40 rivers (Figure 1). Seawater samples were collected during a cargo ship tour in August-September 2013 at 18 off-shore sites (Figure 1) in the Bothnian Bay (*n* = 5, north), the Bothnian Sea (*n* = 3, central), the Baltic Proper (*n* = 6, south), and the west coast of Sweden (Kattegat, *n* = 4).

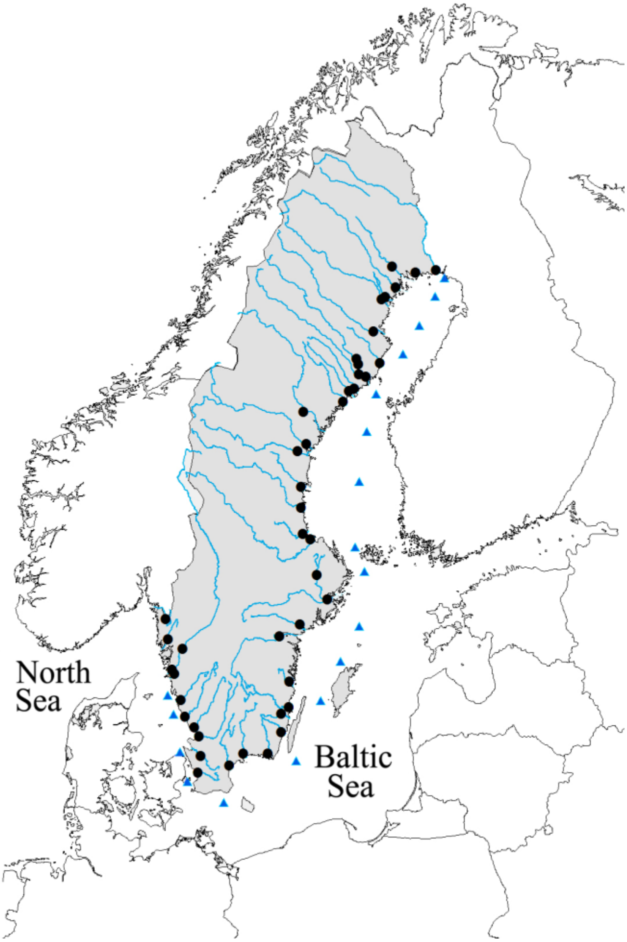


Figure 1. The river and sea sampling sites in Paper I. Black dots (●) represent river water sampling sites and blue triangles (▲) represent sea water sampling sites. The figure is adapted from Paper I.

Paper II: Two study areas were selected based on two different types of point sources for PFASs: fire-fighting training areas at airports (two catchments) and WWTPs (one of the catchments). The sampling was performed monthly at each site from February 2013 to March 2014 to investigate seasonal trends. In the Märsta River catchment, surface water samples were collected at two sampling sites near and downstream from Stockholm Arlanda Airport, Sweden. PFAS-containing AFFFs were frequently used in the airport fire-fighting training area from the 1980s up to 2011 (Ahrens *et al.*, 2015). In 2011, the former PFAS-containing AFFFs were replaced with fluorine-free AFFFs (Moussol FF 3/6, Dr. Richard Sthamer GmbH & Co. KG, Hamburg, Germany) (Ahrens *et al.*, 2015). In the Fyris River catchment near Uppsala, Sweden, samples were collected from three sites. One of the sites was located near Uppsala-Ärna airport and upstream of a WWTP (Kungsängsverket WWTP, 160 000 population equivalents), the second sampling site was downstream of the WWTP, and the third sampling site was upstream of the Fyris River (approximately 20 km north east of Uppsala city) and is referred to as the reference site.

River and seawater samples for Paper I and Paper II were collected by grab sampling at a depth of approximately 0.4 m using 1 L polypropylene (PP) bottles pre-rinsed with methanol. In the field, the sampling bottles were rinsed three times with river/seawater prior to sampling. Directly after sampling, the bottles were stored dark and cool until analysis. Duplicate samples were collected on several sampling occasions (see individual paper for more detail).

Paper III: Atmospheric deposition samples were collected for analysis of PACs at Svartberget field station within the Krycklan catchment study (KCS) area, a 67 km^2 pristine catchment located close to Vindeln, approximately 60 km west of the Baltic Sea in northern Sweden. Atmospheric deposition samples were collected using pre-cleaned adsorbent resin (15 g of Amberlite IRA-743; macroporous styrene-divinylbenzene; particle diameter (Ø) 500-700 μm) packed inside a glass cartridge (25 cm, Ø 2.5 cm, tapered in the bottom end Ø 0.8 cm). This cartridge was connected to a 0.049 m^2 glass funnel with vertical sample sides (collector volume 0.020 m^3). This sampler was employed for collecting bulk deposition (i.e. dry and wet deposition) during a multi-year sampling campaign from July 2012 until October 2016. The cartridges were exchanged every third month. The atmospheric deposition sampler used in this thesis has previously been used for sampling PAHs, PCDD/Fs and PCBs (Bergknut *et al.*, 2011; Gocht *et al.*, 2007).

Paper IV: Water samples were collected for PAC analysis during the period October 2014 to May 2016, and the sampling campaign covered all hydrological seasons at six sites in the Krycklan catchment study (KCS) area and downstream of the city of Umeå, Sweden. Three of the sites within the KCS were monitored, comprising streams *i)* in a forested subcatchment (C2, 100% forest; stream-order 1), *ii)* in a mire subcatchment (C4, 56% forest, 44% mire; stream-order 1), and *iii)* at the outlet of the catchment (C16, stream-order 4) (Figure 2). The remaining three sites were downstream sites outside the KCS area, all representing more densely populated areas (D1-D3, Figure 2). These later sites were the same as the upstream sites mentioned in Paper I. In Paper IV, the particulate fraction was collected by pumping water through glass fiber filters (GF/Fs) with a total of six filters representing from 70 L up to 1200 L of water per sample. For analysis of the dissolved phase, a fraction of the filtered water was collected in stainless steel containers (12 L).

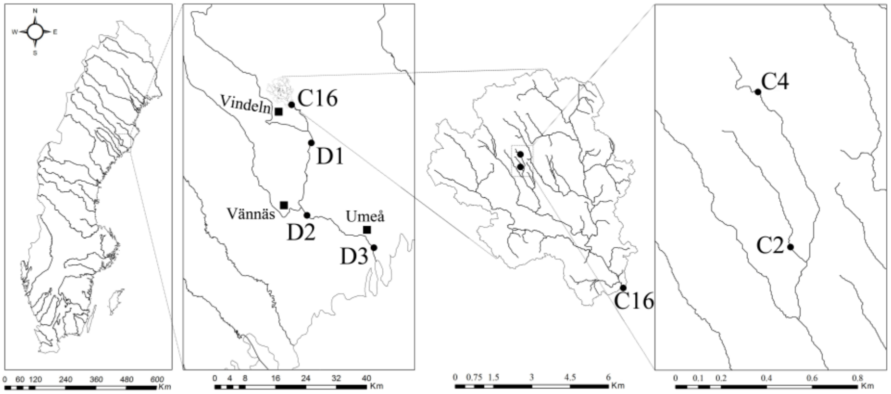


Figure 2. Locations of the six sampling sites (black dots ●) (C2: forest site, C4: mire site, C16: KCS outlet, D1-D3: downstream sites outside KCS catchment outlet) and nearby towns and cities (black squares ■) in a boreal catchment in northern Sweden. The Figure is adapted from Paper IV.

3.2 Extraction

The PFASs (Papers I and II) and PACs (Papers III and IV) studied in this thesis were extracted from the matrices using organic solvents and a combination of different extraction methods. The methods and organic solvents used in this thesis were chosen depending on sample matrix and sample size in order to maximize the extraction efficiency, but also considering consumption of organic solvents.

The surface water samples for PFAS analyses in Paper I and II were filtrated, and the dissolved phase was extracted by using solid phase extraction (SPE) using an Oasis weak anion exchange (WAX) cartridge (Waters, 6 mL, 500 mg, 60 µm for Paper I and 6 mL, 150 mg, 30 µm for Paper II) based on established methods (Ahrens *et al.*, 2009b; ISO, 2009). Solid phase extraction had the advantage of being a low solvent consumption method, and allowed several samples could be extracted simultaneously with high extraction efficiency. Particulate phase water samples in Papers I and II were extracted by shaking with methanol in polypropylene (PP) tubes. The extract for the particulate phase was combined with the extract from the dissolved phase in Paper II, but kept separate in Paper I.

In Paper III, the adsorbent (Amberlite IRA-743) used in the atmospheric deposition sample was transferred into cellulose extraction thimbles before extracting with Soxhlet-Dean-Stark using toluene. Soxhlet-Dean-Stark extraction was chosen for removing water which remained in the adsorbent. More details of the extraction method are given in Paper III.

In Paper IV, the dissolved phase of the surface water samples was extracted using SPE with a hydrophilic-lipophilic balance (HLB) cartridge and dichloromethane (DCM) as elution solvent. The HLB cartridge was chosen because of its suitability for compounds representing a wide range of hydrophobicity, as in the case of the selected PACs in this thesis (log K_{ow} 2.0-6.8). For particulate phase water samples in Paper IV, the extraction was performed using the same extraction method as for atmospheric deposition samples in Paper III.

3.3 Sample clean-up

Due to the complex matrices of environmental samples, interfering substances affecting the target signals can be co-extracted during the extraction process. Thus, one or several clean-up methods are required in order to reduce the impact from potential interferences, while still preserving the integrity of the analytes. In Paper I and Paper II, no clean up after the SPE was necessary due to the selective extraction method, which also included a washing step to remove potential matrix. Adsorption chromatography is often used due to its ability to retain various compounds of a broad range of polarities, from non-polar to more polar compounds (Voogt, 1994). In this thesis, alumina column clean-up using petroleum ether/DCM as elution solvent was employed as a clean-up method for the atmospheric deposition samples (Paper III) and for the particulate phase of the water samples (Paper IV).

3.4 Instrumental analyses, quality assurance and quality control

After sample preparation, the samples were analyzed using liquid chromatography coupled to tandem mass-spectrometry in negative electrospray ionization (ESI) mode (LC(-)ESI-MS/MS) (Papers I and II) or gas chromatography (GC) electron impact coupled to tandem mass-spectrometry (GC-EI-MS/MS) (Papers III and IV). LC(-)ESI-MS/MS was selected for analysis of PFASs since it has been shown to be the most sensitive and selective method for the PFASs studied in this thesis (Ahrens *et al.*, 2009b; ISO, 2009). GC-MS has been shown to be a suitable analytical method for PACs with high volatility (Andersson & Achten, 2015; Bandowea & Wilcke, 2010; Lundstedt *et al.*, 2007). In this thesis, an analytical method was developed for analyzing PAHs and PAH-derivatives in atmospheric deposition and water samples using GC-EI-MS/MS, which introduced high selectivity and sensitivity (see Paper III for more details).

Isotopically labeled internal standards for the target compounds (i.e. PAHs, PAH-derivatives and PFASs) were used to correct for any losses which occurred during the sample preparation processes. When corresponding internal standards were not available, the standards of compounds with similar physical-chemical properties were used. Recovery standards were added to the sample extracts before the injection into the analytical instrument and were used for calculating the recovery of the internal standards during the whole analytical procedure. All internal standards used in this thesis were isotopically labeled (^{13}C or ^{2}H), and their recovery is given in the individual papers.

In order to reduce the risk of any background contamination during sample collection, all sampling equipment and any tools that were in direct contact with samples were cleaned, burned (~400°C if possible), and rinsed with suitable solvents before use. Laboratory and field blanks were extracted and analyzed in parallel with samples to check for potential background contamination of target compounds. When an analyte was detected in blanks, the method detection limit (MDL) of that compound was calculated as the average of blanks + 3 X standard deviation (σ) in Papers I, III and IV, while the MDL in Paper II was calculated as 3 X standard deviation (σ). The sample results in this thesis were not blank corrected. If the analytes were not detected in any of the blanks, the lowest point in the calibration curve was used as MDL. Details on blanks as well as MDLs are given in the individual papers.

4 Results and discussion

4.1 Spatial distribution and source tracing of PFASs in rivers and recipient seas (Paper I)

In general, ΣPFAS concentrations of river samples were approximately two-fold higher than in the sea water. The shorter chained PFASs were the predominant PFASs (i.e. PFBS, PFHxS and PFBA) presumably partly attributed to their higher water solubility (Chen *et al.*, 2017; Shao *et al.*, 2016), which results in a high mobility in terrestrial and aquatic environments. High occurrence of shorter chained PFASs may also reflect the replacement of long chained PFASs (e.g. PFOS and PFOA) in industrial and consumer products with shorter chained PFASs since 2000 (Möller *et al.*, 2010; 3M, 2000). River water has shorter residence times than seawater (Allaby, 1998), and thus rivers respond to changes in source patterns relatively quickly, whereas seawater reflects historical release of PFASs and other POPs over longer times (decades or even longer) (Benskin *et al.*, 2012). The total fraction of shorter chained PFASs (i.e. PFBS, PFHxS, PFBA; 55% of sum of ΣPFCAs and ΣPFSAs) were higher compared to longer chained PFASs in the rivers while this fraction was much lower (26%) in the seawater samples.

Analysis of the spatial distribution of ΣPFASs in Swedish rivers showed that the northern rivers (with river mouths located on the east coast of Sweden) had lower PFASs levels compared to rivers located on the south-east and south-west coast. Both population density and low latitude (south) were strongly correlated to the widely used PFASs PFOS and PFOA as well as to PFHxS. A similar spatial trend was observed for the seawater with lower PFAS levels in the northern sub-basins of the Baltic Sea (Bothnian Bay and Bothnian Sea) compared with the Baltic Proper and Kattegat.

Significant relationships between several PFCAs and PFSAs (i.e. PFBA, PFHpA, PFOA, PFBS, and PFHxS) and dissolved organic carbon (DOC) were detected (p<0.05). This indicates the potential of chemical binding and co-transport of these PFASs with DOC in water. PFCAs were found to be related to the latitude with higher concentrations of the longer chained PFCAs in the north.

Among the 40 rivers investigated, 10 showed higher ΣPFAS concentrations than the others (on average 7.5-fold higher) and, in addition also distinct compositional profiles with a higher fraction of PFSAs than other rivers. The ΣPFSA and ΣPFCA concentrations showed a significant linear relationship for these t10 river sites (p<0.0005) with a slope of 1.8 (i.e. PFSAs dominated), whereas the slope for the other river sites was only 0.34 (i.e. PFCAs dominated; p<0.00001) (Figure 3). This suggests that these 10 rivers were impacted by a similar kind of point source(s). However, it was not possible to determine what this point source type was.

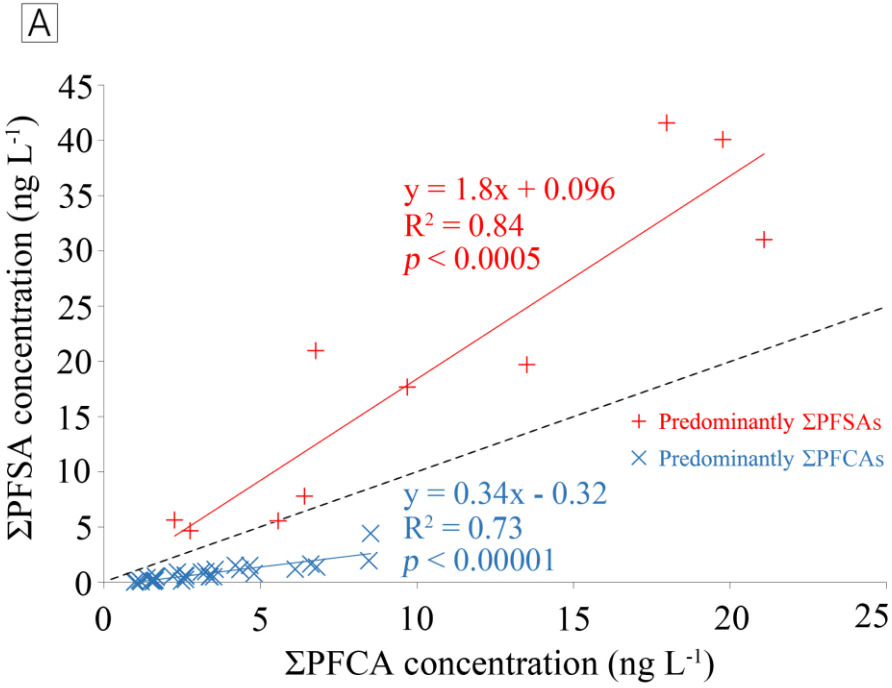


Figure 3. Rivers with predominantly ΣPFSA (in red color) and less-predominantly ΣPFSA concentrations (in blue color) plotted against ΣPFCA concentrations (dotted line represents 1:1 ratio). Figure adapted from (Nguyen *et al.*, 2017) (Paper I).

4.2 Impact of point sources and seasonal changes on of the distribution of PFASs (Paper II)

Point sources such as fire-fighting training sites and WWTP effluents have been shown to have a high impact on the occurrence of PFASs in river water (Gago-Ferrero *et al.*, 2017; Weber *et al.*, 2017; Ahrens *et al.*, 2015; Herzke *et al.*, 2012; Becker *et al.*, 2008). The highest average ΣPFAS concentrations (of the monthly samples during one full year; *n*=14) were observed in the area of Stockholm Arlanda Airport at the site located close to the airport fire-fighting training area and its downstream site in Märsta River. The average ΣPFAS concentration at those sites was 16-fold higher (~300 ng L^{-1}) than the average of ΣPFAS concentration at sites impacted by Ärna-Uppsala airport and the WWTP in Uppsala (19 ng L^{-1}).

The dominant PFASs were PFOS (47% of ∑PFASs) and PFHxS (29%) at all sampling sites. However, different compositional profiles were observed at sites impacted mainly by AFFFs or WWTP. The shorter chained PFASs made a higher contribution at the site located near Uppsala's WWTP (i.e. PFHxS 41% and PFBS 6.7% of the ∑PFASs) in comparison to the AFFF-impacted sites (on average PFHxS 26% and PFBS 2.1% of the ∑PFASs), indicating that products used in households may be the source of the shorter chained PFASs that, have replaced the C_8-based types. The high concentrations of PFSAs found in rivers influenced by point sources in Paper II are in agreement with the findings in Paper I.

All sampling sites were impacted by seasonal changes due to varying hydrological conditions. For example, the ∑PFAS concentrations at the sampling site nearest to Stockholm Arlanda Airport were 1.5 times higher during the high flow season (spring flood) compared to the low flow season indicating that the driving forces for the release of PFASs from contaminated soil at this sampling site was precipitation which results in an increasing run-off and subsurface groundwater flow. The other sampling sites showed generally lower ∑PFAS concentrations during the spring flood indicating that, besides the impact by contaminated soil or WWTPs, the dilution factor plays an important role in influencing the seasonal changes of PFASs. As a consequence, fluxes of PFASs from Märsta (located near Stockholm Arlanda Airport) and Fyris River (located near Ärna-Uppsala airport and Uppsala WWTP) into Lake Mälaren were subjected to change over the year depending on seasons. These seasonal changes potentially also impact the drinking water quality in the region over the year, as Lake Mälaren is the water source area of a major drinking water plant serving approximately two million people.

4.3 Atmospheric deposition and seasonal variation of PACs in a remote boreal catchment (Paper III)

Atmospheric deposition is a source of PAC contamination of boreal catchments (Su *et al.*, 2007) and Arctic areas (Hung *et al.*, 2005; Brun *et al.*, 2004). In Paper III, it was found that chrysene, pyrene and fluoranthene were the dominant PAHs in the atmospheric deposition, while 9-fluorenone and quinoline were the dominant PAH-derivatives. The composition of PAHs in the atmospheric deposition in the KCS area was found to be different to modeled PAH composition for Europe as a whole (including Sweden; (EMEP, 2017), where benzo(*a*)pyrene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene and indeno(1,2,3-*cd*)pyrene were predicted to be the dominant compounds. However, the findings in this thesis were related to a pristine boreal catchment, while the EMEP modeling refers to a more densely populated area with more complex PAH sources (EMEP, 2017).

The atmospheric deposition of PACs in the KCS (boreal forest) area showed higher fluxes during the winter season. For months with average air temperature <0°C, the average deposition rate was 680 ± 540 ng m^{-2} day^{-1} for PAHs and 310 ± 340 ng m^{-2} day^{-1} for PAH-derivatives (not including 9-fluorenone). For months with average air temperature >10°C, the average deposition rate was 260 ± 300 ng m^{-2} day^{-1} for PAHs and 95 ± 39 ng m^{-2} day^{-1} (not including 9-fluorenone). All individual PAHs (n=13) showed higher average values during the cold (<0°C) periods and for PAH-derivatives, 11 compounds out of 12 had higher averages during the cold season (Figure 4).

Seasonal variation of atmospheric deposition fluxes of POPs depends on many factors, such as air concentrations and meteorological conditions (e.g., precipitation type and quantity). It is well known that the source strength of PAH emissions to air is elevated during winter due to increased needs of energy for heating and transport (e.g., combustion of various fuels) (Golomb *et al.*, 2001). The observed higher fluxes of PACs during winter may also be attributed to snow scavenging, whereby PACs bound to particles are efficiently washed out from the atmosphere (Carrera *et al.*, 2001; Franz & Eisenreich, 1998; Wania *et al.*, 1998). Our data suggest that air concentrations of PAH-derivatives could also be elevated during winter.

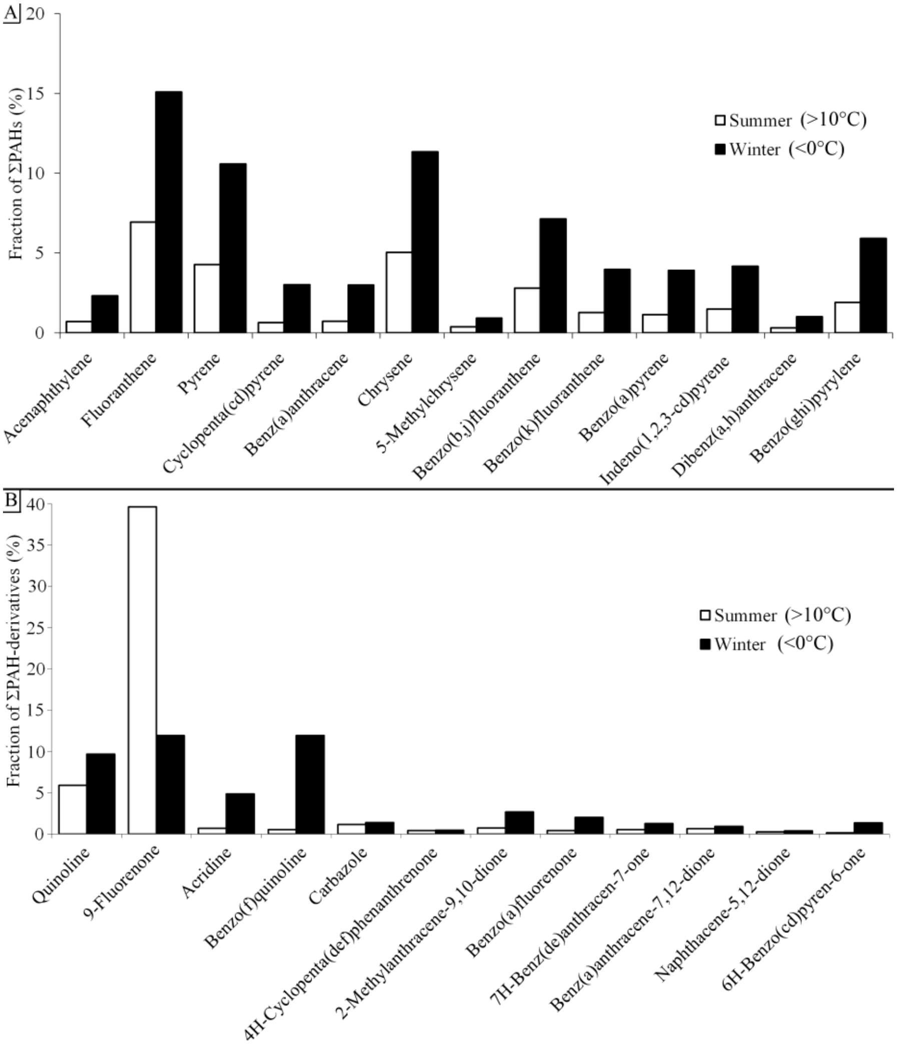


Figure 4. Average fractions of individual PACs in atmospheric deposition over the whole sampling period (2012-2016) separated into cold (<0°C; *n*=4) and warm (>10°C; *n*=4) periods and plotted as fractions in relation to A) ΣPAHs and B) ΣPAH-derivatives. Figure adapted from Paper III.

Modelled fluxes of atmospheric deposition of the four most predominant PAHs in the air (i.e. benzo(*a*)pyrene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene and indeno(1,2,3-*cd*)pyrene) have been found to be >100 g km^{-2} year^{-1} for most European countries (e.g., Portugal, Montenegro, Spain, Slovakia, Germany, Poland, Hungary, Czech Republic, and Romania) , while the predicted flux for Sweden is <50 g km^{-2} year^{-1} (average for the whole residential area) (EMEP, 2017). The results in the current study showed a two-fold lower value (18 g km^{-2} year^{-1}) compared to the modelled value for Sweden as a whole. The average annual amount of ΣPAHs (*n*=13) and ΣPAH-derivatives (*n*=12) deposited to the KCS catchment area (67 km^2) was estimated to be 13 kg yr^{-1} and 12 kg yr^{-1}, respectively. However, it should be borne in mind that the estimated flux in Paper III was for a relatively pristine area, while the modeled value for Sweden included the whole country.

4.4 The role of spring flood and landscape types in terrestrial export of PACs to stream water (Paper IV)

Snowfall plays an important role in scavenging PAHs from the atmosphere (Herbert *et al.*, 2004; Lei & Wania, 2004; Franz & Eisenreich, 1998), and during the winter season, PAHs accumulate in the snow (Meyer & Wania, 2008). In Paper IV, the levels of 19 PAHs and 15 PAH-derivatives were measured in surface waters during all hydrological seasons (snow-free, snow-covered and spring flood; 2014-2016) in streams of a remote headwater catchment in Sweden and in downstream rivers draining also more urbanized areas. It was observed that the spring flood significantly impacts PAC concentrations in the surface water, with e.g., up to 110-fold higher levels of PAHs and up to 7000-fold higher levels of PAH-derivatives than during the preceding snow-covered and snow-free seasons. A clear impact of spring flood on stream water quality was thus observed. The estimated fluxes of PACs at the outlet of the remote headwater catchment during spring flood were higher (9.5-fold for PAHs and 1.3-fold for PAH-derivatives) than total fluxes during snow-free and snow-covered seasons, albeit the short duration of the spring flood season.

Besides seasonal hydrological changes, landscape types (i.e. forested areas or mires) were shown to impact the terrestrial export of PACs to the stream water. Levels of PACs tended to be higher in the stream at the mire site compared with the forested site (up to 20-fold for PAHs and 150 times for PAH-derivatives). Similar trends have been observed for PCBs and PCDD/Fs in the same catchment (Josefsson *et al.*, 2016). The observed trends are suggested to be explained by the different vertical distribution of POPs in the forest soil as compared to the mire, in combination with seasonal variations in hydrological flow paths (Peralta-Tapia *et al.*, 2014).

The potential of the terrestrial environment to retain deposited PAHs and PAH-derivatives was estimated for the studied boreal catchment by comparing the total amount of PACs deposited in the catchment (Paper III) with the total flux of the PACs passing the outlet of the headwater catchment (Paper IV) on an annual basis. The results from these calculations showed that boreal forest catchments have high potential in retaining PACs within the catchment. The estimated fluxes (kg year^{-1}) of ΣPACs at the catchment outlet was <0.8% for

PAHs and <1.7% for PAH-derivatives in relation to the estimated total amount of ΣPACs deposited into the whole catchment over a year. The retention efficiency was, however, calculated conservatively as losses of PACs from the catchment through e.g., volatilization and degradation were not considered. The results for PAHs and PAH-derivatives complied well with corresponding results for PCDD/Fs and PCBs, which have been found to be retained in the terrestrial environment at a fraction of 0.5% for PCDD/Fs and 0.2% for PCBs (Bergknut *et al.*, 2011).

When considering the individual PAHs and PAH-derivatives, the general pattern was that the fraction exported was smaller than the fraction deposited, i.e., the amount exported was lower than the amount deposited on an annual basis. However, for a few of the PAHs (two out of 13; cyclopenta(*c,d*)pyrene, and chrysene) and some of the PAH-derivatives (three out of 12; quinoline, benzo(*f*)quinoline, and carbazole) showed relatively higher export potential (>1%) compared to other PACs (Figure 5). It could be observed that the more highly exported PAHs represented lower molecular mass compounds (MV<240; log K_{ow} < 6.0), while the higher molecular mass compounds (MV>240; log K_{ow} >6.0) were exported to a lower extent. For PAH-derivatives, high export potential was only seen for compounds with log K_{ow} from 2.0 to 3.4 (quinoline, benzo(*f*)quinoline, carbazole), having molecular mass <180, while none of the higher molecular mass compounds (log K_{ow} from 3.9 to 5.3) showed higher export potential. Potential explanations to the observed higher potential export of these PACs might be preferential partitioning due to lower hydrophobicity and post-depositional formation through transformation reactions (particularly for the PAH-derivatives).

Levels of bulk ∑PACs normalized to total volume of water in the river were on average three-fold higher downstream of the most densely populated area than at the outlet of the headwater catchment, but there was no clear increasing downstream trend. When levels instead were expressed as particulate ΣPACs normalized to suspended particulate matter (SPM) (ng g^{-1}), a clear gradually increasing downstream trend was observed, demonstrating the anthropogenic impact of PACs pollution in more urbanized areas.

Observations for the two compound groups studied in Paper III and IV, ∑PAHs and ∑PAH-derivatives, with respect to seasonal variation, impact of landscape type, increasing downstream trend on SPM basis, correlation with environmental parameters, and fraction of exported amounts in relation to deposited amounts demonstrated similar environmental transport behavior for the two groups. Moreover, although less hydrophobic than other planar POPs, such as PCDD/Fs and non- and mono-*ortho*-PCBs, the behavior of the studied PACs comply well with trends observed for the abovementioned pollutants. This is likely attributed to the shared characteristics of the molecules being flat, in contrast to the non-planar (poly-*ortho*) PCBs, which partly behave differently in the same system (Josefsson et al., 2016).

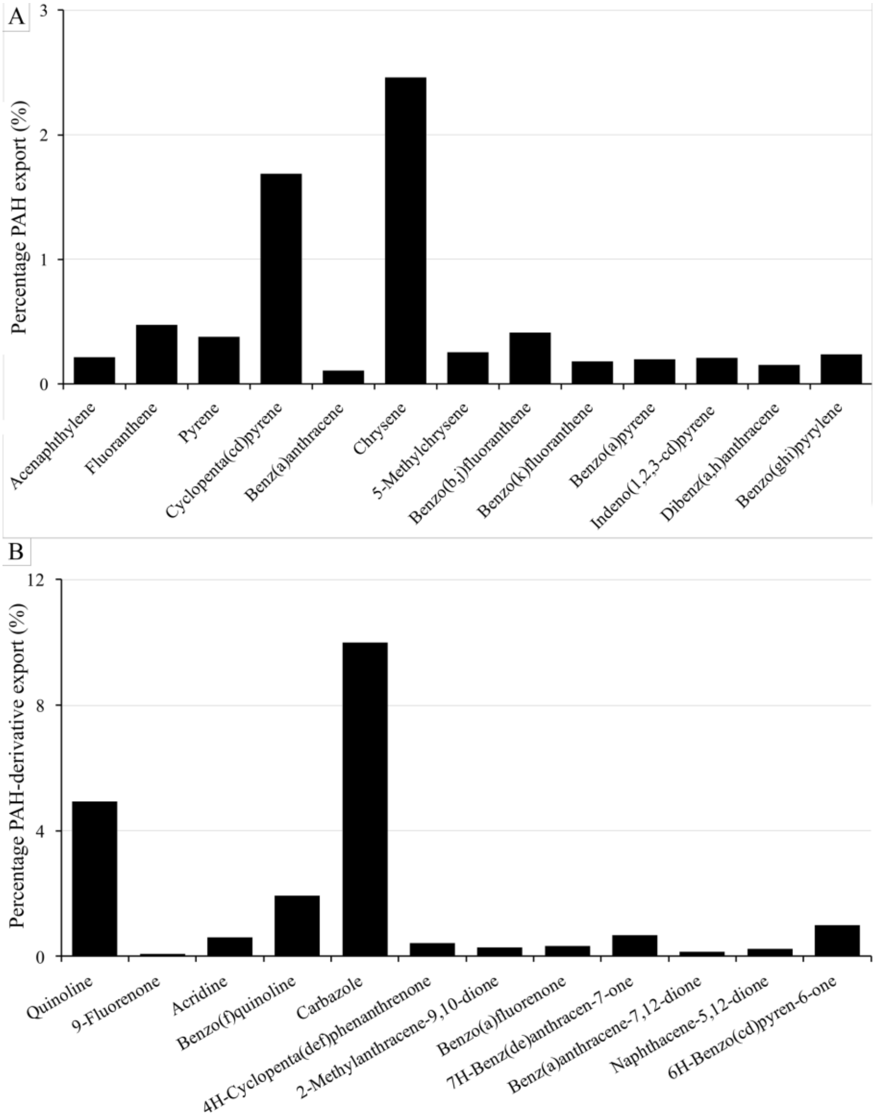


Figure 5. Percentage (%) export of A) individual PAH and B) individual PAH-derivative in comparison to the amount of corresponding PAC deposited to the catchment

5 Conclusions and future remarks

This thesis has contributed to a better understanding of the environmental behavior of legacy and emerging POPs in pristine and polluted boreal catchments by investigating the *i)* spatial distribution of PFASs and PACs in boreal catchments, *ii)* the impacts of point sources and transport of PFASs in water over different seasons, *iii)* seasonal trends of PACs in atmospheric deposition, and *iv)* the role of spring flood and landscape type on terrestrial export of PACs to stream and river water.

PFASs were shown to be ubiquitously distributed in all investigated rivers along the Swedish coasts and their recipient seas (Paper I). Point sources of PFASs including fire-fighting training areas showed strong impact on PFAS pollution in their catchment rivers (Paper I and II). Besides fire-fighting training areas and WWTPs (Paper II), population density was found to be the main factor impacting concentrations of PFASs in river and sea water (Paper I). On a regional scale, the concentration of PFASs in rivers varied depending on water flow (Paper II), with both higher and lower levels following high water flow depending on site. Consequently, fluxes of PFASs in rivers are impacted by hydrological (seasonal) changes. The findings in Papers I and II show that the environmental levels of PFASs highly depend on the characteristics of the region. Potential environmental and human health effects from PFASs exposure even at low levels of exposure cannot be excluded and need to be investigated further.

Fluxes of PACs were also subjected to seasonal changes with higher levels in atmospheric deposition during cold seasons as compared to warm seasons (Paper III). The meltwater from snowpack enriched with PACs over the winter season showed a strong impact on boreal stream water quality by significantly higher levels and fluxes of PACs during the spring flood season compared to the preceding snow-covered and snow-free seasons (Paper IV). Landscape types were shown to impact water levels of PACs, with mire stream water more polluted than the stream water in a forested area. The two substance groups within PACs (i.e. PAHs and PAH-derivatives) showed similar environmental transport behavior (Paper III and Paper IV), reflecting known trends shown by other planar POPs (e.g. PCDD/Fs, non- and mono-*ortho* PCBs, and hexachlorobenzene (HCB) (Josefsson *et al.*, 2016). This indicates that the attribute of flat molecular structure is of critical importance for mode of environmental transport and fate in aquatic, including marine, systems.

There is a need for further investigations of the mechanisms driving long-range atmospheric transport and the magnitude of this transport process for PACs and PFASs, in particular for PFCAs and PAH-derivatives (Paper I and Paper III). Moreover, little is known about the binding mechanism between PFASs/PACs and DOC in fresh water and sea water (Paper I and Paper IV) and the role of DOC in co-transporting these compound classes and other POPs in aqueous and marine ecosystems. For PACs and other planar POPs, directed studies on the role of black carbon (BC) are needed to better understand transport mechanisms of long-range atmospheric transport of PACs (Paper III) and PAC's binding to various carbon fractions (including BC) of suspended particulate matter (SPM) in water (Paper IV). Moreover, little is known about the role of microplastics as carriers of PACs and PFASs in the aquatic environment. In addition, increased monitoring of atmospheric deposition of PAHs and PAH-derivatives in pristine environments is needed to better understand the transport behavior of PAH-derivatives in relation to PAHs (Paper III). Last but not least, there is a lack of understanding of the sorption mechanisms of PFASs and PACs in different soil types and mechanisms on retention and mobilization from soils to stream and river water (Paper II and IV). Research on this is important, as there is an urgent need to prevent future leaching of PFASs and PACs from contaminated soils into the aqueous environments.

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Popular science summary

Persistent organic pollutants (POPs) can be divided into two sub-groups: classical (legacy) or emerging pollutants. The classical POPs have been studied extensively, and have often been regulated and monitored over decades. The emerging POPs, on the other hand, are substances that have only recently got attention. Per- and polyfluoroalkyl substances (PFASs) and polycyclic aromatic compounds (PACs) are examples of POPs that are currently of great concern due to their potential toxicity and high mobility in the terrestrial and aquatic system. PFASs are man-made chemicals with unique properties that can be used for a wide range of industrial and consumer applications. Aqueous fire-fighting foam, dirt and water repellent coating materials, and food packaging materials are examples for applications of PFASs. Polycyclic aromatic compounds can be formed naturally (e.g. in coal and crude oil,) or be produced unintentionally during incomplete combustion of organic materials (e.g. fossil fuels and garbage). Some PACs can also be produced intentionally for industrial use. The overall objective of this thesis was to improve our understanding on the environmental pathways, transport and fate of these legacy and emerging POPs in pristine and polluted boreal catchments.

The first investigation in this thesis (Paper I) focused on PFASs in streams and rivers along the Swedish coast, both on the east coast (the Baltic Sea) and on the west coast (the Kattegat). The results showed that several rivers had higher PFAS concentrations. These rivers also had another composition of the different PFASs than the rivers with lower concentrations, suggesting an impact of a similar kind of point source in these rivers. Potential point sources and their impact on PFAS levels in river water were investigated in Paper II in rivers located close to point sources, such as fire-fighting training areas and wastewater treatment plants. Levels and compositions of PFASs in the river water were highly impacted by point sources and hydrological conditions. There were seasonal trends of PFASs in the river water, probably due to variations in the mobilization of PFASs from contaminated soil and groundwater during the year.

The impact of so-called diffuse sources on fluxes of PACs in atmospheric deposition, for example deposition due to rain, and PACs concentrations in streams in boreal forests were investigated in Paper III and IV. The fluxes of PACs from the atmosphere were higher during winter than during summer. The results showed that the boreal forest can retain PACs: less than 2% of the estimated amount of PACs deposited in the studied area was transported out with rivers. During spring flood, the concentration of PACs in the river draining the area was higher than during the rest of the year (snow-covered and snow-free seasons). Besides seasonal changes, landscape types (forest or mire) were found to have an impact on the export of PACs from land to water, with higher levels of PACs in a mire stream compared to a forest stream. Last but not least, rivers located close to more densely populated areas showed a stronger impact of POPs than in streams at the pristine study area where the population density was very low.

Populärvetenskaplig sammanfattning

Persistenta organiska föroreningar (POPs) är långlivade giftiga kemikalier som kan ackumuleras i levande organismer. POPs kan hittas i miljön över hela världen, och flera av ämnena kan transporteras över långa avstånd. På så sätt kan de röra sig långt från källorna och nå avlägsna miljöer. POPs kan delas in i två undergrupper: klassiska och nya föroreningar. De klassiska POP-ämnena har studerats i stor utsträckning och har ofta reglerats och övervakats under årtionden. De nya POPs är ämnen som nyligen har fått uppmärksamhet. Per- och polyfluorerade alkylsubstanser (PFAS) och polycykliska aromatiska föreningar (PAC) är exempel på POPs som är oroande på grund av sin potentiella giftighet och höga rörlighet i mark och vatten. PFAS är tillverkade kemikalier med unika egenskaper som kan användas i ett brett utbud av industri- och konsumentprodukter. Vattenbaserat brandskum, smuts- och vattenavvisande beläggningsmaterial samt matförpackningar är exempel på produkter där PFAS kan användas. PAC kan bildas naturligt (t ex i kol och råolja) eller bildas oavsiktligt vid ofullständig förbränning av organiska material (t ex fossila bränslen och sopor). Vissa PAC kan också produceras avsiktligt för industriell användning. Det övergripande målet med den här avhandlingen var att öka vår förståelse av hur både klassiska och nya POPs (PAC och PFAS) transporteras och vad som händer med dem i såväl opåverkade som förorenade boreala avrinningsområden.

Den första undersökningen i den här avhandlingen (Paper I) fokuserade på PFAS i vattendrag längs den svenska kusten, både på ostkusten (Östersjön) och på västkusten (Kattegat). Resultaten visade att flera vattendrag hade högre PFAS-koncentrationer. Dessa vattendrag hade också en annan sammansättning av de olika PFAS-ämnena än vattendrag med lägre koncentrationer, vilket tyder på en liknande typ av punktkälla. Potentiella punktkällor och deras inverkan på PFAS-halter i vatten undersöktes i Paper II i vattendrag som ligger nära punktkällor, såsom områden som använts för brandövningar och reningsverk. Halterna och sammansättningen av PFAS i vattnet påverkades starkt av punktkällor och hydrologiska förhållanden. Det fanns årstidsvariationer i PFAS-halterna i vattendragen, troligen på grund av variationer i mobiliseringen av PFAS (hur ämnena rör sig) från förorenad mark och förorenat grundvatten under året. I Paper III och IV undersöktes effekterna av så kallade diffusa källor på flöden av PAC i atmosfärisk deposition, till exempel deposition p.g.a. regn, och PAC-koncentrationer i vattendrag i boreala skogar. Flödena av PAC från atmosfären var högre under vintern än under sommaren. Resultaten visade att boreala skogar kan hålla kvar PAC: mindre än 2 % av den beräknade mängden PAC som deponerades i det undersökta området transporterades ut med vattendragen. Under vårfloden var koncentrationen av PAC i älven som avvattnar det studerade området högre än under resten av året (snötäckta och snöfria årstider). Förutom årstidsvariationer visade sig landskapstyper (skog eller myr) påverka utflödet av PAC från land till vatten: nivåerna av PAC var högre i ett vattendrag som avvattnade en myr än i ett som avvattnade ett skogsområde. Sist men inte minst var vattendrag i tätbefolkade områden mer påverkade av POPs än vattendrag i det mer orörda undersökningsområdet där befolkningstätheten var mycket låg.

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