Project No. SN-01/03

PERSPEC

Perspectives on mobilisation of prioritised contaminants in soil

Final Research Report

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The SNOWMAN partners are:

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PERSPEC

Perspectives on mobilisation of prioritised contaminants in soil

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1   Abstract

Many anthropogenic contaminants such as hydrophobic organic contaminants (HOCs) and metals become airborne and are later deposited and accumulate in distant catchment soils, such as those in northern latitudes. The aim of the PERSPEC project was to compile current knowledge on how atmospheric and hydrological processes such as a change in temperature, groundwater level or change in precipitation pattern influence soil system processes. Special attention has been given to the mobilisation of contaminants to, within, and from soils, with focus on priory substances according to the European water framework directive (WFD). Hence both metals, like mercury, lead, and aluminium, and HOCs, such as polycyclic aromatic hydrocarbons, chlorophenols, PCBs and dioxins were studied. The project was to profit from the results obtained at the Krycklan catchment study (KCS) where long-term hydrological and biogeochemical monitoring has been conducted in combination with 30 years of process based research.

Metals and organic contaminants have in the past often been studied separately, mainly due to their different chemical properties. However, in the environment they coexist and are subject to the same environmental processes. The presented data showed increased concentrations in soil pore water and in soil with increased amount of organic matter (OM) in the soil profile for both metals and HOCs, with maximum values obtained in the top layers of the riparian soil. This indicates that spring flood and other hydrological events affect the stream water levels and loads of contaminants. It is also clear that there is great seasonality of wet and dry atmospheric deposition fluxes in the KCS area, which likely influences the temporal patterns of terrestrial contaminant export. Hence, climate change scenarios including changes in temperature and precipitation will affect both the accumulation and mobility patterns of contaminants in northern latitude boreal regions. The large seasonality in levels and export of contaminants may also have direct consequences for environmental monitoring programs.

As part of the PERSPEC project, levels of HOCs in surface water along the water path from Krycklan to the Gulf of Bothnia were measured and preliminary results are given in this report. The results varied depending on if the concentrations were calculated as amount per water volume or if the values were normalised to the amount of organic carbon present in the water (pg/g OC), once again underlining the importance of organic carbon. Nonetheless, the results show that atmospherically derived diffuse pollution has an impact in addition to downstream point sources.

The data from Krycklan was also modelled with various state-of-the-art models in an attempt to describe the fluxes of contaminants and the processes that regulate these fluxes within the studied catchment and water path. The results from the modelling of HOCs were used to estimate total atmospheric inputs for each season, compare HOC exports for the different seasons and different catchment types (forested / mire), compare exports to total soil inventory, calculate relative contribution of snowmelt to total HOC exports, quantify the role of the spring flood in delivering HOCs to the Krycklan catchment, and estimate the influence of enhanced soil contamination on export of HOCs to the stream. The modelling of metals was focused on comparing two different approaches: WITCH and PHAST. The WITCH code is a geochemical model that allows calculations of soil solution composition and mass balance calculations of elements in different soil compartments based on a series of parallel reactions of dissolution, plant uptake and precipitation. PHAST is a multi-box model that allows hydrology to be connected to both thermodynamic and empirical kinetic rate laws. This permits a more flexible model structure and varying depth in model complexity.

In summary, the presented data shows that although metals, trace elements and HOCs are governed by significantly different chemical properties, they are subject to the same soil - water controlled processes, such as interaction with organic matter (OM) and dissolved organic carbon (DOC), and this has a considerable impact on their environmental fate. The PERSPEC project also serves as a great example on how an interdisciplinary approach where hydrology, soil science, and organic and inorganic environmental chemistry working in tandem contributes significantly to the fundamental understanding of pollution mobility.

2   Sammanfattning (Abstract in Swedish)

Målsättningen med PERSPEC var att samla kunskap om hur atmosfäriska och hydrologiska processer som till exempel förändringar i nederbörd, temperatur och grundvattennivå påverkar de markprocesser som styr transport av föroreningar till, inom och från mark. Ämnen som pekats ut som miljöfarliga enligt European water framework directive (WFD) studerades, och bland dessa återfinns miljöföroreningar som historisk har fått mycket uppmärksamhet, så som kvicksilver, bly, aluminium, PAHs, PCBs, klorfenoler och dioxiner. PERSPEC utgick från resultat insamlade genom Krycklan catchment study (KCS), en övergripande studie av ett avrinningsområde där hydrologisk och biogeokemisk forskning pågått i 30 år.

Metaller och organiska föroreningar har oftast studerats separat, i huvudsak på grund av deras olika kemiska egenskaper. I miljön samexisterar de och utsätts således för samma miljöprocesser. De data som presenteras i denna rapport visar på ökade halter i porvatten och mark med ökad andel organiskt material i marken för både metaller och organiska miljöföroreningar, och de högsta halterna återfinns i de övre marklagren i den bäcknära zonen. Detta visar att vårflod och andra hydrologiska händelser som påverkar vattenflöden och vattenstånd kommer att medföra en förändring av föroreningshalten i ytvatten. Det står också klart att det förekommer en stor säsongsvariation i den atmosfäriska avsättningen av föroreningar inom KCS området vilket också bidrar till att exporten av föroreningar ut från området varierar över året. Detta har en direkt inverkan på hur och när prover bör tas inom olika miljöövervakningsprogram och får också konsekvenser vid framtida eventuella klimatförändringar.

Som en del av PERSPEC mättes halterna av hydrofoba organiska föroreningar (HOCs) i vatten i Krycklan och nedströms mot Bottniska viken. De första resultaten redovisas i denna rapport och visar att diffusa källor så som atmosfärisk deposition och efterföljande mobilisering från mark har en inverkan även i jämförelse med punktkällor. Data från Krycklan användes även i olika modeller för att försöka beskriva hur miljöföroreningar fördelar sig inom det studerade området och vilka processer som styr denna fördelning. Modellerna av hur HOCs fördelar sig användes för att uppskatta tillskottet via atmosfärisk deposition och hur denna varierar över året, hur HOCs fördelar sig vid olika årstider för olika delar av Krycklan (skogsmark vs. myrmark), exporten av HOC från mark, inverkan av snösmältning och vårflod samt för att uppskatta hur förhöjda markkoncentrationer påverkar exporten av HOC till vatten. Modellerna för metaller fokuserade på att jämföra två strategier, en geokemisk modell och en så kallad multi-box modell. Den senare tillät en mer flexibel modellstruktur med varierande modellkomplexitet.

En övergripande lärdom från PERSPEC är att fastän metaller och organiska miljögifter har fundamentalt olika kemiska egenskaper så påverkas de till stor del av samma processer i mark och vatten. Framför allt är andelen löst organisk kol i vattenfasen av avgörande betydelse och har stor inverkan på ämnenas fördelning och transport till olika delar av miljön och på deras mobilitet under året. PERSPEC är sammanfattningsvis ett tydligt exempel på hur en interdisciplinär samverkan mellan hydrologer, markvetare och kemister leder till en värdefull och mycket välbehövd forskningsinsats.

3   Executive summary

By including researchers from Umeå University (Sweden), Lancaster University (UK), and Graz University (Austria), the PERSPEC project brought together experts on all major processes that influence the fate of contaminants in soils and waters in northern Europe. These processes, which are thoroughly described within the PERSPEC project, include accumulation of contaminants from the atmosphere, snow to soil and groundwater transfer of contaminants; hydrological conditions and soil processes controlling the fate of contaminants; contaminant adsorption to soil constituents; leaking of contaminants from soil to water; and transport of contaminants in water systems.

Soil system processes and the mobilisation of contaminants in soil are connected to the hydrological conditions and processes in the soil. In much of the northern and high altitude central regions of Europe, the springtime snowmelt is one of the most important hydrological events of the year. Future climates changes are predicted to drastically alter the precipitation pattern in much of Europe and hence also the mobilisation of contaminants from soils to surface and ground waters. Consequently there is a lot to gain from combining the scientific expertise from countries that share these climate attributes and in this respect are likely to be affected similarly.

Improving the fundamental understanding of the fate of both natural solutes and anthropogenic contaminants is of outmost importance for the wellbeing of our aquatic ecosystems. This is of special urgency in boreal regions in northern latitude. These land areas are experiencing a disproportionate accumulation of anthropogenic contaminants as they are atmospherically transported from more densely populated regions with the prevailing weather systems. This northern zone is also a region where climate change scenarios predict the largest changes in temperature and precipitation in the future, which will affect both the accumulation and mobility patterns of contaminants in the region.

When studying complex systems, such as soil system processes, it is prudent to start with a well-defined system and only expand the area of research once a good understanding of the studied system has been attained. For this purpose the PERSPEC project utilised existing data from a pristine area in Northern Sweden, the Krycklan catchment, representing a low background contamination area. Krycklan is unique in the availability of climatic, hydrological and chemical data collected as well as in the timescale for some of the observations. The upper part of the Krycklan catchment is extremely well documented, as both climatic and hydrological studies have been performed in the area for nearly three decades. It provides an exceptional basis for temporal and spatial analysis of contaminants in the environment usually not available within studies of other areas. The large amounts of climatic, hydrological, and basic and advanced chemical data including pH, level of dissolved organic carbon (DOC), and concentration and speciation of metals and organic contaminants made the Krycklan area an ideal starting point for the PERSPEC project.

In addition to this, the PERSPEC project followed the development throughout the whole river basin down to the Gulf of Bothnia (the northern part of the Baltic Sea). Along this path there are a number of point sources (including Umeå city, a sewage treatment plant, and a chlorophenol contaminated land site). Data from other waters in Europe that experience enhanced contamination levels were also compiled within the PERSPEC project. Knowledge on the presence and behaviour of contaminants in these systems in comparison to headwater catchments such as Krycklan is necessary in the context of understanding chemical loading downstream and the baseline contribution of atmospherically-derived chemicals to Environmental Quality standards within the European Water Framework Directive (WFD).

The focus of the PERSPEC project was on priority substances according to the WFD such as metals (e.g. mercury, lead and aluminium), and hydrophobic organic contaminants (HOCs; e.g. polycyclic aromatic hydrocarbons, chlorophenols, PCBs and dioxins) and hence included studies on both metals and organic contaminants. Metals and organic contaminants have in the past often been studied separately, mainly due to their different chemical properties. However, in the environment they coexist and are subject to the same environmental processes. The data from Krycklan was modelled with various state-of-the-art models in an attempt to describe the fluxes of contaminants and the processes that regulate these fluxes within the studied catchment and water path. The models, combined with a concurrent study of literature, made it possible to identify the key processes of mobilisation, transport, and accumulation of the studied

contaminants. From the presented data it is evident that although metals, trace elements and HOCs are governed by significantly different chemical properties, they are subject to the same soil - water controlled processes, such as interaction with organic matter (OM) and dissolved organic carbon (DOC), and this has a considerable impact on their environmental fate. Hence, an interdisciplinary approach with hydrology, soil science, and organic and inorganic environmental chemistry working in tandem forms a valuable and much needed contribution. The findings from the PERSPEC project are applicable to a wide variety of north European catchments systems and provide an integrated, process-based, understanding of base-line contamination of major catchments from "atmosphere to estuary".

4   Acknowledgements

5   Table of Contents

6   Use of grant

Grants awarded to the PERSPEC project were used in accordance with the individual research grant applications, respectively, directly or indirectly connected to the PERSPEC project. Additional third party funding awarded to individual researchers part of the PERSPEC project was an integral part of the PERSPEC project.

The received funding allowed for the successful implementation of the PERSPEC project as described in this report.

7   Background

Many anthropogenic contaminants such as hydrophobic organic contaminants (HOCs) and metals become airborne and are later deposited and accumulate in distant catchment soils, such as those in northern latitudes. Heavy rainfall and snowmelt events often generate increased concentrations of organic matter from superficial soil horizons. Because of a strong association between organic matter and both metals and organic contaminants, hydrological events can generate an increased mobilisation and hence export of these long range air pollutants to adjacent surface waters. Due to the large export of water during precipitation events the total export of contaminants is further associated to these discrete events. Future climates are predicted to drastically alter the precipitation pattern in much of Europe and alter the timing and magnitude of hydrological episodes and hence the mobilisation of contaminants fluxes from soils to surface waters.

In much of the northern and high altitude central regions of Europe, the springtime snowmelt is one of the most important hydrological events of the year. Because the winter and spring temperature and precipitation patterns is predicted to be most affected in future climatic scenarios, the transport of contaminants from both diffuse and point sources, from the terrestrial to the aquatic environment might be heavily affected.

The transport of contaminants is dependent on the export of dissolved organic carbon (DOC). Large amounts of organic matter are stored in the soils of these regions but the quantitative role and dynamics of organic carbon in mobilising metals and HOCs is not fully understood.

7.1   Accumulation of contaminants from the atmosphere and transfer from snow to soil and ground water

Precipitation in the form of snow and cold winter rain is extremely efficient at scavenging both vapour and particle-bound HOCs from the atmosphere. As a result the standing snowpack may serve as a significant 'reservoir' for atmospherically-derived pollutants to both soil, sand and surface water. For semi-volatile chemicals, the changes to the snowpack, following snow sintering and compaction may result in significant volatilisation prior to the onset of snowmelt thus reducing the contaminant burden actually available to meltwater. Lower volatility chemicals or those possessing sufficiently low Henry's Law constants, are likely to be retained in the 'aged' snowpack and released with meltwater in the spring.

7.2   The role of dissolved organic carbon and water chemistry

Organic matter is the product of degradation and polymerisation of organic building blocks leading to a complex assemblage of organic functional groups. Organic matter may be operationally divided into hydrophilic and hydrophobic fulvic acids, neutrals and bases that may be separated using organic exchanger material. The hydrophobicity of the organic material is affected by the chemical composition and will in turn affect the binding properties of smaller organic molecules. The release of organic matter from solid matter is controlled by a number of factors such as base saturation, pH, temperature and hydrophobic character of the organic matter. Changes in pH tend to neutralize charges on organic matter and lead to higher affinity to the soil fraction. Consequently temporal changes in pH will lead to variability in dissolved and exported organic matter character during a hydrological event. The variables controlling the fate and transformation of DOC, e.g. pH, presence of dissolved ions such CO_3^{-2} and NO_3^-, and ambient conditions such as temperature and light, must hence be assessed in order to predict the fate of metals and HOCs in surface waters.

7.3   The role of snowmelt and spring flood

It is evident that the spring flood results in drastic hydrological episodes resulting in important biogeochemical changes of fundamental importance of the mobilisation and flux of both HOCs and heavy metals. For example, the export of DOC, which is of crucial importance for most contaminants, has been found to be 5-11 times higher during the spring than during any other season. Of similar importance has the spring flood been found for the export of particulate matter bound metals such as aluminium, lead, mercury and other metals. Likewise, recent studies have showed considerable amounts of HOCs adsorbed to mobile fractions (DOC and colloids > 0.2 μm) both in groundwater and soil drainage water. It has also been shown that physical processes have significant importance for redistribution of contaminants.

The transport and export of metals is affected by pH, organic matter and suspended matter all of which vary with the hydrological regime. Recent results from the Krycklan area suggest that metal concentrations correlate with changes in pH and concentration of organic matter but this effect depend both on catchment size and character. The effect of the spring flood on environmental HOC levels is poorly investigated. Several authors have reported increased contaminant levels in sea water after episodes of river flooding and rainfall. However, most spring flood studies have focused on acidification, elevated levels of metals and organic carbon concentrations. The data compiled in combination with the data gathered on HOCs within the PERSPEC project will hence significantly expand the current knowledge on how snow melt and the spring flood influence environmental HOCs levels.

8   Aims and comparison with predetermined objectives

The aim of the PERSPEC project was to compile current knowledge on how atmospheric and hydrological processes such as a change in temperature, groundwater level or change in precipitation pattern influence soil system processes, such as the mobilisation of contaminants to, within, and from soils, with focus on priory substances according to the European water framework directive (WFD) such as metals (e.g. mercury, lead and aluminium), and hydrophobic organic contaminants (HOCs; e.g. polycyclic aromatic hydrocarbons, chlorophenols, PCBs and dioxins). The project was to profit from the results obtained at the Krycklan catchment study (KCS) where long-term hydrological and biogeochemical monitoring has been conducted in combination with 30 years of process based research, thereby allowing the effects of climate change on contaminant mobilisation in soils to be explored.

The primary objective of the PERSPEC project was to:

- Deliver a compilation of current knowledge regarding soil system processes with focus on contaminant mobilisation;

- Gather existing data from a well defined background level system and from systems with elevated contamination levels;

- Produce predictions of contaminant mobilisation by using state-of-the-art modelling tools;

- Identify key processes and parameters needed to expand the necessary knowledge and improve the models.

The deliverables of the PERSPEC project were aligned with the second topic of the SNOWMAN coordinated call, Soil system processes, and includes:

- Models and methods of transport and fate of diffuse contaminants over larger areas and longer periods of time;

- Spatial and temporal changes of soil processes and parameters;

- Transfer mechanisms from soil to other environmental compartments;

- Judgement of existing knowledge and necessary developments from a scientific perspective.

The above listed objectives and deliverables were successfully implemented in the PERSPEC project and are presented in this report.

9   Results

Results are presented according to their deliverable (D). A table listing the workpackages (WP) and associated deliverables included in the PERSPEC project are presented in Table 9-1.

Table 9-1. Work packages (WP) and associated deliverables (D) included in the PERSPEC project.

No. of WP	Title
1	Project management and co-ordination D1: Project coordination and management task as stated by the SNOWMAN coordinated research call.
2	Compilation of current knowledge on how atmospheric and hydrological processes influence the mobilisation of contaminants in and from soils with focus on priory substances according to the European water framework directive (WFD) D2: Compilation of current knowledge on: air to soil/snow surface exchange, including soil/vegetation-air exchange; accumulation of contaminants in snow; and snow to soil and groundwater transfer of contaminants D3: Compilation of current knowledge on hydrological conditions and soil processes controlling the fate of contaminants, contaminant adsorption to soil constituents, leaking of contaminants from soil to water, and transport and transformation of contaminants in water systems
3	Compilation of relevant data from Krycklan (background scenario) D4: Time series of climatic, hydrological and chemical data, including pH, level of dissolved organic carbon, and concentration of contaminants, from the Krycklan catchment.
4	Compilation of relevant data from downstream point sources (enhanced contamination scenarios) D5: Compilation of hydrological and chemical data from enhanced contamination level waters in Europe, including the water path from the Krycklan catchment down to the Gulf of Bothnia
5	Prediction tools (models) for contaminant mobilisation D6: A model assessing the influence of the spring flood on delivering POPs to surface water by snowmelt, soil runoff and mobilisation of DOC and POC using background and enhanced contamination scenarios. D7: A comparison of two approaches, PHAST and WITCH, for modelling the mobilisation of metals within and from catchments. D8: A comparison of key parameters driving the POP and metal models and evaluation of the obtained results in light of the knowledge acquired in WP 2 (Compilation of current knowledge).
6	Interim activity report, draft final report and final report D9: Interim activity report(s) D10: Draft final report D11: Final report.
7	Dissemination of research results D12: Publish information using Internet EUGRIS, PERSPEC website, the Krycklan website, and the websites of the project partners. D13: Kick-off meeting in Umeå, Sweden. D14: Workshop in Lancaster, UK, and participation at conferences.

9.1   D1: Project coordination and management task as stated by the SNOWMAN coordinated research call

Deliverable leader: Magnus Bergknut, Umeå University.

Project management and coordination was an ongoing effort throughout the project and was performed by the PERSPEC project manager in accordance with the SNOWMAN coordinated research call. Contact was maintained within the consortium, resulting in successful transfer of knowledge and data, thus allowing for all PERSPEC partners to contribute according to what was stated in the PERSPEC research application, and thereby enabling all partners to meet their objectives. Information and coordination was achieved by frequent e-mails within the consortium, by an internal PERSPEC Internet based file repository, and two project meetings: a kick-off meeting in Umeå and a workshop in Lancaster. Frequent communication with the SNOWMAN secretariat and the national SNOWMAN contacts was also a central part of the PERSPEC project coordination.

Initially, the project manager coordinated the process of establishing national agreements between the universities and national funding agencies in each participating country. These activities were followed by a final agreement between the PERSPEC consortium and the SNOWMAN secretariat to start the project. A homepage was launched presenting the project for the broader community. The economical frame for each partner was set in the application and economical administration was performed at each university, respectively. Funding was handled via the individual national SNOWMAN funding partners but was coordinated by the PERSPEC project manager who maintained an overall control function.

The PERSPEC project manager was in charge of common activities such as the kick-off meeting in Vindeln (Sweden) and the workshop in Lancaster (UK). The PERSPEC project manager was also in charge of the PERSPEC interim activity reports, the draft final report and the final PERSPEC report.

9.2   D2: Compilation of current knowledge on: air to soil/snow surface exchange, including soil/vegetation-air exchange; accumulation of organic contaminants in snow; and snow to soil and groundwater transfer of organic contaminants.

Deliverable leader: Crispin Halsall, Lancaster University.
Contains contributions from all PERSPEC partners

9.2.1   Overview

Remote catchments and headwaters receive organic contaminants via deposition from the atmosphere. Semi-volatile chemicals such as POPs, pesticides and other HOC are subject to medium and long-range atmospheric transport in both vapour and particle-bound phases. In northerly or upland areas, colder air temperatures coupled to higher rates of precipitation, serve to promote deposition of these chemicals, with cold rain (approaching 0°C) and snow efficiently scavenging semi-volatile organic chemicals from the atmosphere (Lei and Wania, 2004). In turn, soils rich in organic matter favour the accumulation of hydrophobic contaminants with accumulation in soils enhanced in forested-regions due to the 'forest-filter' effect – enhanced scavenging of HOCs with certain physical-chemical properties by the forest canopy – resulting in increased deposition (through-fall and leaf/needle litter), relative to non-forested regions. In areas where snow plays a significant role in the hydrological cycle, then the efficiency of snowfall in removing trace contaminants from the atmosphere results in the standing snowpack providing a significant reservoir to spring melt waters, although re-evaporation back to the atmosphere may reduce this burden available to meltwater to some extent. Nonetheless, baseline concentrations of HOCs in surface waters within remote catchments will be controlled by several factors: the prevailing climate (air temperatures, rainfall and snowfall), the presence of forests and the nature of the soil (i.e. the % OM content). Knowledge on the presence and behaviour of contaminants in these headwater catchments is necessary in the context of understanding chemical loading downstream and the baseline contribution of atmospherically-derived chemicals to Environmental Quality standards within the European Water Framework Directive. The following sections attempt to address key scientific aspects behind the transfer of HOCs from the atmosphere to boreal catchments.

9.2.2   Air/vegetation transfer and scavenging of atmospheric HOCs in forested areas.

HOCs, such as POPs, can undergo long range atmospheric transport following emissions in source areas (Wania and Mackay, 1993; Breivik et al., 2004) with the atmosphere considered the major source of these chemicals to remote catchments: 'remote' indicating that point sources of these pollutants within a given catchment are negligible or absent. Semi-volatile organic pollutants, present in the atmosphere in the gas phase or bound to particles, can partition to available environmental media, including soils (Meijer et al., 2003), water bodies (Dachs et al., 2002) and vegetation (Calamari et al., 1991). Due to their relatively hydrophobic nature i.e. high octanol-water partition coefficients (log K_{OW}), the environmental stocks of organic carbon play a key role in this partitioning (Ockenden et al., 2003), with vegetation providing an important, carbon rich interface with which HOCs interact (Calamari et al., 1991; Gouin et al., 2002).

As forests present a large unit area of standing biomass and high carbon turnover rates, then forest canopies have the potential to affect air-surface POP partitioning significantly (Dixon et al., 1999; Malhi et al., 1999). In a mature forest canopy, there is as much as 8 - 10 m^{2} of organic leaf surface per unit of ground area which is available for HOC exchange with air (Nizzetto et al. in press). In addition, the organic carbon pool of the forest canopy is structurally organized to optimize light harvesting and gas exchange (Monteith and Unsworth, 1992), thereby inadvertently enhancing the rate of air-leaf gaseous exchange of HOCs (Barber et al., 2004). Horstmann and McLachlan (1998) investigated the air-canopy exchange of HOCs and showed that yearly averaged deposition fluxes to forest soils were 3-5 times higher than to bare soils. Building on the result of their field study, they then used a mathematical model to identify the physical-chemical partitioning properties, which result in a pronounced filtering effect (Gouin et al. 2002).

Wania and McLachlan (2001) included a canopy compartment into an existing fugacity-based non-steady-state multimedia fate model (CoZMo-POP) utilizing the physical parameters of the forest in the field study of Horstmann and McLachlan (1998). In essence, application of the CoZMo-POP model both with and without a forest canopy, resulted in a 'forest filter effect', whereby the forest canopy serving to increase net

atmospheric deposition to the terrestrial environment. This was most pronounced for gas-phase chemicals with octanol-air (K_{OA}) and air-water (K_{AW}) partitioning properties of log K_{OA} 8.5 to 11 and log K_{AW} -1 to -3.5. To illustrate this effect, Figure 9.2-1 highlights the reduction of average summer air concentrations due to the presence of a forest canopy (i.e. the ratio of modelled air concentrations without a forest canopy, to modelled air concentrations with a forest canopy). Interestingly, the filter effect is most pronounced for the hydrophobic chemicals, with PCBs and PCDD/Fs showing reduced air concentrations (by a factor of 5) compared to concentrations without a canopy, indicating their propensity to be removed from the atmosphere by the presence of a canopy. This effect should also be evident for a large number of pesticides, given the "window" of partition property combinations yielding the highest forest filter effect.

SVOCs are efficiently deposited to the forest during the spring and summer when deciduous forest canopies have their highest uptake capacity, and unstable atmospheric conditions increase the rate of deposition (Nizzetto et al., 2006). For coniferous forests - typical of remote catchments in northerly latitudes or upland areas - there are only limited studies which have measured deposition of HOCs to the forest floor. A recent Alpine study measuring PCB deposition under the forest canopy (coniferous forest) and in adjacent clearings found that at a high altitude site (1800 masl), the deposition of PCBs was on average ~200ng ΣPCB/m^2/month compared to <100 ngΣPCB/m^2/month in an adjacent forest-clearing (Nizzetto et al., 2006). These 'under-canopy vs. clearing' fluxes were similar to findings from the Swedish west coast, in a study conducted in the late 1990s, where the average beneath-canopy deposition flux was ~400 ΣPCB/m^2/month (Brorström-Lundén and Lofgren, 1998). Furthermore, under-canopy deposition fluxes appear to show seasonal fluctuations, with deposition in coniferous forests highest during the autumn (akin to deciduous woodland), when needle/litter fall is at its highest.
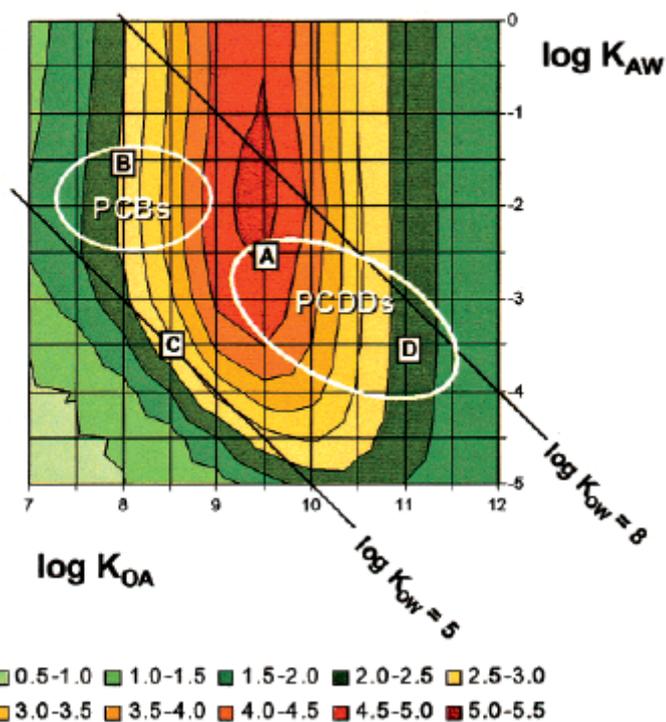
Figure 9.2-1. Chemical partitioning 'map', illustrating the chemical property combinations, where the largest reduction in modelled air concentrations are evident due to the inclusion of a forest canopy in the model. The colour scale is the ratio of modeled air concentrations both with and without a forest canopy. Hydrophobic chemicals such as PCBs (A) and PCDD/Fs (B), fall in the region with the largest 'filter effect' (C) represents the current use pesticides of methoxychlor and chlorpyrifos, while D represents the in-volatile (particle-bound) heptachloro-dioxin. The figure is taken from Wania and McLachlan (2001). Courtesy of the American Chemical Society.

9.2.3   The role of "cold" rain and winter snow in scavenging HOCs

The snowpack plays an important role in providing atmospherically derived pollutants to catchments in sub-Arctic and upland environments (Tranter et al., 1986, Gregor and Gummer, 1989, Gregor et al., 1995, Blais et al., 1998) Pollutants like acidic ions and heavy metals have been observed to accumulate in the winter snowpack, only to be released during spring melt, affecting freshwater chemistry (Tranter et al., 1986) and

aquatic biota, possibly at a sensitive stage of their life-cycle with the onset of spring. A recent Arctic study has shown that a significant fraction of both methylmercury and total-mercury present in wetlands within the Canadian Arctic originate from snowmelt (Loseto et al., 2004).

For polar, temperate and upland environments, HOCs have also been reported in the seasonal snowpack (e.g. Kawamura and Kaplan, 1986, Gregor et al., 1995, Blais et al., 1998, Masclet et al., 2000, Carrera et al., 2001, Herbert et al., 2005a&b). These chemicals have also been observed in older layers of firn and ice, providing accumulation time-series (Peters et al., 1995, Donald et al., 1999, Villa et al., 2001, Masclet et al., 2000). Spring snowmelt has now been shown to have a major impact on the loading of organochlorine pesticides to lakes in the Canadian Rockies, with the contribution from snow greatly exceeding the contribution from direct atmospheric deposition to lake surfaces (Blais et al., 2001a, Blais et al., 2001b). The recent interest in both mountain and boreal environments as possible repositories for atmospherically transported POPs, is likely to prompt further interest in the mechanisms concerning snow contamination and subsequent accumulation of organic chemicals in the deeper snowpack, and the role of snow in providing toxicologically-relevant chemicals to sensitive habitats, such as mountain lakes (Carrera et al., 2001, Carrera et al., 2002).

The accumulation of HOCs in the snowpack is driven by two related processes. Firstly, the "cold condensation effect", whereby lower temperatures will promote a shift of partitioning equilibria for chemicals in the vapour phase towards sorbed "condensed" phases, will serve to promote HOC accumulation in cold environments (Wania et al., 1998, Lei and Wania, 2004). Secondly, precipitation in the form of falling snow and cold winter rain is highly efficient in removing HOCs from the atmosphere (both vapour and particulate bound chemicals) (Franz and Eisenreich, 1998, Wania et al., 1999, Lei and Wania, 2004). Cold temperatures coupled to the presence of snow are therefore likely to enhance air to surface transfer processes for HOCs in regions with substantial snowfall. In order to understand and predict chemical accumulation in snow, as well as quantify chemical transfer to meltwater and ice, then post-depositional behaviour needs to be examined and understood. There is growing evidence that a significant fraction of HOCs deposited with fresh snow may volatilise from the snowpack with snow ageing, resulting in heavier, less volatile or more water-soluble contaminants may remain in the snow until spring melt (Gregor and Gummer, 1989, Wania et al., 1997, Herbert et al., 2005a, Villa et al., 2004). Importantly, those chemicals remaining in the snowpack may also have the potential to undergo photochemical transformation, possibly to more long lived and/or toxic by-products (Klan et al., 2001, Klan and Holoubek, 2002).

9.2.3.1   HOC concentrations in snow

A number of studies over the last 15 years or so, have measured organic contaminants in snow and ice (e.g. Gregor and Gummer, 1989, Donald et al., 1999, Herbert et al., 2005a&b), but these studies are relatively compared to measurement of organic contaminants in soil and vegetation. The chemicals subject to study usually include chemicals such as polychlorinated biphenyls (PCBs) and organochlorine (OC) pesticides. In addition, PAHs, n-alkanes and phthalates have also been measured in snow in remote regions (e.g. Masclet et al., 2000, Garbarino et al., 2002). Table 9.2-1 provides a summary of HOC concentrations in snow from several studies conducted in both alpine and arctic regions and, while not exhaustive, highlight the general paucity of HOC data. These studies reveal a wide range in measured concentrations for the same chemical classes. This range in concentrations within data sets may, in part, be explained by temporal and spatial differences, reflecting change in global emissions with time, as well as different regional usage patterns.

Table 9.2-1. Polychlorinated biphenyl (PCB) and organochlorine (OC) pesticide concentrations in snow (concentrations reported as pg/L of snowmelt).

(pg L^{-1})	Canadian Arctic[1]	Ny-Ålesund Norwegian Arctic[2]	Agassiz Ice Cap Canadian Arctic[3]	Amituk Lake Canadian Arctic[4]		Gossenkolle (European Alps)[5]	
Analyte	Winter 1987	Spring 2001	1987	1994		1996-1997	
	Range	Mean (range)	Mean (SD)	Analyte	Range	Analyte	Mean
ΣPCB	257-1770	742 (116-2000)	972 ± 344	ΣPCB$_{(116)}$**	118-1317	ΣPCB$_{(7)}$	730
α-HCH	143-42700	15.3 (N.D.-47.6)	6576 ± 1441	ΣHCH	651-1943	HCH$_{(\square)}$	1110
γ-HCH	83-10500	1150 (186-3090)	4080 ± 909				
ΣDDT	ND*-1380	25.6 (0.39-59.5)		ΣDDT	174-347		330
HCB	ND –104	17.8 (3.10-35.3)					
ΣChlordane		29.3 (N.D.-47.6)	760 ± 89	ΣChlordane	105-309		

[1]Gregor and Gummer (1989); [2]Herbert et al. (2006); [3]Gregor et al. (1995); [4]AMAP (2004); [5] Grollert et al (1997). * N.D. (Not detected); ** no. of individual congeners for the SPCB

For example, the highest snowpack concentrations of α–HCH (the major isomer comprising the pesticide technical-HCH) were from studies conducted during the 1980/90s in the Arctic (e.g. Gregor and Gummer, 1989) and were found to be an order of magnitude higher than concentrations reported in later snow studies in 2001 and 2003 (Herbert et al., 2005a&b). This may reflect the decline in technical-HCH usage following bans in North America during the 1970's, and later by China and Russia in 1990 (Li, 1999; Halsall, 2004). However, it is apparent that snowpack concentrations may vary by over an order of magnitude within the same study. For example, Herbert et al. (2005a) showed that surface snow layers in the Norwegian Arctic, had polychlorinated biphenyl (ΣPCB) concentrations ranging from 160-2500 pg L^{-1} (snowmelt). This raises the question as to why such wide ranges in contaminant snow concentrations have been observed, both between studies and within an individual study (Gregor et al., 1995, Herbert et al., 2005a&b. There are possibly three factors that may account for this. Firstly, different sampling and extraction methods may reduce the level of precision for measuring trace organics in snow. Secondly, fluctuating atmospheric concentrations may influence levels present in the snowpack, and thirdly, varying snow physical properties (which change with snow age) may influence the capacity of snow to retain vapour-sorbed HOCs.

9.2.3.2   Snow properties and chemical interaction

Snow comprises a mixture of ice, air, water and particles and can be viewed as a relatively homogenous porous surface compared to snow-free surfaces such as soil and vegetation (Bidleman and Leone, 2004; Meijer et al., 2003; Thomas et al., 1998; Smith et al., 2001). There are relatively few studies that have undertaken to categorise and measure the properties of different snow types with respect to trace gas transfer between the snow surface and the atmosphere (e.g. Sumner and Shepson, 1999, Legagneux et al., 2002). Closer examination of the seasonal snow pack usually reveals a degree of stratification, with layers comprising of different snow types, each of which is more or less homogenous within its own boundaries (Colbeck et al., 1990). Snowpack heterogeneity arises due to the accumulation of different snow layers, followed by snow metamorphosis brought about by changes in temperature, wind speed, relative humidity and solar radiation both during and after snowfall (e.g. Colbeck 1983). Snow metamorphosis generally results in an increase in density (ρ) and a decrease in the specific snow surface area (SSA) (the latter usually expressed in units of cm^2 g^{-1}) (Cabanes et al., 2003). Density is a measure of the mass of snow per unit volume (e.g. kg L^{-1}) and can be readily determined in the field. SSA however is a difficult parameter to measure, but is a very useful property with respect to vapour sorption of trace gases and has been the focus of recent research in understanding the sorptive capacity of different snow types (e.g. Hanot and Dominé, 1999, Legagneux et al., 2002). Measurement of SSA involves a technique based on CH$_4$-adsorption, using the Brunauer-Emmett-Teller (BET) isotherm. SSAs generally fall between 100 – 1500 cm^2 g^{-1} depending on the age and "weathering" of the snow (Domine et al., 2002, Legagneux et al., 2002). The total surface area of the snowpack (TSA) can then be calculated as a product of the SSA, ρ and snowpack depth.

Snow is a highly transient medium with physical properties open to rapid change, often over a period of hours following snowfall (Cabanes et al., 2002, Herbert et al., 2005b). Fluctuating temperatures and wind speeds are processes that will change the physical structure of snow, affecting both ρ and SSA, which in turn affect the vapour-sorbed quantity of a chemical in the snow. Cabanes et al. (2002) examined the evolution of SSA and crystal morphology of fresh snow at Alert (Nunavut, Canada) and demonstrated that measured SSA values decreased with snow metamorphosis, with rates of decrease accelerated in periods of rising temperature and wind speed. The mechanisms involved in the reduction of SSA, include the rounding of snow crystal edges, the sublimation of crystal microstructures and the dilution of snow by surface hoar of a lower SSA (Cabanes et al., 2002).

The mechanisms that control the exchange of trace organic contaminants between the atmosphere and both falling snow and the standing snowpack need to be resolved to incorporate winter snow cover into atmospheric and chemical fate models. The major processes illustrated in Figure 9.2-2, include bulk transport from the atmosphere (vapour and particle scavenging) by falling snow, vapour sorption/desorption to surface snow layers - with diffusion into deeper layers through wind ventilation - and leaching with meltwater during spring melt. These processes dictate the quantities of chemicals available to meltwater and for deeper burial in areas of permanent snow and ice.
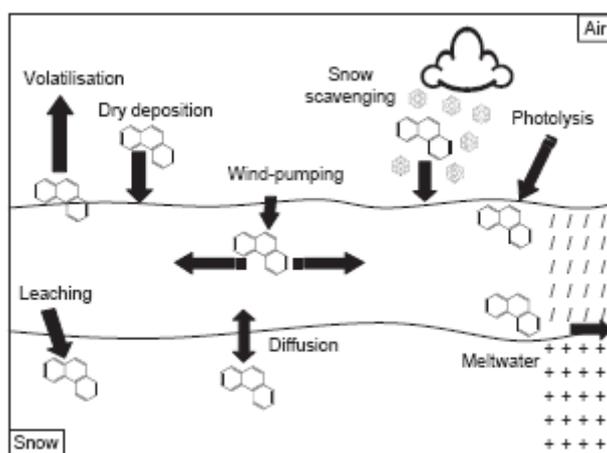
Figure 9.2-2. Organic contaminant interactions with snow. Adapted from Herbert et al. (2006).

The most important parameter controlling vapour scavenging of organic contaminants by snow fall and contaminant retention within the standing snowpack, is the ice interfacial – air partition coefficient (K_{IA}). The interaction of low polarity organic vapours with ice has been investigated in a number of laboratory studies (e.g. Orem and Adamson, 1969; Goss, 1993; Hoff et al., 1995). Several of these studies found that snow/ice-air partitioning was akin to that observed on water films (coated onto mineral surfaces) at temperatures >0°C. Hoff et al. (1995) examined the partitioning of a number of chlorinated volatile/semi-volatile chemicals directly to snow and concluded that partitioning at the ice-air interface (through derivation of experimental interfacial-air partitioning coefficients), was akin to water surfaces and can be estimated at temperatures near melting by extrapolating adsorption constants for the air-water interface. In this case, K_{IA} can be determined according to a chemical's aqueous solubility (subcooled) (C_W) and Henry's Law constant (H) according to;

$$LogK_{IA} = -0.769 \times LogC_W - 5.97 + Log\frac{RT}{H}$$ (1)

where R is the universal gas constant, and T is temperature (293 K). Note that RT/H is the water-air partition coefficient (K_{WA}). Vapour partitioning for ice (i.e. $K_{IA\ snow}$) can be approximated by adjusting K_{IA} to sub-zero temperatures with knowledge of the heat of adsorption (ΔH_a) for the chemical in question, assuming that the liquid water and ice interface is similar. At temperatures between –30°C and 0°C the ice-surface is assumed to behave like a sub-cooled water surface with respect to sorption of volatile (often polar) organics (Sokolov and Abbatt, 2002).

At present the dominant sorptive process to the ice surface is still unknown. However, Roth et al. (2004) have empirically measured $K_{IA\ snow}$ for 57 organic compounds that covered a wide range of physical-chemical properties. $K_{IA\ snow}$ was determined from compound retention volumes, using inverse gas chromatography for field snow cores at –6.8°C. To test the approach used by Hoff et al. (1995), Roth et al. compared

measured K_{IA} values for selected compounds of their study, with water surface-air adsorption coefficients that had been extrapolated down to -6.8°C. It was shown that sorption of both non-polar and polar compounds to the snow surface were underestimated by these extrapolated water values. This suggests that the sorptive process to snow is more complicated than simple adsorption to a sub-cooled water surface, and that there is some uncertainty in extrapolating K_{IA} values, derived for water, to ice surfaces at temperatures below freezing. Roth et al (2004) developed a linear free energy relationship based on intermolecular interactions:

$$\log K_{IA}(-6.8^o C) = 3.60\Sigma\alpha_2^H + 5.11\Sigma\beta_2^H + 0.635\log L^{16} - 8.47 \qquad (2)$$

Where log L^{16} is the hexadecane/air partition coefficient at 25°C (an expression of the van der Waals interactions) and α_2^H and β_2^H are the measures of a compound's ability to act as electron acceptor and donor, respectively. K_{IA} can then be corrected to a relevant temperature using the van't Hoff equation.. It is worth noting that K_{IA} is not dimensionless, but has the units of m (i.e. ng m^{-2}/ng m^{-3}). A snow/air partitioning coefficient (K_{SA}), essential in vapour flux calculations to and from the snow pack, is therefore given by:

$$K_{SA} = K_{IA}xSSAx\rho \qquad (3)$$

Where SSA is the specific snow surface area (m^2/g) and ρ is the snow density (g/m^3).

9.2.3.3   Chemical fate following snow metamorphism

Significant reductions in the burden of OC pesticides and other HOCs in fresh snow, have been observed with snow ageing (Gregor and Gummer, 1989, Hargrave et al., 1988, Herbert et al, 2004; Herbert et al., 2005b). For example, a study conducted in the Canadian High Arctic, (Hargrave et al., 1988), observed HCB in snow samples collected during May-June, but not in snow collected in the same location in August-September. Similarly, in a study by Gregor et al. (1989) conducted on the Agassiz Ice Cap (Ellesmere Island, Nunavut), OC pesticide concentrations from the snow layer representing 1985/86 were up to an order of magnitude higher than those measured in the subsequent year. Unfortunately, neither of the above studies provide details on contaminant loss rates, nor infer the physical processes that may have accounted for this loss.

Snow intercepted by a boreal forest canopy is particularly susceptible to sublimation and evaporation processes. Sublimation of snow over the winter period substantially decreases the amount of melt water released during the melt period and typically accounts for 15 to 40 % of the cumulative snowfall (see Marsh, 1999). Sublimation increases the concentration of non-volatile chemicals within the bulk snow. Interception and storage of snow within dense boreal forest canopies can amount up to 70% of cumulative winter snow fall (Pomeroy and Schmidt,1993). The air-snow interface of intercepted snow greatly exceeds that of surface snow (Pomeroy and Schmidt, 1993) and wind ventilation velocities are an order of magnitude higher than in snow on the ground (Claasen and Downey, 1995). Hence, semi-volatile organic chemicals stored in canopy snow are likely to be much more affected by evaporation prior to melting than substances deposited in snow on the ground.

In an attempt to quantify the rate of HOC loss from a fresh snow layer on the ground, Herbert et al. (2005b) took consecutive snow samples over an 11-day period at Tromsø in the Norwegian Arctic. It was shown that the concentration of PCBs decreased significantly throughout the sampling period from an initial concentration of 2500 to 340 pg ΣPCB L^{-1} (meltwater). The most rapid decrease was seen within the first 96 h, with ~75% of the total PCB burden lost during this period (ΣPCB $t_{1/2}$ = 65 h). Between 96 and 240 h the PCB concentration remained stable (~380 pg L^{-1}), with no significant change in concentrations. Interestingly, PCB concentrations in this snow layer increased significantly from 300 pg L^{-1} to 5400 pg L^{-1} after a fresh snowfall event (this fresh snow now overlying the sample layer), indicating the propensity for PCB exchange between snow layers, and possible downward migration of PCBs into deeper snow layers.

Rates of loss in the snow (k_s) were calculated for selected PCB congeners and OC pesticides and were found to follow first order kinetics. Values of k_s were found to be similar for both PCB congeners and OC pesticides, where k_s = 0.01 h^{-1}. Surprisingly, a relationship between k_s and physical-chemical properties, such as vapour pressure or Henry's Law constant was not apparent, although the precision between samples may have blurred any relationship. The decrease in PCB and OC pesticide concentrations was mirrored by a steep increase in snow density of the sampled snow layer with a significant relationship (r^2 =

0.85, $p<0.05$) (fitted to all compounds studied) between the fraction of chemical remaining in freshly fallen snow (ϕ_s) and changes in snow density ($\Delta\rho$). This exponential relationship is given by:

$$\phi_s = 0.6923e^{-6.2609\Delta\rho} \tag{4}$$

As an exponential decrease in ϕ_s was apparent, only a small increase in ρ will result in a sizeable decrease in ϕ_s. It must be noted, however, that this relationship may be applicable only for freshly fallen snow, since similar changes in ρ for aged snow (months) are unlikely to result in an exponential decline in any remaining chemical residue. Nevertheless, use of equation (2) may prove useful in quantifying POP accumulation in a seasonal snowpack, although it is likely to overestimate evaporative loss. Importantly, the decrease in ρ will result in a decrease in SSA, and hence, will reduce the capacity of the snow layer to retain the vapor-sorbed fraction. This will ultimately result in repartitioning of the chemical from the ice crystal surface back into the interstitial pore spaces for subsequent migration within the snowpack or re-release to the overlying atmosphere.

Seasonal snowmelt may also result in re-emission of HOCs from aged snow back to the atmosphere, but more importantly, will result in their release to meltwater and subsequently to catchment systems. During snowmelt, water is preliminary lost from the snowpack by drainage and sublimation (Wania, 1997). At the start of snowmelt, liquid water released into the snowpack is generally retained in-situ by capillary action and by damming at the bottom of the snowpack (Wania, 1997). Once the snowpack water content increases to approximately 0.1 m^3 m^{-3} then substantial draining occurs (Bergstrom, 1975). During snowmelt, the fate of organic contaminants present in the snow is largely dictated by the physical-chemical properties of the chemical; namely solubility, but also K_{OA} and K_{OW}. For example, K_{OA} and K_{OW} will play a role in the re-partitioning of HOCs between particles and air pore-spaces, and between particles and meltwater respectively. Furthermore, a chemical with a relatively high H value such as hexachlorobenzene (HCB) may also be lost through volatilisation from the melting snowpack. In contrast, a chemical with a relatively higher water solubility, such as γ-HCH, is predicted to have a large fraction (~98 %) released with the draining meltwater (Wania, 1997).

9.2.4   Organic contaminant release from the melting snowpack.

There is large uncertainty with respect to the fate of HOCs during snowmelt, but the limited observations in the field, supported by modelling work, would suggest an elution order based on chemical solubility. The process of re-partitioning to particulate-matter during the melt process and the fate of particle-bound chemicals is similarly unclear. To date, there are very few studies that have investigated the release of organic compounds from melting snow. Recently, Meyer (2008) reviewed these studies to set the basis for a series of laboratory-based simulations using artificial snow spiked with chemicals of varying physical-chemical properties (i.e. Meyer et al., 2006). An earlier, laboratory-based study conducted by Schöndorf and Herrmann (1987), investigated the fractionated release of five organic chemicals (with widely variable partitioning properties) from large cylindrical glass columns filled with aged, coarse snow. The compounds included the hexachlorocyclohexanes: α-HCH and γ-HCH, and the polycyclic aromatic hydrocarbons, (PAHs): phenanthrene (Phen) pyrene (Pyr) fluoranthene (Fla), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P) and benzo[ghi]perylene (B[ghi]P). The first melt water fractions were highly enriched with the dissolved fractions of both HCH isomers, along with a large fraction of inorganic and metal ions, reflecting earlier field work conducted by Tranter et al. (1986). Approximately 90% of the PAHs, which are more hydrophobic and therefore more likely to be attached to particles than the HCHs, were eluted with the last 20% of melt water. A fraction of the HCHs, presumably also attached to particles, was enriched in the last sample. The very hydrophobic B[ghi]P and B[a]P were more strongly enriched in the late melt water samples than the somewhat less hydrophobic Fla which was released more uniformly over the entire melt period. The concentration ratio between Fla and BghiP decreased after a short initial increase. These findings were confirmed by preliminary results from a laboratory study (Meyer et al., 2006) which relied on a much larger, rectangular snow vessel. Figure 9.2-3 shows the elution profile of γ-HCH and the PAHs for the respective Schöndorf and Herrmann (1987) and Meyer et al (2006) studies. Both experiments show that the particulate-bound PAHs were released late during the melt experiment whereas the more water-soluble PAHs were eluted from the snow pack relatively uniformly over the meltwater elution period. Approximately 85% of the very hydrophobic B[ghi]P and B[k]F were released in the last third of the snowmelt. These two PAHs were completely sorbed onto particles while phenanthrene and pyrene occurred also within the dissolved phase.
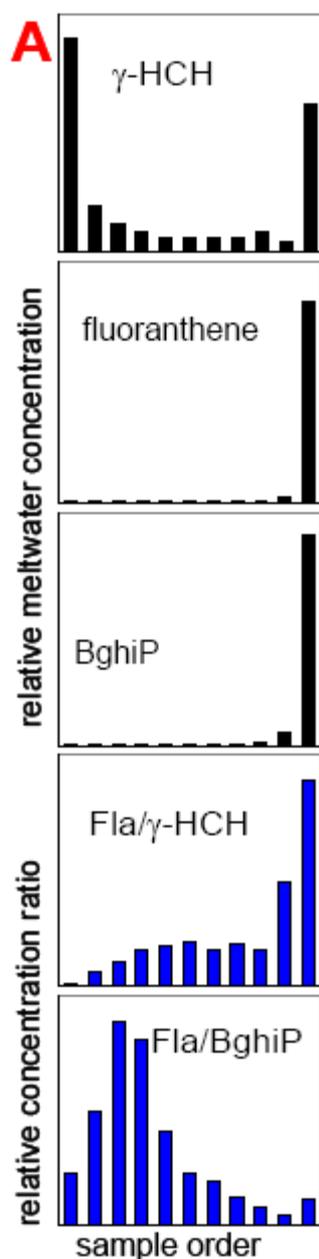
Figure 9.2-3. Relative elution sequences of □HCH, Fla, Pyr and B[ghi]P reported by Schöndorf and Herrmann (1987) and later discussed and confirmed by Meyer (2008). Figure adapted from Meyer (2008).

Meyer et al. (2006, 2008) suggest that there are essentially two patterns of organic contaminant enrichment in snow melt water. One leads to preferential elution with the early melt water fractions and affects the more water soluble substances, and sometimes also particle-sorbed organic contaminants (depending on the layering and age of the snowpack) and is called 'Type 1' by Meyer (2008). The other pattern (Type 2) leads to enrichment of particle-sorbed substances in late melt water fractions. Both patterns can lead to temporarily increased contaminant exposure of aquatic organisms in water receiving snowmelt. Type 1 enrichment, leading to a "first flush" of organic contaminants in early melt water fractions, mimics the melt behaviour of inorganic ions, which is relatively well studied in the field (see Tranter et al., 1986). This early release is attributed by Meyer (2008) to a freezing-out of chemicals and small particles from the ice lattice during snow metamorphism occurring prior to snowmelt or during melt/freeze cycles. As downward percolating melt water front picks up the contaminants concentrated on the ice-grain surface and thus becomes enriched. Differences in the extent of first flush behaviour may therefore be due to differences in either the extent of dry and wet snow metamorphism prior to melt, or the melt water hydraulics during the melt.

Using the snow cover classifications of Meyer (2008) regarding organic contaminant fate, then snow cover within a boreal forest catchment, such as Krycklan, can be regarded as "taiga" and/or "maritime" snow cover.

That is, snow cover in late winter is typified by being thin to moderately deep (~30 – 120 cm deep) with a low density, high SSA, a strong temperature gradient within the snowpack and reduced wind ventilation due to the presence of trees. The likely behaviour of HOCs will therefore be a strong release back to the atmosphere prior to spring melt and heavy 'peak' concentrations of both dissolved and particle-bound chemicals during initial melt, due to either dry or wet snowpack metamorphism, especially in areas where the snow pack is deep.

9.2.5   Summary and outlook

Northern boreal catchments dominated by coniferous woodland and organic rich surface soils are likely to be a sink for airborne HOCs, present in the atmosphere through long-range or regional transport. Air-vegetation partitioning favours the forest "filter effect" for many of these chemicals, and is likely to account for a significant fraction of the HOCs present in forest/catchment soil. In addition, cold rain and winter snow also efficiently scavenge airborne HOCs. The melting snowpack in the boreal catchment (where snowfall plays a significant role in the catchment hydrology) is also likely to be a significant source of HOCs to spring melt water, with early elution of the more water soluble chemicals, followed by release of particle-bound HOCs as melt progresses. There are significant knowledge gaps in our understanding of these processes and modelling efforts at the catchment scale, aimed at quantifying chemical transfer from the atmosphere must be viewed as best estimates only. Specific research needs include:

- Field measurements of atmospheric deposition (including beneath canopy measurements)

- Measurements of HOC in forest soils and soil-water

- Laboratory and field measurements of HOC in the snowpack – with focused efforts on spring-melt

- Temporal measurements of HOCs in catchment surface waters – especially during spring melt.

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9.3   D3: Compilation of current knowledge on hydrological conditions and soil processes controlling the fate of contaminants, contaminant adsorption to soil constituents, leaking of contaminants from soil to water, and transport and transformation of contaminants in water systems

Deliverable leader: Hjalmar Laudon, Umeå University.
Contains contributions from all PERSPEC partners

9.3.1   Background

Although many northern latitudes can be characterized as pristine environments due to their remoteness and their lack of industry, many anthropogenic contaminants, such as organic compounds and metals, become airborne in more populated regions and then later deposited in remote catchments. This has resulted in accumulation of contaminants in many northern areas because of the prevailing weather patterns. How these contaminants are accumulated and transported from the catchment soils to adjacent surface waters is a complex question. It is generally known that the transport is dependent on a complex set of variables that include hydrological flow pathways and water transit times, concentration and charge of the contaminant, soil matrix characteristics, organic and inorganic colloids and redox conditions. A further complication is that the boreal region is comprised of a mosaic of forest, wetlands and lakes which results in a complex and dynamic hydrology and a hydrochemistry that can vary with stream size, flow conditions and season.

The movement of water is a prerequisite for the mobility of contaminants from soils to adjacent streams, rivers and lakes. The transport of contaminants is further dependent on the export of dissolved organic carbon (DOC), which forms strong complexes with both metals and organic contaminants. Large amounts of organic matter are stored in the soils of the boreal region but the quantitative role and dynamics of organic carbon in mobilizing contaminants is far from understood. Because of a strong association between organic matter and most contaminants, hydrological events can generate an increased mobilization and hence export of these long range air pollutants to adjacent surface waters when flushing of DOC occurs. Due to the large export of water during precipitation events, the total export of contaminants is strongly associated to these discrete episodes. Future climates are predicted to drastically alter the precipitation pattern in much of Europe and alter the timing and magnitude of hydrological episodes which inevitable will affect the mobilization of contaminants from soils to surface waters.

The patchy nature of biogeochemistry in soil and stream water occurs on scales ranging from plot (Allan et al., 1993) to regional (Hutchins et al., 1999; Cresser et al., 2000). This variation is typically related to natural variation in geology, soils, vegetation and/or sea-salt deposition (Hutchins et al., 1999), or gradients of anthropogenic impact from point sources (e.g., mining) and atmospheric acid deposition (Galloway, 2001). At the watershed scale, high spatial variability in stream water chemistry has been noted in many regions including the temperate Catskill mountain region of New York (Wolock et al., 1997) and the boreal zone of northern Sweden (Ivarsson and Jansson, 1994; (Temnerud and Bishop, 2005).

A prerequisite for a better understanding of the fate of contaminants in the boreal landscape is to have appropriate field data and a conceptual understanding of how the ecosystem functions. While the transport rate of groundwater primarily is determined by hydrological conductivity in combination with the hydrological gradient, the rate of solute movement is, in addition, retarded by a set of chemical and physical mechanisms. Another important step forward is to improve our knowledge on critical zones and critical moments for biogeochemical processes. As the kinetics and rate of processes vary greatly in space and time a better understanding of the role of these critical interfaces could greatly aid in directing future research.

This compilation of current knowledge on hydrological conditions and soil processes controlling the fate of contaminants is primarily focused on northern ecosystems characterized by long winters and rapid snowmelt-dominated hydrographs. All of the presented field data is from the Krycklan Catchment Study (KCS) located in a boreal setting in northern Sweden. The purpose is to use one of the most well studied catchments in Europe to show what data and process understanding is available to guide future efforts in understanding the mobility of contaminants in these and similar settings.

9.3.2   Hydrology and hydrological pathways

Water and the movement of water from soils to adjacent surface waters is a prerequisite for contaminant mobility. The flow pathway defines the route which water takes from the soil system to surface waters. This can generally be divided up into two main pathways; overland flow and subsurface flow. The most widely used method for understanding and quantifying hydrological pathways in catchments is the use of natural stable isotopes as environmental tracers for isotopic hydrograph separation (IHS). The use of IHS has provided important understanding for questions related to water resource management, transport of contaminants and biogeochemical cycling. Its use dates back to the pioneering work by Dinçer et al. (1970) and has since been used in various environments around the world (Rodgers et al., 2005; Sklash et al., 1986; Stadnyk et al., 2005; Uhlenbrook et al., 2002). The general finding from these studies has been that so called old, or pre-event, water dominates the hydrograph during events whereas contribution from new, or event, water during rain storms and snow melt events remains generally small.

In the boreal setting of the Krycklan catchment forest, dominated catchments follow this general pattern of a dominance of pre-event water during the spring flood (Figure 9.3-1). In contrast, wetland dominated catchments have a much larger event water fraction. This indicates that overland flow, especially at the onset of the snow melt period, is an important pathway during snow melt in catchments with large extent of wetlands caused by a continuous soil frost layer inhibiting melt water from infiltrating into the peat (Laudon et al. 2007).
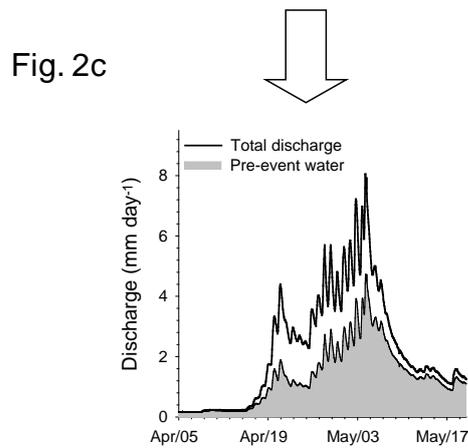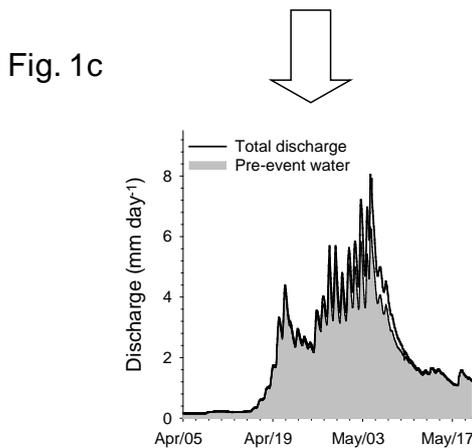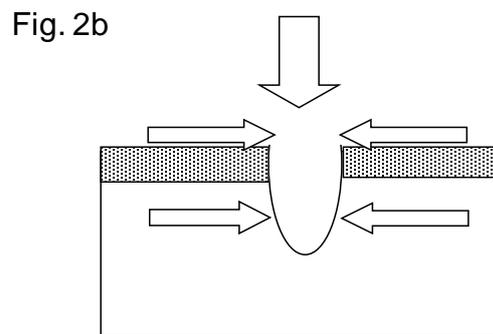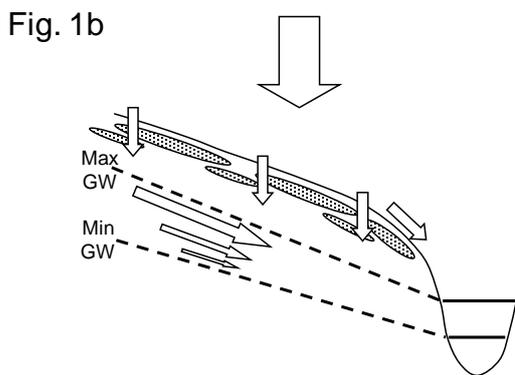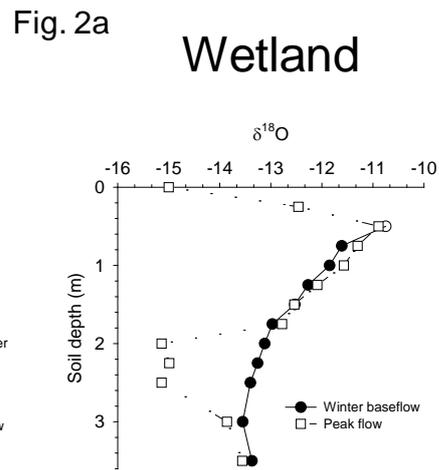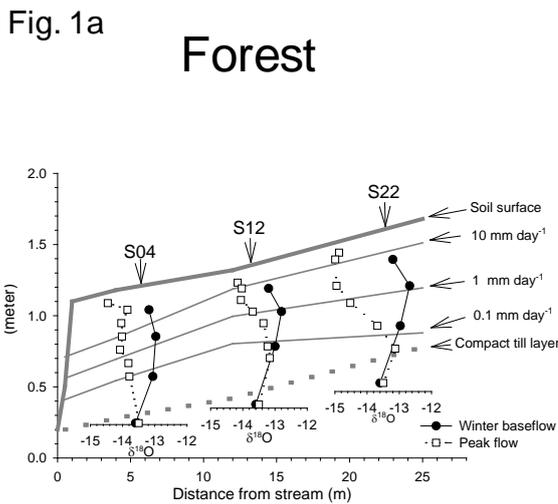
Figure 9.3-1. Evolution of event and pre-event water during the spring flood through the forested catchment soils, in C2 (a). A schematic view of the soil hydrological flow pathways during snow melt, where snow melt water infiltrate through the topsoil because of permeable soil frost (grey ovals), raise the groundwater level into soil horizons of higher hydrologic conductivity which results in more rapid lateral flow (b). The resulting stream spring hydrograph in the forested catchment is dominated by pre-event water (c). From Laudon et al. 2007.

Figure 9.3-2. Evolution of event and pre-event water during the spring flood through the wetland peat, in catchment C4 (a). A schematic view of the subsurface hydrological flow pathways where snow melt water cannot infiltrate the soil because of impermeable soil frost (grey rectangles) and instead runs off as overland flow or through preferential flow pathways (b). The resulting stream spring hydrograph in the wetland catchment have similar proportion of event and pre-event water (c). From Laudon et al. 2007.

How the flow pathways change as one move from small well defined catchments to larger heterogeneous systems remains a more open question. The effect of catchment size and the influence of landscape characteristics on runoff generation are still not fully understood because of a complex multi-scale dynamics with numerous processes operating at the same time (Blöschl, 2001; Gergel et al., 1999; McGlynn et al., 2004). Evidence from hydrometric as well as isotopic and chemical tracer studies has been used to infer how the partitioning of event and pre-event water during episodes (Brown et al., 1999; Shanley et al., 2002) and mean transit time (McGuire et al., 2005; Shaman et al., 2004) are affected by catchment scale. Although some evidence of self-similarity of hydrological pathways and transit times across scales has been

presented, the construction of hydrological models and river management tools that operate at different spatial and temporal scales remains a challenging task.

As with most other process-oriented hydrological investigations, previous IHS studies are mainly based on small individual catchments or hill slopes. The few multi-scale IHS studies that have been conducted provide inconclusive results (Buttle, 2005). For example, Rodhe (1987) compared the pre-event fraction for a number of runoff events from different small catchments. He found a decrease of pre-event water fraction for larger episodes, but no relation to catchment size. Brown et al. (1999) showed that catchment size was negatively correlated with event water contribution during heavy rainstorms, whereas Shanley et al. (2002) found a positive correlation during snow melt episodes (i.e., the amount of event water increased with catchment size). In contrast, Laudon et al. (2007) found a strong dependency of wetlands for the partitioning of event and pre-event water during snow melt (Figure 9.2-3). This finding of varying hydrological pathways depending on catchment characteristics has important consequences, as we will see below, for both natural solutes and contaminants of anthropogenic origin.
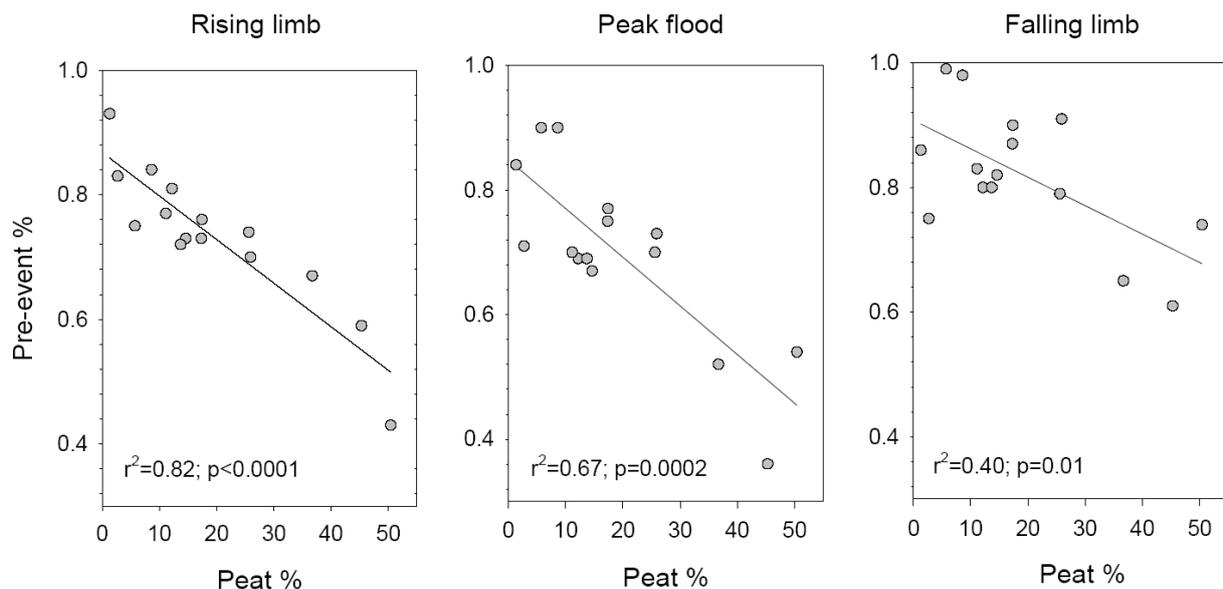
Figure 9.3-3. Correlation between peat percent coverage and pre-event water fraction during rising limb, peak flood, and falling limb in 15 streams in the Krycklan catchment. The strong correlation between peat percent and pre-event water fraction at the onset of the spring flood becomes less pronounced at the later stages of the hydrograph. This was suggested to be caused by a melting of soil frost which then allowed infiltration to the deeper soil layers. (Adapted after Laudon et al. 2007).

9.3.3   Water chemistry and DOC

Surface water chemistry is the end product of a number of interacting biogeochemical processes in the landscape. In most pristine environments, chemical weathering is the most important primary source of solutes. However, cation exchange reactions, plant uptake and exudation and leaching of organic material form variable sources and sinks of individual chemical species. Conceptually, the evolution of stream water chemistry can be formulated as a function of i). The number and types of hydrological reservoirs in the landscape, ii). The net chemical reactivity of each reservoir, iii). The volume flux rate of water within each hydrological reservoir, and iv). The sequence of which the reservoirs becomes activated. In other words, the chemistry of streams depends on how long water resides in the different soil compartments, the chemistry of those compartments and the sequence in which these compartments are encountered by the water on its way to the stream.

As a consequence, transient changes in stream water chemistry associated with increasing discharge during rain or snow melt episodes is the result of a change in the hydrological flow pathways and/or activation of soil compartments (soil horizons) that were not hydrologically connected with the adjacent surface waters during the lower flow stages. One of the more studied transient changes in stream water chemistry in the boreal region is that of episodic acidification. These short lasting episodic events results in decreased pH and increased concentration of monomeric aluminium which is toxic to fish (Kahl et al., 1992; Campbell et al., 1992; Molot et al., 1989; Evans et al., 1995; Wigington et al. 1996; Laudon and Bishop, 1999). The episodic pH decline, which is typical for most boreal surface waters (Figure 9.3-4), is preceded by a change

in the concentration of most major dissolved solutes due to a shift in the sources and pathways of water. During low flow periods, or base flow conditions, water is derived mainly from deeper mineral soil horizons and the groundwater zone with longer water residence times where the accumulated effect of mineral weathering renders the water relatively alkaline. During hydrological events, rain or snowmelt input generates a rising water table activating water flow through more superficial layers. These upper soil horizons are often more acidic due to higher concentrations of natural organic acidity and/or acid deposition. In many recently glaciated regions such as northern Sweden, the upper horizons typically have a higher hydraulic conductivity allowing more rapid water transfer through the soil (Rodhe, 1987). Thus, the pH and buffering capacity of the surface water originating from these episode-activated hydrological reservoirs are often depressed considerably relative to base flow (Bishop et al, 2000).
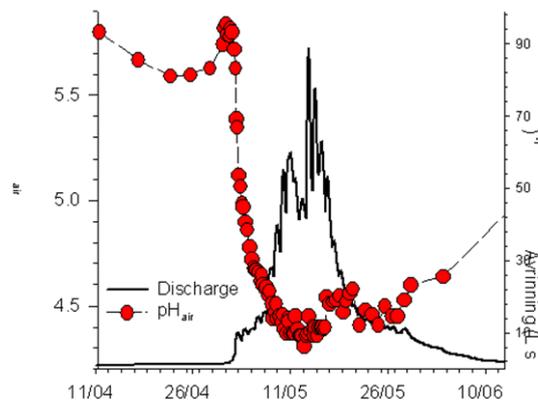
Figure 9.3-4. One example of a typical pH decline associated with the spring flood in northern Sweden. Note the very rapid change in pH as soon as the discharge starts increasing.

At the landscape scale, wetlands are of particular relevance for controlling the stream water chemistry at both base flow and peak flow conditions (Hope et al., 1994; Aitkenhead et al., 1999; Gergel et al., 1999; Mulholland, 2003; Ågren et al. 2007). Boreal catchments with high wetland percentage provide high concentrations of organic acids associated with DOC, resulting in acidic waters in areas where mineral weathering rates are low. In regions which have experienced relatively low levels of acid deposition, these naturally-occurring organic acids frequently play a primary role in controlling the acidity of surface waters [Campbell et al., 1992; Kortelainen and Saukkonen, 1995; Laudon et al., 1999]. In a study by Buffam et al. (2007) in the Krycklan catchment, the natural changes in Acid Nautralization Capacity (ANC) and DOC resulted in a pH drop in 14 out of 15 streams during the spring flood (Figure 9.3-5). Buffam et al. (2007) were able to explain the change in pH during the transition from winter base flow to peak flood by two processes: (1) a shift from mineral to upper riparian organic soil flowpaths in forested catchments, and (2) dilution of peat water with snowmelt via overland flow in wetland catchments.
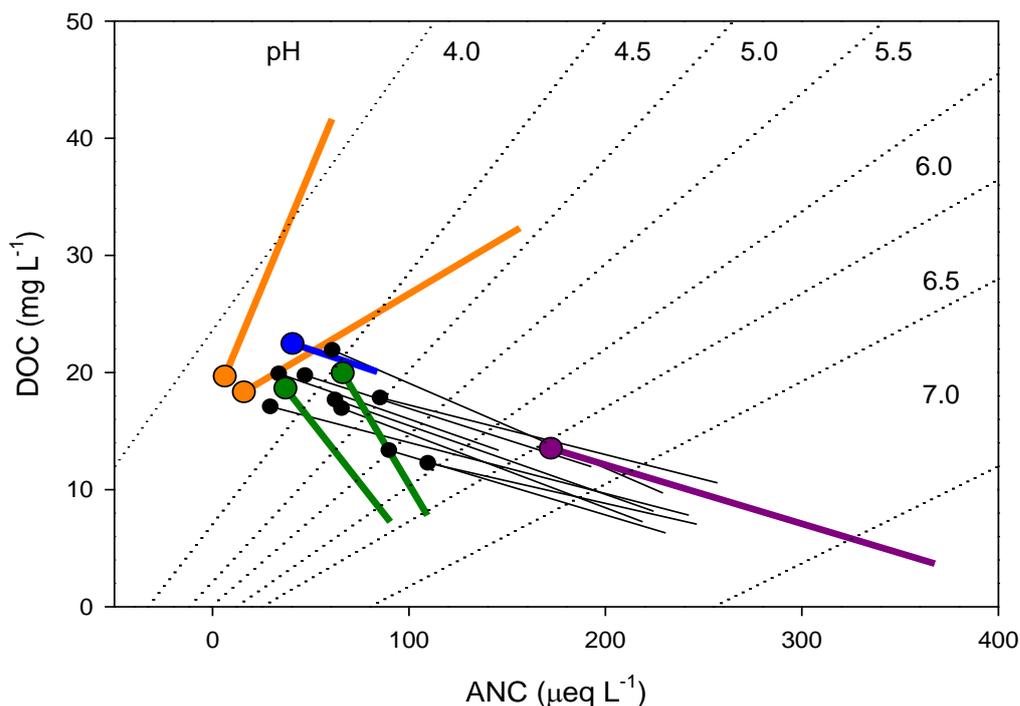
Figure 9.3-5. Data from the 15 monitored streams in the Krycklan catchment during the spring flood. Arrows represent change from winter base flow (tail of arrow) to spring flood concentrations (head of arrow) of DOC and ANC. Orange arrows are headwater wetland sites, green arrows are headwater forested sites with no wetlands, the blue arrow is the outlet of a humic headwater lake, and the purple arrow is the 68 km^2 Krycklan outlet site. High inter-stream variability in ANC and DOC is reduced at spring flood, especially with regards to DOC. The ANC and DOC concentrations can be used to calculate pH as indicated by the aired pH isolines, shown as dotted lines and ranging from pH 4.0 to pH 7.5 as indicated by labels around the perimeter. Figure modified from Buffam et al. (2007).

Besides being of large importance for controlling pH in boreal surface waters, DOC also plays an integral part in many other biogeochemical processes. For example, DOC is a source of energy and carbon for heterotrophic bacteria and the mineralization of allochthonous DOC makes boreal aquatic systems net heterotrophic and net a sources of CO_2 to the atmosphere (Duarte and Prairie, 2005, Jansson et al. 2007). DOC also affects the export and toxicity of metals (Bishop et al., 1995; Tipping et al. 1993), but its effect on metals is complicated and double-edged. For example, the lowering of pH by the organic acids increases the aluminium levels and speciation towards more toxic forms in the aquatic system. At the same time, DOC decreases the toxicity of Al by binding it into a less toxic organic form, thereby having a positive effect on the survival of fish during acid episodes (Laudon et al. 2005; Serrano et al. 2008).

In recent years, the dynamics of DOC during episodes have received much attention. In northern Sweden for example, an emphasis has been focused on better understanding the importance of the type of landscape which is drained (Laudon et al. 2004; Temnerud and Bishop, 2005; Ågren et al. 2008). While forested areas often dominate total watershed area in most areas, they are historically believed to contribute a minority of the exported DOC through surface waters, due to retention of DOC by the underlying mineral soils (Thurman, 1985). Instead flat topography (Clair et al., 1994; Mulholland, 2003) and proportion of wetlands have been reported as being the major contributor of DOC to streams and lakes (Hemond, 1990; Dillon and Molot, 1997; Hope et al., 1997a). However the role of forested areas, and especially organic rich riparian soils (Ågren et al. 2008) and less well defined (cryptic) wetlands (Creed et al. 2003) make many seemingly wetland poor areas important for the total flux of DOC. The finding from these studies have been that while the concentration generally increase with increasing discharge in streams draining forested catchments, DOC decrease in concentration when draining wetland dominated systems (Figure 9.3-6). This results in a source switching (Berggren et al. 2008) where the downstream locations receives a majority of its DOC from wetlands during low flow conditions but from forested areas at high flow.
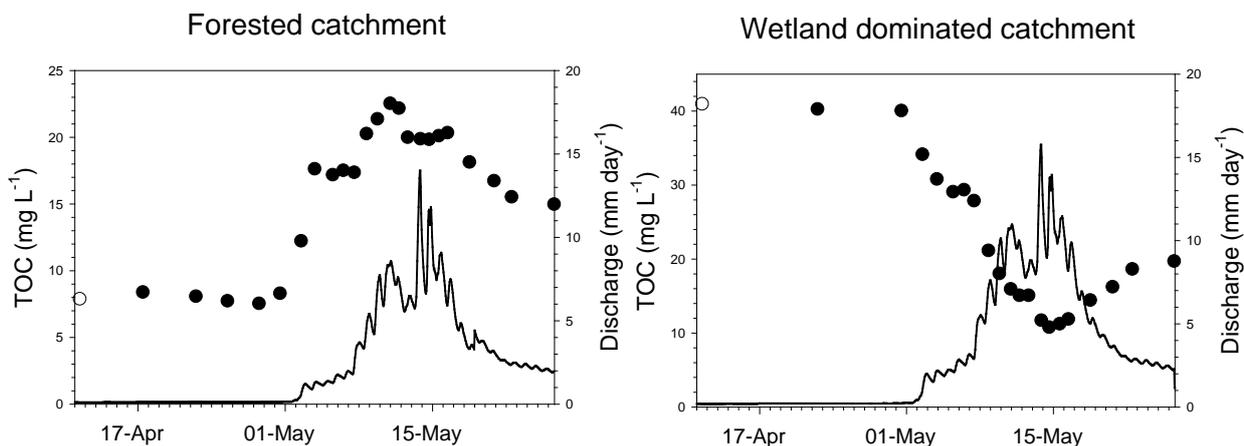
Figure 9.3-6. Example of responds in DOC concentration (black circles) during spring flood in a forested dominated (left) and a wetland dominated (right) catchment, respectively.

The dynamic DOC responses during the spring flood, is, again, an effect of changes in the hydrological flow pathways during the spring flood in combination with the configuration of the riparian zone. In forested areas, the riparian zone is composed of organic-rich soil material. When the groundwater level increases during rain or snow melt episodes, new more surficial soil horizons become activated and water with higher concentrations of DOC are flushed out in the stream (Figure 9.3-7). Wetland dominated catchments, which often experience declining DOC concentrations during the spring flood, have a larger component of overland flow which bypass the soil on its way to the stream. This results in a dilution of DOC during the spring flood (Figure 9.3-6).
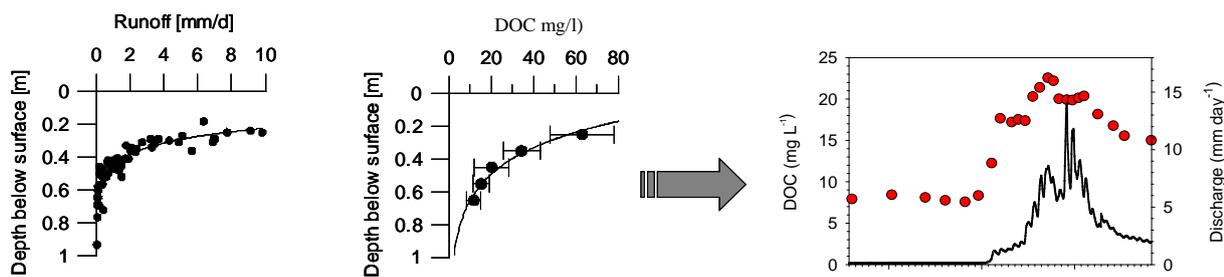
Figure 9.3-7. The relationship between DOC in the riparian soil and runoff DOC. To the left, the correlation between groundwater level and stream runoff. In the centre, the relationship between DOC and soil level. To the right, how the hydrology and DOC concentration of the riparian soil is translated into the dramatic concentration increase in the stream observed during the spring flood (modified after Bishop et al. 2004).

Climate change will likely affects DOC in surface waters of the boreal forest region, but the total effects are not well understood. How a change in the climate will affect DOC in surface waters of the boreal forest region is not well understood. Due to the strong connection between DOC, hydrological pathways and the structure of the riparian zone, even a small change in the conditions affecting the hydrological pathways and/or hydrology could result in a large influence on the flux and concentration of DOC during episodes. Along the same line, Köhler et al. (2008) showed that the total export of carbon is extremely sensitive to the annual precipitation. They demonstrated that during the last 20 years, the wettest years in the period exported over seven times as much DOC compared to the driest year. As the climate scenarios for the region predict an increase in temperature of approximately 4-6 degrees and increased precipitation of 20% to 30% over next 100 years (Mellander et al. 2007) a larger variability in export of DOC can be expected between years in the future (Köhler et al. Manuscript).

9.3.4   Metals and radio nuclides

To gain increased understanding of the processes influencing stream and river biogeochemistry in the heterogeneous boreal landscape, it is necessary to have better knowledge on how the elements behave under various conditions in the landscapes, both temporally and spatially. Recent results from the Krycklan catchment suggest that metal concentrations in soils and stream water are strongly controlled by the concentration and mobility of DOC (Cory et al. 2006; Björkvald et al. 2008). As the temporal variability of

stream water DOC primarily is determined by the riparian zone (Figure 9.3-7), the near stream area has also been shown to be important for controlling the metal and radionuclide export from forested to aquatic ecosystems. It has also been shown that DOC has a first order control on certain metal concentrations e.g. for Hg (Bishop et al. 1995), Pb (Klaminder et al. 2006), Al (Cory et al. 2007), as well as for U and Th (Köhler et al. submitted). Since practically 100% of the water in forested ecosystems must pass through the organic rich riparian zone in order to reach the stream, the riparian zone is also likely to be a critical zone for the accumulation of many natural and anthropogenically derived elements.

For example, the activity of ^{232}Th in the soil follows the same pattern as DOC with increasing concentrations in the riparian soil (Figure 9.3-8 and Figure 9.3-9a). The close similarity between DOC concentration and thorium activities suggest a strong connection between the two elements. This agrees well with what is known about the biogeochemistry of thorium, namely that it has a low solubility and a high affinity for particles and colloids, especially those of organic origin.

Recent work by Köhler et al. (submitted) has confirmed that DOC governs thorium mobility. When DOC is removed from the soil sample through precipitation, a majority of the ^{232}Th activities are co-precipitated (Figure 9.3-9). This suggests that the DOC concentration has a first order control on the ^{232}Th activity.
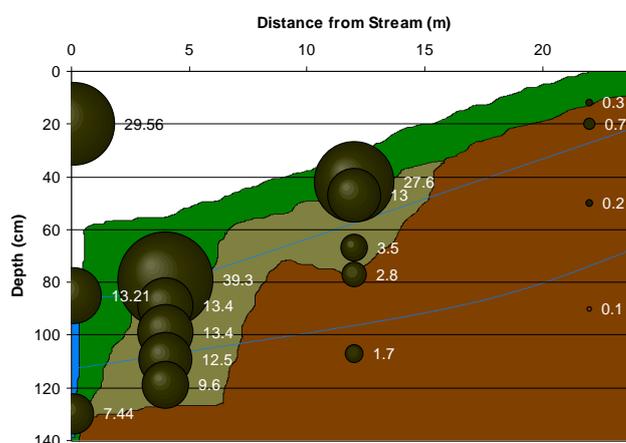
Figure 9.3-8. Concentrations of DOC in soil water (mg/l) along the S transect. The circles to the right show the minimum, median and maximum DOC concentrations in the stream. The indicated distance is along the flow path of the groundwater.
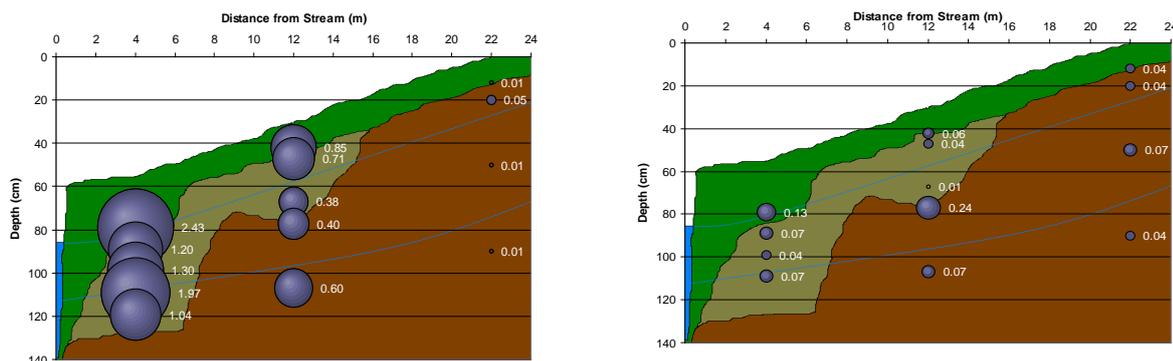
Figure 9.3-9. A: ^{232}Th activity (mBq/l) in soil water along the S transect.

B: ^{232}Th activity (mBq/l) in soil water after precipitation of DOC.

Up-scaling the biogeochemical processes understanding from small scale to the large-scale patterns found at the landscape scale remains a challenge. Without proper understanding of the fundamental processes governing the transport, the predictive power of any such landscape model or statistical relationships will unavoidably be weak. Preliminary results from the Krycklan catchment (Lidman et al. Unpublished data) show that the export of both U and Th are strongly dependent on the amount of wetlands within each subcatchment (Figure 9.3-10). The data suggest that more thorium and uranium are exported from forest-dominated catchments. This is not surprising, since the major source of uranium and thorium is weathering of mineral soils. The annual export is, however, out of proportion with the percentage of mineral soil in the

present in the catchments, suggesting that uranium and thorium are being accumulated in the peat. However, the concentrations of these elements in the wetlands are very low, which indicates that the elements are accumulated at the interface between the upland mineral soil and organic rich organic soil (McClain et al. 2003). These findings are consistent with recent experimental work in Canada (Mitchell et al. 2008) where they showed the importance of biogeochemical reaction at this critical zone was shown.
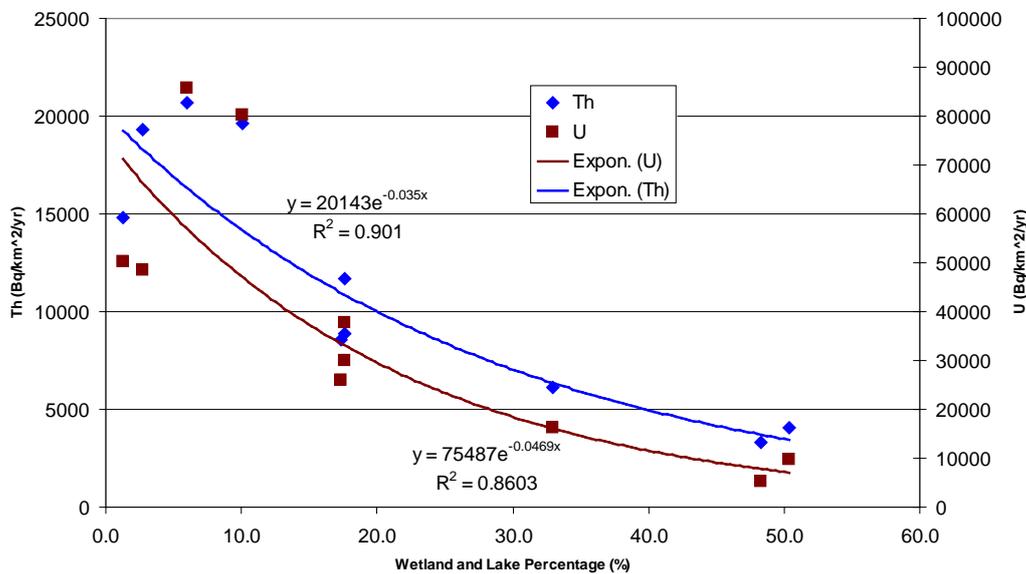
Figure 9.3-10. Annual export of thorium and uranium for the studied subcatchments as a function of the lake and wetland cover. The remaining area is almost entirely forest. (From Lidman, unpublished)

It is, however, not only U and Th that are disproportionate affected by wetlands. In preliminary work by Lidman (unpublished), budgets for a number of other elements within the Krycklan catchment were estimated. Where significant regressions could be established for some elements, these correlations were used to calculate the effect of introducing 25% and 50% wetlands respectively in a forested catchment (Figure 9.3-11). The results from these estimations suggest that the effect of mires on various elements varies significantly. The findings suggest that the affinity for organic matter is an important factor for determining the transport and accumulation patterns for various elements on the landscape level.
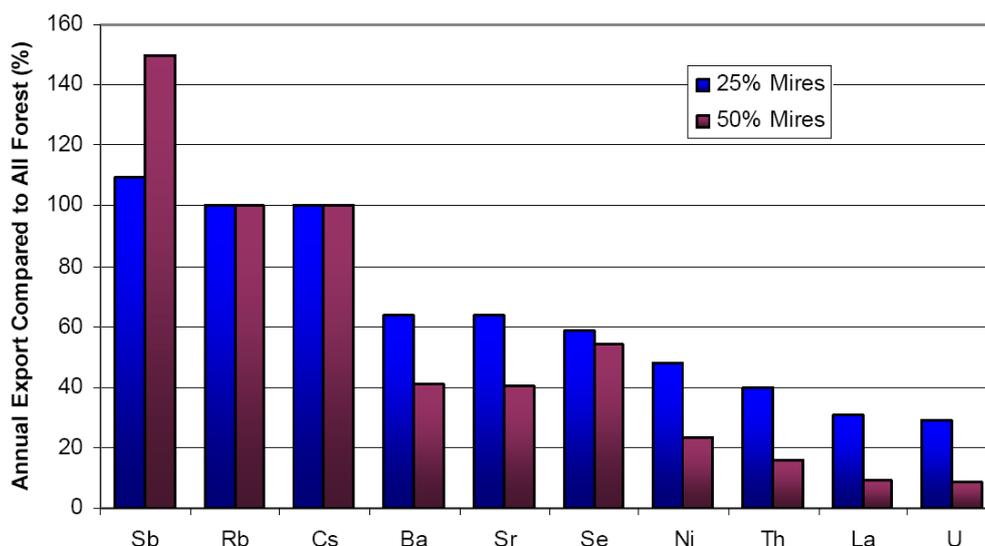
Figure 9.3-11. The effect of mires on the annual export of some selected elements. The effect of 25% and 50% mire respectively on the annual export was assessed based on regressions from estimated budgets. The results are compared to the statistically expected export from an entirely forested catchment, which corresponds to the 100% line on the y axis (from Lidman, unpublished).

The results suggest that a high wetland percentage favours the export of antimony (Sb). It is likely that this is explained by a significant atmospheric deposition of antimony, which has been observed, for instance, in similar systems in southern Sweden (Lidman, in press). Similar trends have been observed for other elements with a high atmospheric deposition. For the alkali metals, rubidium (Rb) and cesium (Cs), no significant correlation between the export and the mire coverage could be established. Although there were some variations between the sub-catchments, these variations could not be explained by the proportion of wetlands.

The export loads of barium (Ba) and strontium (St) were proportional to the reduction in forested area, while selenium (Se) apparently was appear to be somewhat affected by wetlands. Due to the complex chemistry of selenium, which involves e.g. several redox reactions and volatilization, it is hard to give a plausible explanation to this pattern without more thorough investigations.

For nickel (Ni), thorium (Th), lanthanum (La) and uranium (U), there is a significant reduction in the export with increasing proportion of mires in the catchment was predicted. Lanthanum was included as an analogue for the rare earth elements. The most extreme case is, however, uranium, whose export was estimated to decreases to less than 10% of the export from an entirely forested catchment if 50% mire was introduced (Lidman, unpublished results).

The importance of mires on for the biogeochemistry of other elements has also been clearly demonstrated previously. For example Björkvald (2008) showed that SO4 concentration was significantly negatively correlated with the amount of mires in the 15 streams of the Krycklan catchment (r^2= 0.89, p<0.0001). Iron and manganese are other elements that are strongly related to the amount of wetlands in the same catchment (Björkvald et al. 2008), whereas the role of wetlands for controlling the aluminium was shown by Cory et al. (2007).

The findings from the Krycklan catchment follow that of other recent work from the boreal region. For example, Mitchell et al. (2008) suggested that the interface between the terrestrial and aquatic ecosystem is a hot spot for many biogeochemical reactions, including mercury methylation. Kerr et al. (2008) demonstrated that the wetlands constitute sinks for certain chemical compounds while being a source of others. While interfaces, such as riparian soils and mineral soils-wetland soils, are critical zones for many elements at the local scale, wetlands shape much of the biogeochemistry variability at the scale of landscape. This large influence of interfaces and wetlands do not only provide spatial heterogeneity but are also responsible for providing much of the temporal variability that can be found in the boreal region. For example, the strong seasonality caused by wetlands cause overland flow which allows most of the snow melt water to bypass the soil on its route to the stream. This has of course large implications for atmospherically derived compounds such as antimony.

9.3.5   Organic contaminants

As for many metals and radio nuclides, it has been demonstrated that soil-to-water export of hydrophobic organic contaminants (HOCs) is highly mediated by mobile organic carbon (DOC and colloids) (Frankki et al. 2007; Persson et al. 2008). Variation in the physical and chemical properties of the HOCs results in alternative scenarios for different organic pollutants. Generally, the hydrophobicity determines the strength of the interaction with organic carbon, and it is possible to estimate the fraction sorbed to organic carbon by using the octanol-water partition constant coefficient (K_{ow}) (se section 9.6, ref Seth et al, 1999). The more hydrophobic the compound is, the higher affinity for particulate (non-mobile) organic carbon (Mackay et al. 2001; Frankki et al. 2006). The transfer of HOCs from soils to water is, due to the sparse water solubility of HOCs, primarily mediated by DOC and small particles (colloids). Hence, the transport in water may be viewed as a two-phase system where the substances are partitioned between mobile particles (i.e. DOC and colloids) and the aqueous phase. This has been shown to be fundamental for the mobilization of organic pollutants at contaminated sites and significant export of hydrophobic compounds may therefore still occur from soils rich in DOC and fine particles (Persson 2007).

The exact nature of the mechanism controlling contaminant adsorption to soil constituents and DOC is not known, which in large is due to the complex and heterogeneous nature of organic matter (OM) such as DOC (Sutton and Sposito 2005, Piccolo 2001). Although the sorption of HOCs to DOC is believed to occur through a hydrophobic partitioning mechanism, specific molecular interactions, for example involving phenyl groups or other functional groups, may still be significant. Noncovalent interactions such as hydrogen bonds (H-bonds), stacking interactions, electrostatic interactions and charge transfer interactions are considered as possible contributing mechanisms of HOC – OM interactions (Muller-Dethlefs et al. 2000). It is assumed that functional groups are mainly interacting with OM through H-bonds, while phenyl or aromatic ring structures mainly interacts trough electrostatic edge-to-face aromatic interactions (which may or may not be simplified into the π-π interaction theory, (Muller-Dethlefs et al. 2000, Hunter et al. 2001)). However, improper H-bonds may also be present, either as C-H••π bonds, C-H•••O bonds, or C-H•••X- (X- = halogen) bonds (Muller-Dethlefs et al. 2000).

The type and quality of OM will greatly influence the interactions between HOCs and DOC. The soft, rubbery, or expanded, versus the hard, glassy, or condensed domain theory is an often used concept used to describe the sorption process between HOCs and OM (Xing and Chen 1999). According to this theory, sorption of HOCs to expanded matter is linear and reversible, while sorption to condensed matter is characterized by a non-linear, fast adsorption and slow desorption (Leboeuf and Weber 2000). A number of studies have demonstrated that a high fraction of black carbon, i.e. condensed organic matter, enhances the sorption of HOCs to particles, especially the planar compounds (Cornelissen et al. 2005; Cornelissen et al. 2005; Accardi-Dey et al. 2002). The size distribution of OM macromolecules may also be a controlling factor with large hydrophobic intramolecular volumes linked to an increased affinity for hydrophobic molecules (Kopinke et al. 2001). The aromatic and aliphatic property of OM is also of importance. Some HOCs, like polycyclic aromatic hydrocarbons (PAHs), have been suggested to sorb mainly to aromatic structures in OM (Pan, et al. 2007, Borisover et al. 2006, Laor and Rebhun 2002, Uhle et al. 1999). In contrast, other studies have shown that aliphatic structures may be of equal importance (Kang and Xing 2005, Chefetz et al. 2000), either by providing a discrete hydrophobic region or by forming micelle structures.

The ratio of aromatic structures versus aliphatic carbons within DOC has at the Krycklan Catchment been assessed by UV measurements (Ågren et al. 2008). Differences in the aromatic to aliphatic quota have been found for wetland dominated versus forest dominated sub-catchments and ongoing research is investigating if the ratio of aromatic structures versus aliphatic structures within DOC plays a significant role when assessing the partitioning of HOCs to DOC at the catchment scale. Significant export of hydrophobic compounds may still occur from soils rich in DOC and fine particles (Persson 2007). Recent advances within HOC mobility research also include the findings of differences in the interaction strength between organic carbon and HOCs depending on quality of organic matter. A number of studies have demonstrated that a high fraction of black carbon enhances the sorption of HOCs to particles, especially the planar compounds (Cornelissen et al. 2005; Cornelissen et al. 2005; Accardi-Dey et al. 2002)

Fundamental understanding of terrestrial transport of HOCs to adjacent waters is largely lacking, and changes of HOC levels in aquatic environments following hydrological events is poorly investigated. Some authors have reported increased levels of HOCs in seawater after episodes of river flooding (e.g. Bergqvist et al. 1998; Witt et al. 2000, see also 9.5.2). It has also been shown that pollutant levels of truly dissolved HOCs in surface water near an urbanized area varied seasonally and were particularly high during hydrological episodes (Sethajintanin 2006) and that for streams in urbanized areas, the main load of HOCs

occurs during hydrological events (Robson et al. 2008). Most studies have, however, focused on highly contaminated areas and little is known about basic mechanisms and processes in pristine environments with lower levels of contaminants.

Strong spatial correlation between surface soil organic matter (SOM) and HOCs have previously been shown at local, regional and global scales (Meijer et al., 2002; Ribes et al. 2002; Meijer et al. 2003). It has also been demonstrated that forests act as scavenging filters for a wide range of HOCs (see also 9.2.2). Surface soils in forested areas therefore show higher levels of HOCs than open areas outside the forests (McLachlan and Horstmann M 1998).

The transformation of HOCs in soil and water systems occurs through a number of processes, including biodegradation and photodegradation. However, the rate of photodegradation is generally limited as it only occurs in the topmost layers of the soil or in the water body. In this context, it is important to stress that HOCs hold large inherent property variation (Mackay 2006) and HOCs like dioxins are for example generally resistant to biodegradation, while smaller PAHs are rapidly mineralized. The half life of HOCs in soil or the aqueous phase vary from hours to years, and when the effects of sorption to soil, DOC, or colloids are considered, half-life's may increase to decades (Mackay 2006), hence the environmental stability or persistence of HOCs. This effect is e.g. reported for decabromodiphenyl ether (BDE209) showing photolytic half-life in solution of approx. 15 minutes which can be compared to estimated half-life of 150-200 days in soil (Söderström et al, 2004). The persistence is in particular high in soil, especially in cold climates, and half-lives generally increase with molecular size or degree of halogenation. The volatility, tendency of long range air transport (LRAT), and repeated air-surface exchange is higher for low molecular weight / lower chlorinated molecules as compared to the high molecular weight / highly chlorinated ones, while hydrophobicity generally increases with size or increasing degree of chlorination. The discussed properties are all controlling reactions with SOM and consequently spatiotemporal enrichment.

The described spatiotemporal pattern seen for DOC and metal export described in the previous sections ("Water chemistry and DOC" and "Metals and radio nuclides") may also apply for HOCs or for selected HOCs, and investigations are under way. Field sampling for HOC measurements started in 2007 in the Krycklan Catchment Study (KCS) area (Table 9.4-5). Similar to [232]Thorium and DOC, concentrations in soil pore water (Figure 9.3-8 and Figure 9.3-9), soil concentrations of selected HOCs showed increasing concentrations in the riparian soil (Figure 9.3-10, Figure 9.3-12, Wiberg et al. unpublished data), indicating that spring flood and other hydrological events affect the stream water levels and loads of HOCs. It is also clear that there is great seasonality of wet and dry atmospheric deposition fluxes in the KCS area, which likely influences the temporal patterns of terrestrial HOC export.
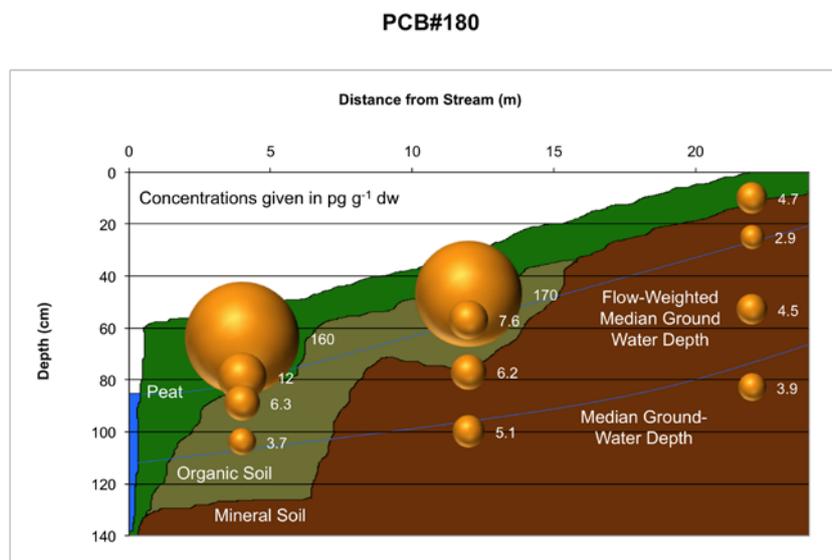
Figure 9.3-12. Soil concentrations of PCB#180 showing increasing concentrations in riparian soil.

9.3.6   Summary and outlook

Terrestrial-aquatic interfaces and wetlands shape much of the temporal and spatial variability in stream water chemistry in the boreal region. Without a proper process understanding of these critical zones our ability to predict the fate of contaminants in the boreal systems will remain rudimentary. Improving the understanding of the fate of both natural solutes and anthropogenic contaminants is of outermost importance for the wellbeing of our aquatic ecosystems. This is of special urgency in boreal regions in northern latitude as this is an area that are experiencing an disproportionate accumulation of anthropogenic contaminants, which are atmospherically transported from populated areas with the prevailing weather systems. This northern zone is also a region where climate change scenarios predict the largest changes in temperature and precipitation in the future, which will affect both the accumulation and mobility patterns of contaminants in the region.

It is well known that the mobilization of natural and anthropogenic contaminants from the terrestrial to the aquatic systems is controlled by a complex set of variables that includes soil types, meteorological conditions and anthropogenic influence. While the transport rate of groundwater primarily is determined by hydrological conductivity in combination with the hydrological gradient, the rate of solute movement is, in addition, retarded by a set of chemical and physical mechanisms. From the presented data is evident that although metals, trace elements and HOCs are governed by significantly different chemical properties, they are subject to the same soil - water controlled processes, such as OM and DOC, which have a considerable impact on their environmental fate. Hence, an interdisciplinary approach where hydrology, soil science, and organic and inorganic environmental chemistry are working in tandem forms a valuable and much needed contribution.

The most common, yet simplest, method for estimating contaminate retardation in soils is based on a single partition coefficient (K_D-value), which gives an empirical partitioning relationship between the solid and aqueous phases for a specific solute. The K_D-value can, in turn, be estimated from K_{ow}. Several successful examples of the use of K_D-values exist in the literature from diverse fields such as natural element transport (Curtis et al. 2004), assessing the chemical contaminants movement in drinking water supplies (Bergvall et al. 2007) to long-term dynamics assessments of radionuclides (Avila et al. 2006). A major limitation with the single K_D-value approach is that it is only valid for the particular conditions for which it has been calibrated (e.g., temperature, solute concentration, mineral soil matrix and organic matter conditions). Variation in either the soil characteristics or aqueous chemistry of a system can result in differences in K_D values of several orders of magnitude (Shiao et al. 1979). At the other end of the model complexity spectra, fully mechanistic chemical speciation models are found (see also section 9.7). Many of these complex models explicitly accommodate for the dependency of contaminant concentration and charge, competition with other elements, variable soil matrix characteristics, organic and inorganic colloids and redox conditions. Incorporating a more mechanistic approach into transport models is often desirable, as it will make the models more robust and more scientifically justifiable. However, truly mechanistic models can seldom be tested under natural conditions, and hardly ever applied to environmental questions that deal with landscape scale issues and longer time spans.

One way of providing more scientifically justifiable tools and models for understanding of the fate of contaminants in heterogeneous landscapes in a changing climate is to use fully mechanistic models to better characterise the most important processes that determine the accumulation and mobility in the system. The next step is to use these processes that determine the accumulation and mobility of contaminants to improve the simple K_D approach by adding model complexity as needed. For this to be successful, one need to do apply this on a well defined systems such as the Krycklan catchment where soils and surface water are well defined and appropriate field data is readily available. By doing this, one can move towards a more scientifically based modelling approach to and eventually assess how organic and inorganic contaminants will impact surface waters in a changing climate in the future.

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9.4   D4: Time series of climatic, hydrological and chemical data, including pH, level of dissolved organic carbon, and concentration of contaminants, from the Krycklan catchment.

Deliverable leader: Anneli Ågren, Umeå University.
Contains contributions from all PERSPEC partners

The Krycklan catchment is a 68 km2 catchment in the Vindeln Experimental Forests (64º14'N, 19º46'E), 60 km northwest of Umeå, Sweden (Fig. 1). The catchment is divided into subcatchments and two of the catchments have been used as model catchments; a forested catchment and a mire catchment (see also section 9.6, catchment C2 and C4). The forest catchment (the diamond in Figure 9.4-1), Västrabäcken, drains a 13 ha forested catchment and then joins the eastern tributary just above the Nyänget outlet. The catchment is forested with 80 year old Norway Spruce (Picea abies) in wetter areas and Scots pine (Pinus sylvestris) on drier soils. The mire catchment (triangle in Figure 9.4-1) is dominated by Sphagnum species.
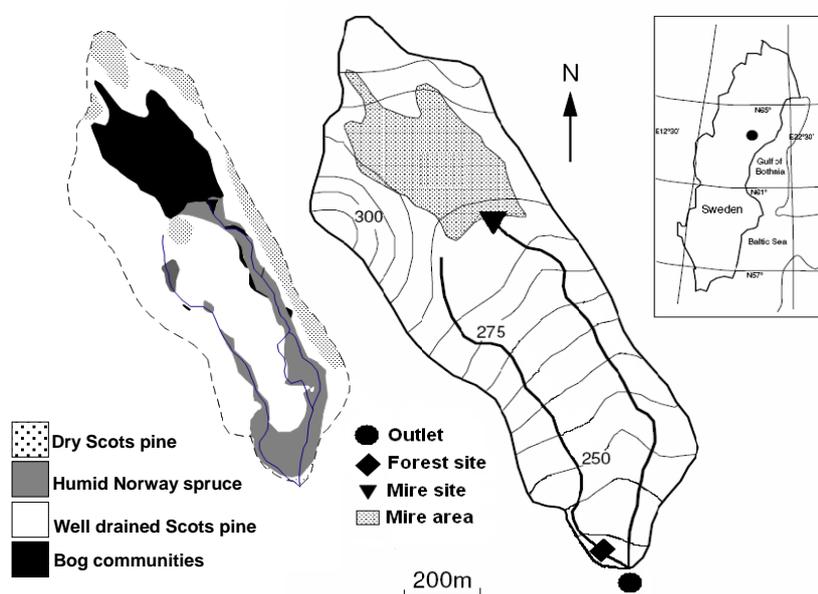
Figure 9.4-1. Map of the studied subcatchments in the Krycklan area. The left tributary is the forested catchment and the right catchment is the wetland catchment.

An important characteristic of the Krycklan catchment is the spring flood that normally starts in April or May and lasts for a couple of weeks. During this event, around 40 % of the total annual runoff occurs. Later in autumn, important runoff occurs due to the autumn rain period (Figure 9.4-2). During both periods, important changes in stream water chemistry occur. The dissolved organic carbon (DOC) concentrations vary in a predictable way based on the hydrology and the time of the year. Since DOC is an important carrier of contaminants (both metals and POPs), we have used this information to divide the year into 3 distinct seasons: the snowmelt season, the snow-free season, and the snow covered season. In the Krycklan catchment comparison between DOC and TOC (total organic carbon) show no measurable difference, not even during the most high flow situations, and the terms DOC and TOC are used interchangeably (Ågren et al, 2007). Averages on climatic, hydrological and chemical data were calculated for each of these seasons (Table1). In addition to the seasonal variation in DOC, the landscape variation has also been taken into account. The two major boreal landscape types, forests and wetlands, show different characteristics when it comes to DOC export. During the snowmelt period, they behave contrastingly with DOC concentrations increasing in the forested areas and decreasing in wetland areas (by melt water dilution). To catch these variations, two model catchments; forest and wetland were selected and included in this report (Figure 9.4-1, Table 9.4-1).

9.4.1   Time series of climatic, hydrological and chemical data, including pH, level of dissolved organic carbon.

Time series of data from the Nyänget/Krycklan catchment were collected and compiled for this report. This includes measurements on: continuous discharge (Figure 9.4-2) (daily averages based on hourly measurements), high frequency sampling of water chemistry during episodes with less frequent sampling during low flow periods. At present the stream water chemistry includes basic chemistry: pH, absorbance spectra (190-510 nm), major cat- and anions, a suite of stable and unstable isotopes, metals and persistent organic pollutants (POPs) (Table 9.4-5). The outlet (Figure 9.4-1) is one of the national environmental monitoring sites for stream water chemistry, and a more than 20 year record of water chemistry data can be found in a publically available database (http://info1.ma.slu.se/ma/www_ma.acgi$Station?ID=Intro&S=1262).
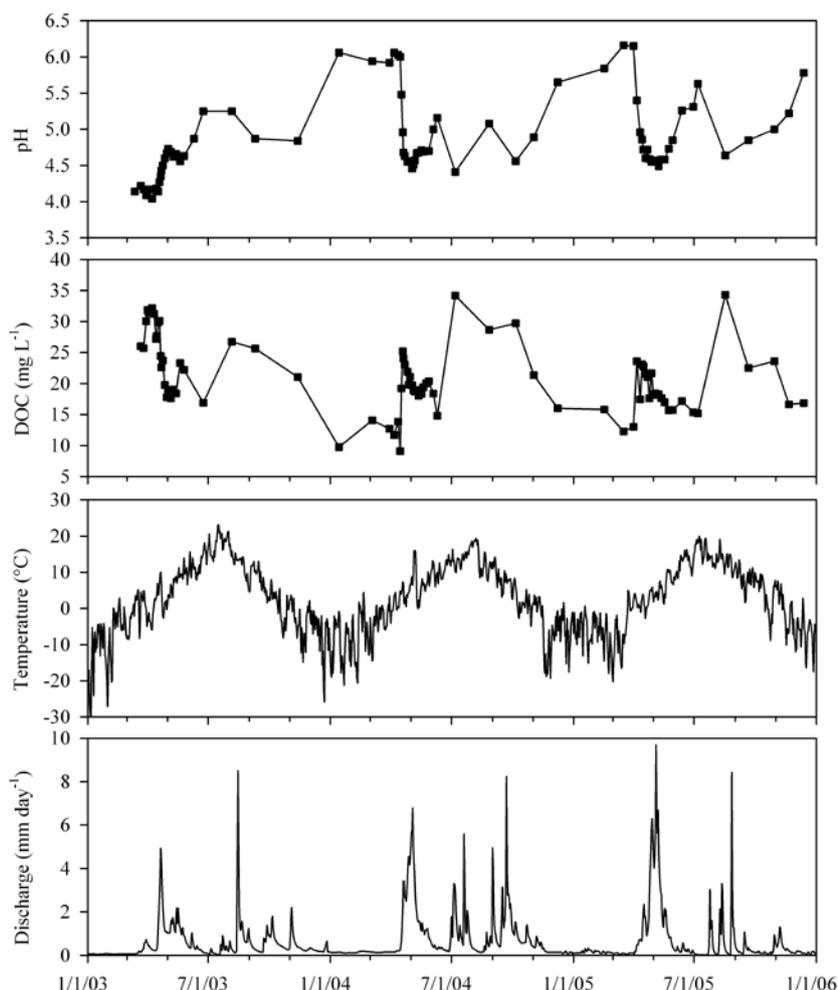
Figure 9.4-2. Time series of some of the climatic and water chemistry data that were compiled within this study: daily mean discharge (mm day-1), daily mean temperature (°C), DOC (mg L-1), and pH.

An advantage of the location of the Krycklan Catchment Study is that it includes the field station at Svartberget, where above and below ground climate data have been monitored since 1979. These climatic time series (from the SLU Unit for Field Based Research in Vindeln) has also been incorporated in this study and includes: daily mean temperature (Figure 9.4-2), daily precipitation, daily mean solar radiation, and daily potential evapotranspiration.

The amount of data collected in this project is immense and only a selected fraction of the available information is presented here (Figure 9.4-2, Table 9.4-1).

Table 9.4-1. The discharge, export of DOC, and pH for the wetland catchment and the forest catchment during the different seasons.

	DOC export (kg)	Discharge (m3)	Specific DOC export (kg C ha-1 period-1)	Specific discharge (m3 ha-1 period-1)	Average pH
Forested catchment					
Snowmelt period	178	10868	13	805	4.99
Snow-free period	257	13866	19	1027	5.11
Snow-covered season	26	2380	2	176	5.56
Wetland catchment					
Snowmelt period	354	15296	19	805	4.28
Snow-free period	787	19515	41	1027	4.40
Snow-covered season	105	3350	6	176	4.95

9.4.2   Time series of contaminants from the Krycklan catchment.

Total organic carbon (TOC) is known to co-transport both metals (see Figure 9.4-3) and POPs, which is why we chose to present both time series and export data of TOC. The export of TOC is closely connected with the driving variables temperature and flow (c.f. Figure 9.4-5, Figure 9.4-6, and Figure 9.4-7 in the attachment). Large variations occur in between years that are mostly related to warm and wet summers (c.f. Figure 9.4-6 and Tab 9.4-3). The export for most of the major elements is closely related to the water flux (c.f. Tab 1 and 4). Concentrations of aluminium in the stream are closely related to concentrations of TOC in the stream while this is not the case for lead (c.f. Figure 9.4-3 and Figure 9.4-4). Further analysis is needed to better elucidate the lead mobility. A better understanding of the dynamics of TOC will help to confine periods of time where elevated concentrations of aluminium occur in the stream. We are currently developing a model to describe the temporal variation of TOC as a function of temperature and flow which may be used to estimate metal and POP export for those compounds that are tightly related to TOC.
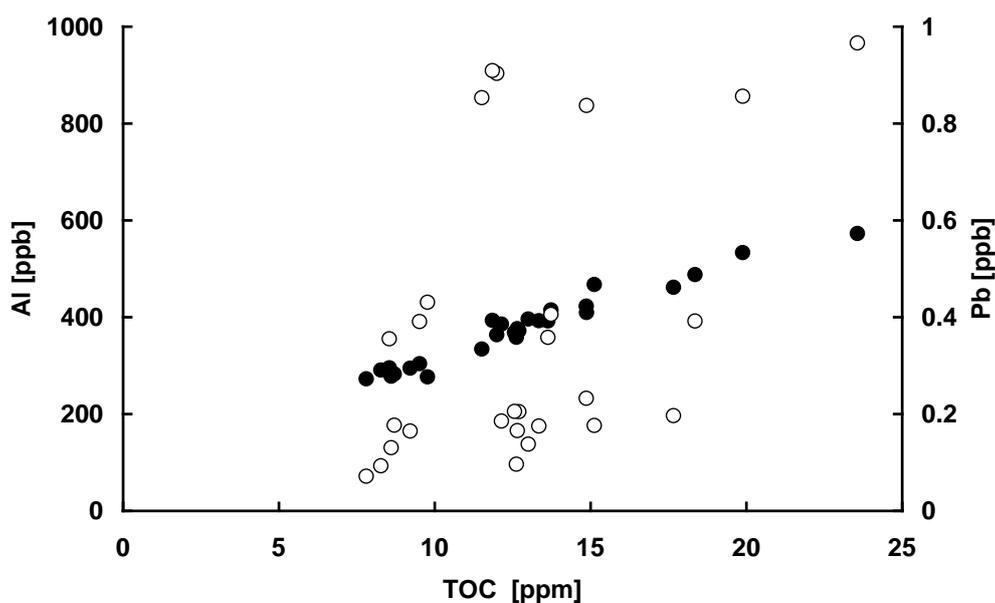
Figure 9.4-3. Stream concentrations of TOC vs. concentrations of aluminium • [Al] and lead □ [Pb]

The time series of aluminium, lead, DOC and pH are presented in graphical form (Figure 9.4-4).
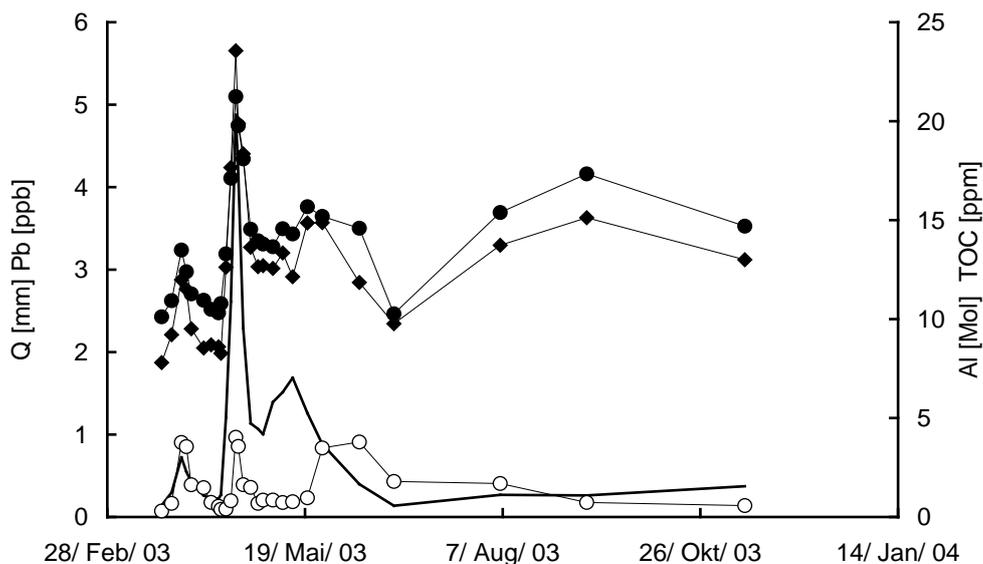
Figure 9.4-4. Temporal variation of Al [mMol] •, TOC [ppm], Pb □ [ppb] and flow Q • [mm] during 2003.

The sampling for measurements of POPs started in December 2006 (Table 9.4-5). So far, a complete time series covering one full year exist only for atmospheric wet & dry deposition sampled in an open field near the Svartberget field station. The data for 2,3,7,8-substituted PCDD/Fs (polychlorinated dibenzo-p-dioxins and dibenzofurans) for the different seasons are given in Table 9.4-2. Stream water has also been sampled during the various seasons and is being analyzed for the content of POPs (total and freely dissolved concentrations). In addition to this, soil and snow melt sampling has been conducted. The target POPs include PCDD/Fs, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs) and hexachlorobenzene (HCB).

Table 9.4-2. Wet and dry deposition of POPs.
Sum-PCDD/F (2,3,7,8-substituted) (pg m-2)

Snowmelt period	220
Snow-free period	2100
Snow-covered season	1300

9.4.3   Attachments
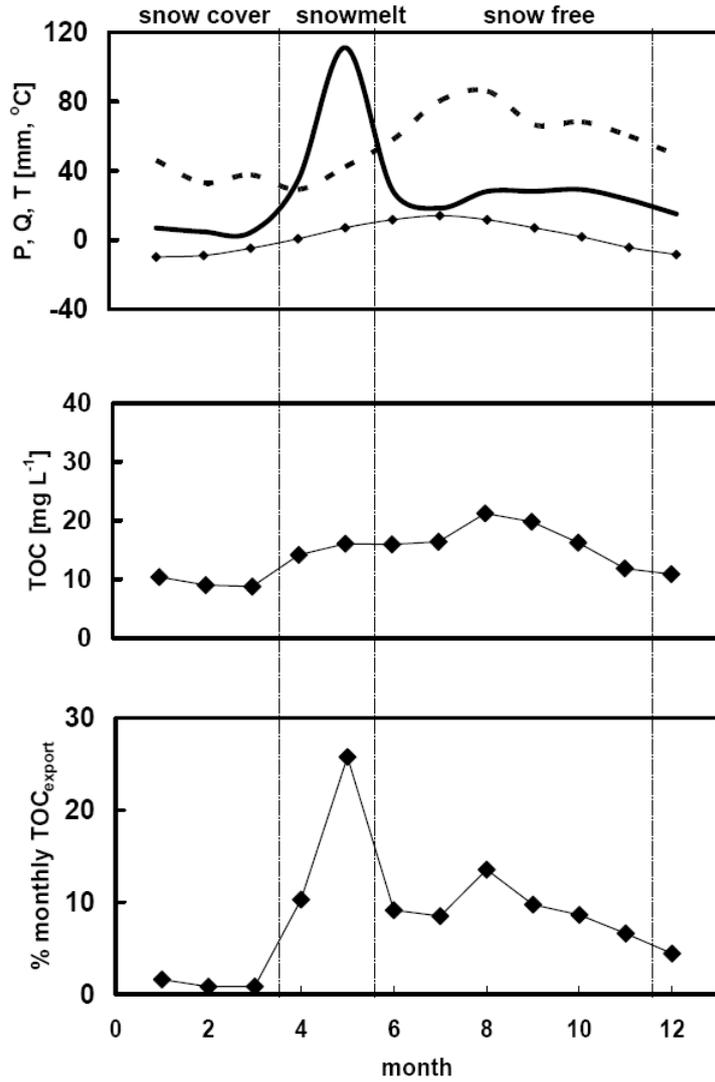
Figure 9.4-5. Upper panel: long-term (1983-2003) mean monthly climate variables: air temperature (black diamonds), flow (black line) and precipitation (dashed line). Middle panel: long-term (1993-2003) monthly average TOC in the forested site. Lower panel: mean percentage of annual TOC export occurring in each month for the 3 studied catchments.
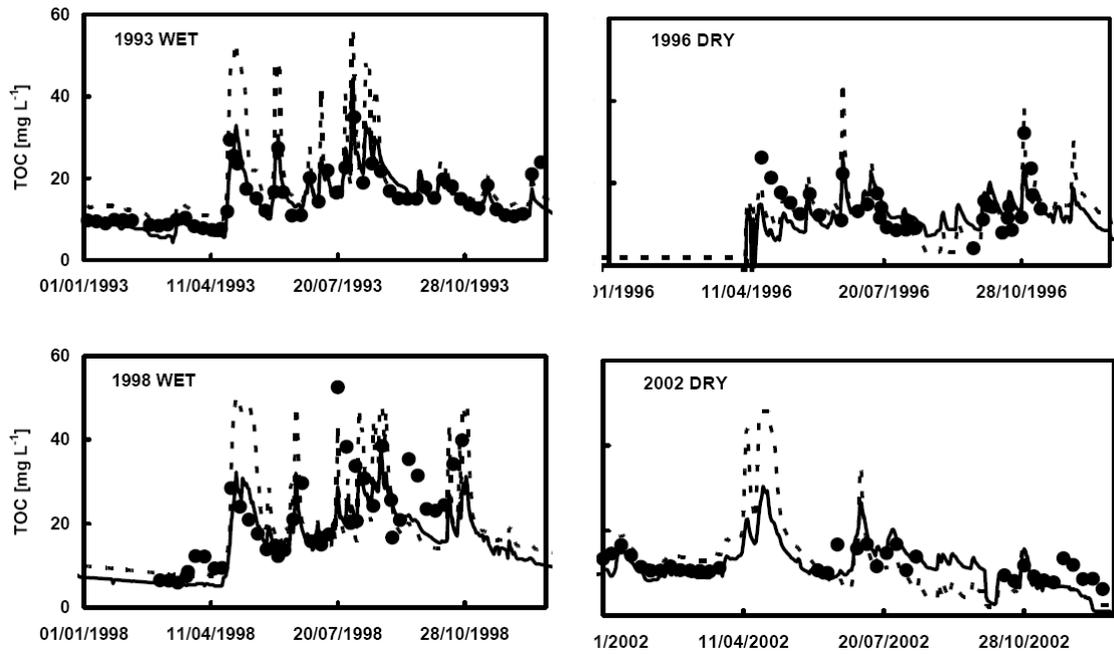
Figure 9.4-6. Time series of TOC and runoff for four characteristic years. The hyphenated lines indicate the modelled TOC values.
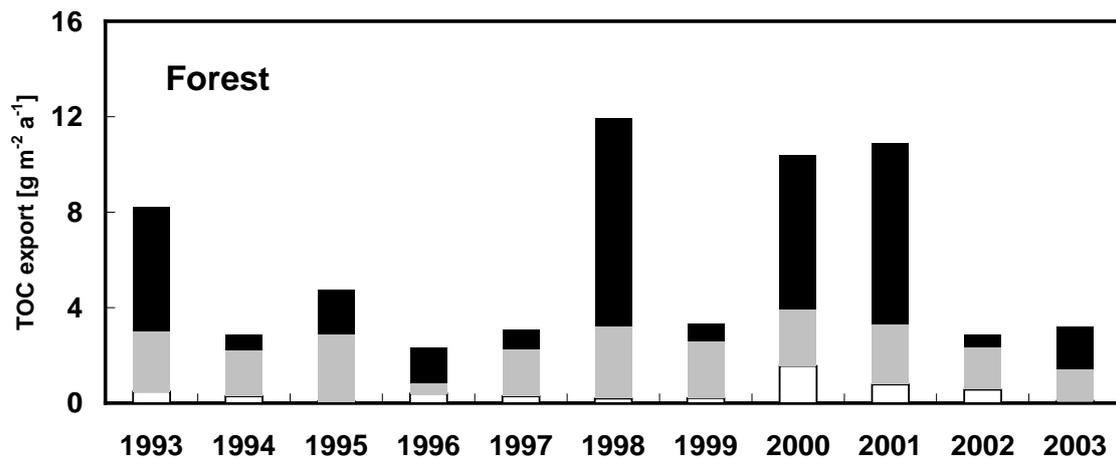
Figure 9.4-7. Annual TOC export in the forested site for the period 1993 through 2003, with each year divided into snow cover (white),snowmelt (light grey) and snow free (black) periods.

Table 9.4-3. Average annual climate data, annual and snow free season volume weighted TOC export.

year	Q [mm]	Q* [mm]	P [mm]	P* [mm]	Tair [°C]	Tair* [°C]	Forest TOC [mg L^{-1}]	Mire TOC [mg L^{-1}]	Outlet TOC [mg L^{-1}]	Forest$_{total}$ TOC-export [g m^{-2} a^{-1}]	Forest$_{snow free}$ TOC-export [g m^{-2} a^{-1}]	Mire$_{total}$ TOC-export [g m^{-2} a^{-1}]	Mire$_{snow free}$ TOC-export [g m^{-2} a^{-1}]
1993	418	240	711	474	1.6	5.6	15.4	31.0	22.5	8.2 (8)	5.2 (5.1)	10.3 (9.5)	7.2 (6.6)
1994	262	48	446	238	1.2	7.2	10.6	24.2	15.4	2.9 (2.9)	0.7 (0.6)	4.9 (4.9)	1 (0.9)
1995	291	75	550	265	1.9	7.2	11.7	29.3	16.8	4.7 (4.6)	1.8 (1.6)	7 (6.4)	2.3 (1.9)
1996	128	80	553	390	1.2	7.1	14.4	41.8	25.3	2.3 (2)	1.5 (1.3)	4.8 (4.3)	3.2 (2.9)
1997	212	50	514	307	2.5	8.4	13.9	36.2	21.5	3.1 (2.7)	0.8 (0.7)	4.8 (5.7)	1.5 (1.5)
1998	508	286	847	579	1.5	6.8	20.0	37.8	25.1	11.9 (12.4)	8.7 (8.8)	12.6 (13.8)	7.5 (8)
1999	257	56	549	268	2.2	8.8	13.4	22.3	15.7	3.3 (3.4)	0.7 (0.7)	4.6 (5.1)	1.1 (1)
2000	558	286	828	523	3.3	8.7	14.5	35.3	20.3	10.4 (10.1)	6.4 (6.3)	12.4 (13.7)	6.7 (7.4)
2001	523	329	825	570	1.8	8.3	20.1	31.2	23.7	10.9 (11)	7.6 (7.7)	15.1 (17.1)	11.1 (12.7)
2002	212	39	470	278	2.5	7.6	11.7	25.5	15.7	3.1 (2.4)	0.5 (0.5)	6.5 (4.2)	1.4 (1.1)
2003	232	130	597	412	2.6	8.1	12.8	35.8	24.4	3.2 (3.2)	1.8 (1.9)	7.5 (6.1)	4.9 (4.2)
AVERAGE	351	147	626	391	1.9	7.6	14.4	31.9	20.6	5.8 (5.7)	3.2 (3.2)	8.2 (8.3)	4.3 (4.4)
STD	155	114	149	129	0.7	1.0	3.1	6.2	4.0	3.7 (3.9)	3.1 (3.1)	3.8 (4.5)	3.4 (3.8)

Q* is the amount of flow measured at the Outlet occuring during the snow free period june to november

P* is the amount of precipitation occuring during the snow free period june to november

Tair* is air temperature measured during the snow free period june to november

(values in parenthesis are calculated as $TOC_{flux} = \dfrac{\sum\limits_{i=1}^{total\ days\ in\ seasons} q_i}{\sum\limits_{j=1}^{days\ with\ sampling} q_i} \sum\limits_{j=1}^{days\ with\ sampling}\left(TOC_j * q_j\right)$, and

annual TOC concentration for the three sampling sites on the Nyänget catchment).

Table 9.4-4. Available export data for the years 1995 through 2003 for selected major elements (TOC, Al, Ba, Ca, Fe, K and Mg) given in g m^{-2} a^{-1}.

[mm] Q	year	unit	FLUX TOC	FLUX Al UF	FLUX Ba UF	FLUX Ca UF	FLUX Fe UF	FLUX K UF	FLUX Mg UF
262	1995	[g m-2 a-1]	3.672	0.102		0.370	0.086	0.071	0.177
123	1996	[g m-2 a-1]	1.764	0.055		0.316	0.041	0.056	0.128
174	1997	[g m-2 a-1]	2.857	0.086		0.277	0.063	0.049	0.124
455	1998	[g m-2 a-1]	13.299	0.265		0.713	0.262	0.060	0.275
	1999	[g m-2 a-1]							
	2000	[g m-2 a-1]							
	2001	[g m-2 a-1]							
	2002	[g m-2 a-1]							
226	2003	[g m-2 a-1]	3.535	0.100	0.002	0.499	0.107	0.076	0.201
328	2004	[g m-2 a-1]	1.369	0.037	0.002	0.562	0.225	0.089	0.238
294	2005	[g m-2 a-1]	4.756	0.129	0.002	0.422	0.184	0.064	0.185
330	2006	[g m-2 a-1]	5.844	0.186	0.002	0.762	0.231	0.104	0.265

Table 9.4-5. Example of measurements done in the Krycklan Catchment.

Major Anions	Major Cations	Carbon	Stable/ unstable isotopes	Metals/ Trace elements	POPs
Cl	Ba	total organic	^{18}O	Al	polychlorinated
SO$_4$	Ca	carbon	D	Fe	biphenyls (PCBs)
F	Mg	(TOC)	^{14}C	Cu	
NO$_3$	Na		^{137}Cs	Zn	polychlorinated
	K		^{15}N	Hg	dibenzo-p-dioxins
	Sr	dissolved	^{13}C	Ba	and dibenzofurans
		organic	$^{224/226/228}$Ra	Cd	(PCDD/Fs)
		carbon	$^{206/207/208}$Pb	Be	
		(DOC)	^{34}S	Pb	polyaromatic
			$^{234/235/238}$U	Co	hydrocarbons
		dissolved	$^{228/230/232}$Th	La	(PAHs)
		inorganic	$^{220/222}$Rn	Cr	
		carbon		S	hexachlorobenzene
		(DIC)		Mn	(HCB)
				Li	
		CH$_4$		Mo	
				Ni	
				P	
				Rb	
				Si	
				Cs	
				Se	
				U	
				Th	
				Sr	
				Ti	
				V	
				Y	
				Rare earth elements (REEs)	

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9.5   D5: Compilation of hydrological and chemical data from enhanced contamination level waters in Europe, including the water path from the Krycklan catchment down to the Gulf of Bothnia

Deliverable leader: Karin Wiberg, Umeå University.
Contains contributions from all PERSPEC partners

9.5.1   Introduction

The chemical analysis of hydrophobic organic contaminants (HOCs) in water is challenging. This is because HOCs have low water solubility and prefer to adsorb to organic material and surfaces rather than being freely dissolved in the water. In order to investigate the degree of water contamination, measurements of sediments or aquatic biota are often performed, since the concentrations in these compartments are higher than in the water phase. Sampling and analysis of sediment or biota has advantages – analysis of various layers in sediment cores gives a good picture of the contamination history in the area, and the actual levels in biota are interesting from an ecotoxicological perspective (since HOCs may harm organisms and the eco-system functioning). However, there are also drawbacks. Choosing sediment and biota for chemical analysis instead of water leads to poor knowledge of the situation in the water phase. This makes it difficult to evaluate the dynamics of the terrestrial-aquatic transport. Even for well-known HOCs, which have been contaminants of concern for many years, there is not sufficient information about their mobilisation from land to aquatic systems. To obtain more knowledge, HOCs have been measured in the water phase in the Krycklan area in Northern Sweden within a project run by our research group. The HOCs investigated are polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB). These are ubiquitous contaminants that are considered to be chemicals of concern under the Stockholm convention, and they are present even in background areas as a result of long range atmospheric transport.

There is a global interest in understanding the transport and fate of pollutants in the environment. The interaction between the terrestrial and the aquatic system is of special interest for aquatic and marine ecosystems. The Water Framework Directive (WFD) is aimed at achieving a good environmental status of the waters of the EU, and it is an important driving force for controlling and understanding water pollution. The EU has supported several projects concerning pollutant behaviour, such as the ongoing project AquaTerra, which has the goal to achieve a better understanding of the behaviour of pollutants in the soil-sediment-water system, including the effects of changes in climate and land use (Gerzabek et al., 2007).

The Krycklan catchment is an area where hydrology as well as soil and stream water chemistry is extraordinarily well studied, and measurements of HOCs in this area will provide more understanding on how these contaminants are mobilised from the terrestrial to the aquatic system. Krycklan is a pristine area, i.e. there are no known point sources of HOCs affecting the contamination loads. Studies of this area will thus provide a general baseline case in a boreal system. In order to be able to relate the Krycklan catchment baseline scenario to a scenario with a slightly higher degree of anthropogenic impact, the sampling area was extended and three sites downstream the Krycklan catchment were included, i.e. sampling was also conducted in the Vindeln and Umeå Rivers. In general, these rivers have a relatively low degree of contamination, but there are point sources along the river, for example one town (Vindeln, approx. 6000 inhabitants), one city (Umeå, approx. 110 000 inhabitants), and a contaminated saw mill site, of which the latter has been investigated by Persson et al. (2008). Some of the results from the first year of sampling are reported in this deliverable (Chapter 9.5.3).

The deliverable will also report on levels of the selected HOCs in aquatic media from sites and events in Europe with distinctly enhanced contamination to enable a comparison of different waters and the mechanisms behind the transport. Although PCDD/Fs, PCBs and HCB have been of environmental interest for many years and there are a large number of studies investigating their presence in the environment, the compilation and comparison of data from literature is troublesome. There are several reasons for this:

- Chemical measurements of environmental media are expensive. Thus, field data are limited. The compounds are frequently not included in monitoring programmes; instead of systematic long-term monitoring, data is available from less systematic single studies. This is true especially for the dioxins (PCDD/Fs), which are present in water at very low concentrations, making not only the analysis but also the sampling a challenge. For instance, in the Czech monitoring programme, PCDD/Fs are not measured in the dissolved phase; instead the water contamination is evaluated from the determination of PCDD/Fs in particulates or sediment (Holoubek et al., 2003).
- Data exists, but are difficult to access. Databases with open access, where data is compiled in a standardised way, are needed.
- Heterogeneity in methodologies for measurement (sampling and chemical analysis) and for reporting data makes it problematic to compare results. For instance, some sampling methods do not distinguish between particulate and dissolved fractions in the bulk water phase. Moreover, when the particulate fraction is filtered off, the filter pore size varies from one study to another. The unit to which the concentrations are normalised also varies – sometimes they are reported per volume of water, sometimes normalised to the dry weight of particles or to organic carbon (OC) content. The analytical methodologies have changed over the years. For instance, PCBs were previously quantified and reported as technical mixture equivalents (e.g. Aroclor-equivalents) due to lack of reference calibration compounds. This complicates comparisons over time. Moreover, studies differ in the number or identity of congeners reported, and thus a reported sum of PCBs can consist of different congeners in different studies. For dioxins (PCDD/Fs), the congeners examined are in general the seventeen 2,3,7,8-substituted congeners, which are the most toxic congeners. Commonly, the toxic equivalent (TEQ) value is reported instead of reporting the concentration of the individual congeners. The TEQ is the sum of all products of the congener concentration and their toxic equivalency factor (TEF). The TEF expresses the toxicity of the congener in relation to the most toxic congener, which is 2,3,7,8-TCDD. There are, however, several different TEF scales. This is due to that several organisations have adopted different TEF schemes and it is also due to that the TEF-values have been changed as a result of new findings on the toxic potency of the various congeners. For instance, there are I-TEFs (NATO/CCMS 1988), WHO-TEFs from 1998 and from 2005 (van den Berg et al., 1998, 2006). There were also other, more regional, TEF systems, e.g. TEFs from Ahlborg (1989). The consequence of the various TEF-schemes is that reported values can often not be directly compared, unless the concentrations of individual congeners are known.
- The concentration in freshwater is highly influenced by the hydrological conditions at the time of sampling, and the response of HOC concentrations to different hydrological conditions tend to be specific for different streams. This is further discussed in the following section (Chapter 9.5.2).
- Levels change over time, for example as a result of a ban and varying environmental conditions. However, it is also possible that data variation partly can be explained by differences in sampling and analytical techniques. Agrell et al. (2001) suggested that this was the reason for observed differences in water concentrations of two Polish rivers. One important reason for differences in contaminant levels between sampling occasions can be the hydrological regime at the time of sampling.

9.5.2   Effects of hydrological conditions on the concentration of HOCs in surface waters

Several authors have reported that the levels of HOCs in surface waters are dependent on the discharge at the sampling time (e.g. Bremle & Larsson, 1997, Gómez-Guitérrez et al., 2006, Meharg et al., 2003). However, there are also investigations that have indicated the opposite – that there is no dependence of concentrations on the flow regime (e.g. Agrell et al., 2001, Fingler et al., 1992). Among the studies reporting a dependence on the flow regime, some authors report lower concentrations at high flows (Bremle & Larsson, 1997) while others have found more complex relations between flow and contaminant levels (Gómez-Guitérrez et al., 2006). This demonstrates that the link between hydrological conditions and HOC concentrations is complicated, and dependent on the contamination situation of the specific stream, for example how large the input is from different sources.

In the study by Bremle & Larsson (1997), PCB levels in the river Emån in the south of Sweden were measred during two years (1993-1995) and a distinct seasonal variation was found. During high water

discharge (>10 m^3 s^{-1}), the median bulk water concentration (dissolved and particulate) of PCBs (as a sum of 53 chromatographic peaks) was 1.2 ng L^{-1} (range 0.4-4.5 ng L^{-1}), while at lower water discharges (<10 m^3 s^{-1}), the concentration increased up to 4 ng L^{-1}. The authors concluded that the higher concentrations during low flow indicated an internal source of contamination in the stream, namely contaminated sediments. The concentration was also positively correlated to temperature, maybe due to more desorption from sediments during warm periods (generally corresponding to low flow). At high flow, the water in the stream was diluted with less contaminated rainwater, thus lowering the PCB concentration in the stream. This conclusion was supported by the fact that rainwater from a nearby region had a concentration of 1.3 ng L^{-1}, and that a principal component analysis (PCA) of the congener patterns pointed at two different sources of PCBs during high and low flow. Bremle & Larsson (1997) saw no increase in resuspension during high flow, and the concentration of suspended matter was rather low, 2.2 mg L^{-1}. The authors thus concluded that the major part of the transport will take place in the dissolved phase. Although Bremle & Larsson saw no increase in resuspension during high flow in Emån, a high flow can give an increased resuspension of sediments, which could lead to increased contaminant levels during high flow. This is of course dependent on the situation in the specific stream.

Agrell et al. (2001) found that the Vistula and Odra rivers, with around 1 ng L^{-1} of PCBs, showed no relationship between PCB concentration and water discharge, unlike the River Emån. Agrell et al. argued that the difference in behaviour between these rivers can be due to a difference in the source of contamination. In Emån, sediments were postulated to constitute a major source, while the source of PCBs in the Polish rivers could be precipitation.

Similar to the study on Emån, Meharg et al. (2003) found higher concentrations of PCBs during low flow and high water temperature, up to almost 10 ng L^{-1} (sum of 11 congeners) in the Aire/Calder catchment (NE England). They estimated that the particle-bound PCBs accounted for half of the bulk water concentration of PCBs. Also in this study, a PCA revealed different congener patterns during high and low discharge. Moreover, particles suspended in the water were more contaminated than the bed sediments (53.8 and 4.0 ng g^{-1}, respectively). Meharg et al. (2003) concluded that the major PCB source was ongoing fluxes from sewage treatment plants (STP), rather than remobilisation of bed sediments. This input was more pronounced during low discharge, due to less dilution of the STP outflow in the recipient stream. The source of contamination in Aire/Calder is thus believed to be different than in Emån, but the results in terms of contamination levels are the same – higher PCB concentrations during low discharge.

Even if concentrations are lower during high-flow periods, the major part of contaminant transport can still occur during high flow since the discharge is higher. For example, Bremle & Larsson (1997) calculated that during their two-year study, a total load of 884 g PCBs was being transported downstream from the sampling site. Of this, 655 g was during high flow (>10 m^3 s^{-1}). Gómez-Guitérrez et al. (2006) also observed that high discharge periods were most important for the load of PCBs and HCB from a river, due to an increase in suspended particulate matter (SPM). During the month with highest discharge (February), more than 500 g PCB day^{-1} and 100 g HCB day^{-1} was transported downstream, due to an increased amount of particle-bound contaminants. Over the entire year, the load was 80 kg of PCBs and 11 kg of HCB, of which the dissolved phase contributed 75 and 64%, respectively.

In the study by Gómez-Gutiérrez et al. (2006), the levels of particle-bound contaminants were highest at periods of high discharge, while the concentrations of dissolved HOCs were higher during low discharge, possibly as a result of less dilution. They studied the input of various HOCs, including PCBs (9 congeners) and HCB, from the Ebro River into the Mediterranean Sea during nine months in 2002/2003. Ebro is the second largest river in the NW Mediterranean, with a discharge of 9.2 km^3 yr^{-1}. Gómez-Guitérrez et al. found that the concentration of dissolved PCBs was highest at low water discharge during May-October (up to 18.1 ng L^{-1}; <180 m^3 s^{-1}). However, during another period with low discharge (November, 121 m^3 s^{-1}) the dissolved concentrations remained low. This shows that the connection between levels of HOCs and discharge is not straightforward, not even for the same stream. It is possible that part of this difference in behaviour can be explained with temperature effects, as in the study by Bremle & Larsson (1997), where an increased temperature was connected to an increased PCB level in the water.

The concentration of particle-bound contaminants in the study by Gómez-Guitérrez et al. (2006), on the other hand, had a maximum concentration in February, 2.5 ng L^{-1} when the discharge was 1236 m^3 s^{-1}. However, the amount of SPM was at a maximum in February (19.6 mg L^{-1}). Thus, if the concentrations are expressed as ng g^{-1}, the concentration of particulate PCBs was not at a maximum value in February. The increase in SPM was attributed to increased sediment resuspension as well as an increased runoff. The maximum SPM occurred at the highest flow rate, but there were also high values in May and August when the discharge was low. The OC content in the particles was highest in June, and lowest in February. This might indicate a more minerogenic composition of the particles in February. HCB followed a similar trend as the PCBs, with

high values in February and May for the particulate phase (maximum 0.67 ng L^{-1}), and in June for the dissolved phase (1.19 ng L^{-1}).

Although many studies have pointed at a dilution of the contaminant levels during high flow, there are also studies which illustrate the opposite scenario – higher levels during high flows (e.g. Teil et al., 1998, Sethajintanin et al., 2006). The hydrological event can activate contamination sources, for instance due to an increased runoff from contaminated sites or overflows at sewage treatment plants. Sethanjintanin et al. (2006) looked at the dissolved fraction, and found higher PCB concentrations as well as higher loads during high river flow and precipitation, which they attributed to sewer overflows. Teil et al. (1998) also looked at the behaviour of PCBs, and discovered that the concentration and loads increased as the river flow increased. However, maximum concentration and load was not at maximum river flow, but prior to this. They also observed that the peak in concentration before the peak of flow occurred for all observed PCB congeners, and that the higher the chlorination level (i.e. more hydrophobic and with a higher tendency to partition to particles), the higher the peak concentration. As precipitation creates runoff from contaminated surfaces, it is likely that the highest runoff of contaminants occurs in the beginning of the precipitation event. At later stages of the high-flow event, concentration levels drop.

Rivers are important routes for the transport of HOCs to coastal areas (e.g. Tolosa et al., 1995, Salo et al., 2008) and the transport of HOCs increases during floods, leading to increased levels of contaminants in the sea water. For instance, PCB concentrations were found to increase with 1.5-3.7 times in surface sediments in the Szczecin Lagoon in southern Baltic Sea as a result of flooding of Polish rivers as Odra and Vistula in Poland in 1997 (Konat & Kowalewska 2001). Similarly, Witt & Siegel (2000) found an increase in the concentrations of PAHs in surface sediment in the estuary of the Oder River in the Baltic as a result of the flooding in 1997, and attributed this to flooding of municipal and industrial waste disposal areas.

The spring flood during snow-melt is an example of a hydrological event, when large amounts of water are transported through rivers to the sea. Large amount of particles or colloids are also put to movement. HOCs are well-known to sorb to particles and co-migrate with these in the water. Studies have also shown that their transport is likely to be facilitated by colloid movement (Persson et al., 2008). The transport of HOCs from terrestrial to aquatic systems is therefore probably highly dependent on flow conditions also in places where there are no point sources that can be flooded, such as the Krycklan catchment.

9.5.3   Levels of hydrophobic compounds (PCDD/Fs, PCBs, HCB) in surface water from the Krycklan catchment and along the water path down to the Gulf of Bothnia

The overall and long term goal with this field measurement project is to establish spatiotemporal patterns for HOCs in a baseline environment, as has been done for many metals and radionuclides. This will be done by multiple sampling occasions covering all seasons (snow free season, snow melt season and snow covered season) and a time span of several years. Ultimately, the behaviour of HOCs will be so well characterized that reliable predictions can be made by environmental fate modelling. The sampling sites in the Krycklan catchment area were selected so that importance of landscape type as well as stream order can be evaluated. The sampling is conducted at 7 sites; 4 in Krycklan (Figure 9.5-1) and 3 downstream Krycklan (Figure 9.5-2), and the location and characteristics of the sites are summarised in Table 9.5-1.

Table 9.5-1. Location and characteristics of the sampling sites.

Site 2	Krycklan: Low wetland
Site 4	Krycklan: High wetland
Site 13	Krycklan: Stream order 3
Site 16	Krycklan: Stream order 4
Site A	Ytterrödå (at Vindel river)
Site B	Berg (downstream town of Vännäs; after confluent of Vindeln with Umeå river)
Site C	N. Bergsboda (downstream town of Umeå)

The levels of PCDD/Fs, PCBs and HCB are being determined in the surface water in Krycklan and further downstream the watercourse, with the final site located just downstream of central Umeå. To be able to differentiate between the particulate and the dissolved phase of the contaminants, active sampling is used. The water is pumped through filters (<0.7 μm), which collect the particulate phase, and through polyurethane foam (PUF) plugs, which collect the dissolved phase. Since the compounds investigated are present at very low concentrations (e.g. the concentrations of PCDD/Fs in 1 L of water are in the magnitude of femtograms; 1 fg = 10^{-15} g), approximately 500-800 L are pumped through the filters and PUFs for each sample.

The target PCDD/Fs are the 2,3,7,8-substituted congeners, i.e. the congeners that have been assigned TEFs, and the sum of the 2,3,7,8-substituted congeners is hereafter referred to as ΣPCDD/Fs, although the non-2,3,7,8-substituted congeners are not included. For PCBs, the target congeners are seven congeners known to be abundant in the technical products and in the environment (PCB 28, 52, 101, 118, 138, 153, 180; denoted ΣPCB_7). HCB is also analysed, as are the polycyclic aromatic hydrocarbons (PAHs), but the results from the PAH-analyses are not discussed here. In addition to this, the water is sampled for analysis of total organic carbon (TOC).

Extraction, clean-up and final analysis are performed at the Department of Chemistry, Umeå University. Filters and PUF plugs are extracted in a Soxhlet apparatus. The extracts are then cleaned on open columns containing neutral, acid and basic silica gel. Thereafter, the PCDD/Fs are separated from the PCBs by fractionation on an activated carbon column. The concentrations are determined by injecting the final extracts on a GC/HRMS-system.

During 2007, the sites were sampled twice. The first sampling for the Krycklan sites (2-16) took place in May, during the spring flood. The sampling was then extended further downstream in July (sites A-C). Since the sites were not sampled in the same campaign it is difficult to draw conclusions about the patterns of contamination along the river from just this sampling. However, in October 2007 a new sampling took place, this time for all sites during an 8-day period.
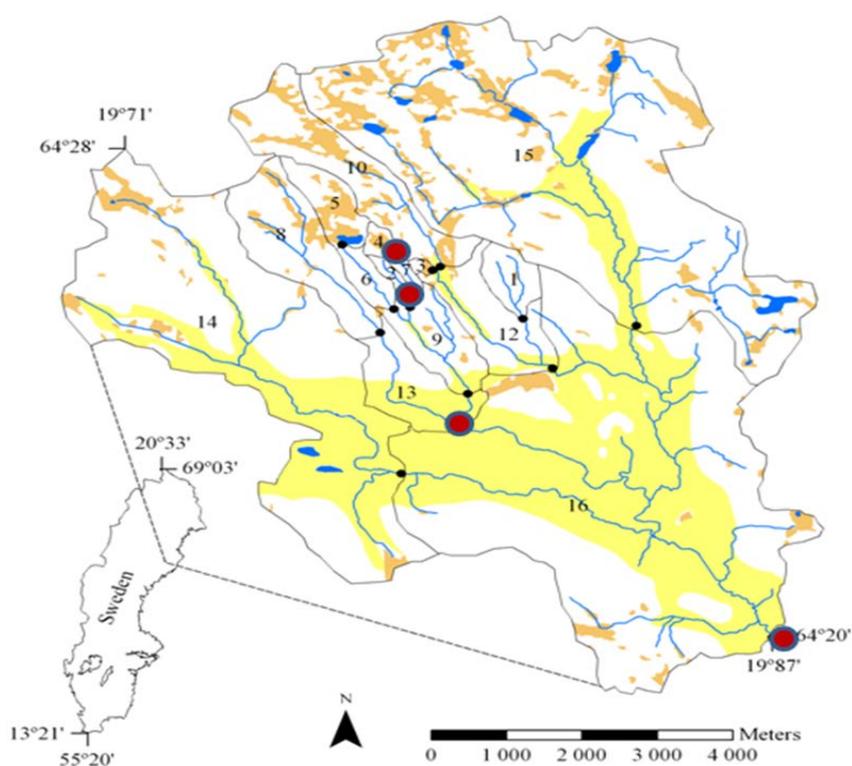
Figure 9.5-1. The location of the four sampling sites in Krycklan.
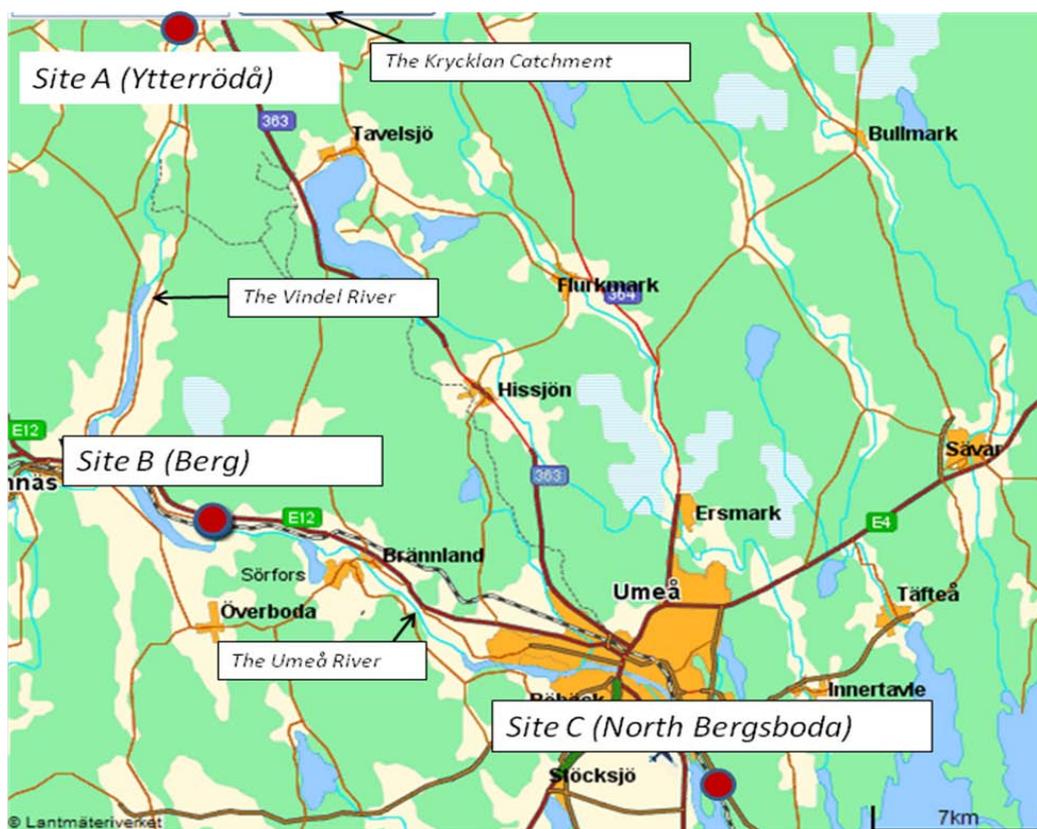
Figure 9.5-2. The three sampling sites downstream of the Krycklan catchment.

This study is ongoing, and the results discussed here are the results from the sampling carried out during 2007. It is important to bear in mind that the results are from only two sampling occasions, and that conclusions about the behaviour of HOCs and their mobilisation from the terrestrial system to the aquatic therefore are preliminary. To get a more reliable picture of the fluxes during a year, it is necessary to carry out sampling several times during the year, as well as sampling during more than one year. Due to that the project is in a relatively early stage, the following results and discussions focus on differences between the baseline and the downstream sites, and differences between sampling occasions during 2007.

The results show that the bulk concentrations (i.e. the sum of the particulate and dissolved concentrations) of ΣPCDD/Fs are rather constant along the stream: during the sampling in May/June most sites display concentrations ranging between 110 and 140 pg m^{-3}. The Krycklan catchment and the Vindeln and Umeå Rivers thus have a low level of contamination. One site deviated from the others, but results from more sampling occasions are needed before it is possible to conclude that this site has a different contamination pattern than the other sites. Moreover, the results from the first sampling campaign point at no difference in PCDD/F concentrations between the sampling sites within the Krycklan catchment and the downstream sites along the Vindeln and Umeå Rivers. It is not only the concentration levels that are of interest. A change in composition of the pollution may reveal information on transport routes and emission sources. Here, we limit the pattern analysis to compare the fractions of PCDFs (furans) and PCDDs (dioxins). In general, the concentration of furans (PCDFs) were found to be higher than the concentration of dioxins (PCDDs), but not consistently so, and the differences were small.

For ΣPCB$_7$, a trend of increasing concentrations downstream can be seen. The concentrations tend to be higher at the downstream sites (>20 000 pg m^{-3}) compared to the upstream sites, but also here one site displays an exceptional value. For HCB the situation is similar: a tendency of increased concentration downstream. However, the difference in concentrations between upstream and downstream sites are less marked than for the PCBs, and concentrations of HCB range in general between 2000 and 5500 pg m^{-3}. It is important to bear in mind that the three sites downstream Krycklan (A, B and C) were sampled more than two months later than the sites within Krycklan (July compared to May) during the first sampling campaign, so it is not possible to draw definite conclusions about the contamination pattern along the watercourse from the first sampling campaign.

In the second sampling campaign, all sites were sampled during eight days in October, which gives a better picture of the contamination pattern along the watercourse. The contamination levels seem to have increased compared to the levels measured in May/July. For ΣPCDD/Fs, the range was now 70-700 pg m^{-3}, and the average level in October was 159% of the level in May/June, i.e. a modest increase. During the

May/July sampling, the fraction of furans was rather consistent along the watercourse, but in October, values are more different. Some sites show smaller values (i.e. higher concentrations of PCDDs than PCDFs), while a few sites have a marked increase of the PCDF fraction. This pattern is interesting, but there are too few data points for any definite conclusions to be drawn. However, this observation will be given further attention in future data evaluations.

For ΣPCB_7, the concentration range in October was 18 000-77 000 pg m^{-3}, a large increase compared to the previous sampling. The levels in October constitute on average 648% of the levels in May/July. This is due to a large increase in PCB concentrations at the three most upstream sites. In May, the concentrations at these sites were below 6 000 pg m^{-3}, while in October concentrations were >25 000 pg m^{-3}. For the downstream sites, concentrations were relatively similar as in May/July. For HCB, the concentration range in October was 5 000-14 000 pg m^{-3}. The levels increased at all sites in October compared to May/July; on average, the concentration of HCB was doubled.

The concentrations of HOCs in the Umeå River are generally low compared to other rivers flowing into the Baltic Sea. A study by Agrell et al. (2001) showed that the median concentration of PCBs (51 chromatographic peaks, corresponding to 84 congeners) in Umeå River was 0.21 ng L^{-1}, compared to 0.61-1.44 ng L^{-1} for rivers Mörrum (Sweden), Wistula and Odra (Poland). The value 0.21 ng L^{-1} corresponds to 210 000 pg m^{-3}, which is substantially higher than what has been found in this study (at most 77 000 pg m^{-3}). Agrell et al. (2001) did not use filters to separate the particulate and dissolved fractions, and considered the amounts in the PUF to be the bulk concentrations. The difference between the value from Agrell et al. and the value found in this study can be due to differences in quantification (i.e. different number of congeners), that the levels actually have decreased during the last decade, or that the sampling took place at different hydrological conditions, since it is clear from this study that the amount of contaminants in the water varies during the year.

Looking at the average contamination levels for HOCs at each site (average of PCDD/Fs, PCBs and HCB), it is obvious that there was a large increase in the three most upstream locations in October as compared to the earlier sampling (300-700% of the levels in May), while this was less noticeable downstream (109-168% of the levels in May/July). This could be a consequence of the different sampling times, i.e. for the downstream sites the sampling took place in July and October, while for the upstream sites it took place in May and October. There was thus a larger difference in water flow conditions between the sampling campaigns at the upstream locations than at the downstream locations. Future field measurements will provide better insight into this issue.

It is obvious that the concentrations of organic carbon are higher in the Krycklan streams than in the downstream sites, at both sampling times (Table 9.5-2). The Krycklan sites (sites 2-16) have TOC concentrations of approximately 10-35 mg L^{-1}, and the downstream sites (sites A-C), contain 2-4 mg TOC L^{-1}. During both campaigns, the OC content is highest for site 4 (21 and 35 mg L^{-1}), the high wetland site, followed by site 13, 2 and 16. It is also worth to notice that the OC content of the water was generally higher in October than in May/July. The organic carbon (OC) has been analysed as total organic carbon, i.e. on unfiltered water, but detailed investigations of the organic carbon in Krycklan have shown that the TOC in Krycklan is almost only present in the form of dissolved organic carbon (DOC), and not as particulate organic carbon (POC) (Åberg 2008). For the downstream samples, no such investigation has yet been carried out.

Table 9.5-2. The total organic carbon (TOC) content and the flow type during the two HOC sampling campaigns in 2007.

Site	2	4	13	16	A	B	C
Sampling time	*May*	*May*	*May*	*May*	*July*	*July*	*July*
Flow type	high	high	high	high	summer	summer	summer
TOC (mg L^{-1})	13.6	21.1	13.9	11.4	2.18	2.56	2.29
Sampling time	*Oct*	*Oct*	*Oct*	*Oct*	*Oct*	*Oct*	*Oct*
Flow type	mixed	mixed	mixed	mixed	mixed	mixed	mixed
TOC (mg L^{-1})	16.76	34.8	22.0	9.44	4.17	3.03	2.83

Since hydrophobic organic contaminants tend to partition to organic carbon, it is common to normalise the concentration of HOCs to OC. An increase of the amount of OC in the water volume could explain the increase of the amount of HOCs in the water. The normalisation to OC does give the HOC concentrations during the two sampling campaigns a different appearance. For PCDD/Fs, there was still an increase in concentrations from the first to the second campaign. The average value (average of six sampling sites) in May/June was 30 pg g^{-1} OC, while in October it was 38 pg g^{-1} OC. HCB also displayed an increase: from 990 to 1 200 pg g^{-1} OC, and in fact, the concentration increased at all sites. For PCBs, however, only the upstream sites displayed an increase of the amount of PCB g^{-1} OC in October compared to May/July, while the downstream sites experienced a decrease.

Since the levels of organic carbon were substantially higher at the Krycklan sites than at the downstream sites, the normalisation to OC also gives another picture of the concentration trends along the watercourse. When normalised to OC, there was an increase downstream for all three compound groups. The levels were by far highest at the most downstream site (site C) for all three compound groups, almost twice as high as the second highest value. HCB showed the least marked difference: 3 300 pg g^{-1} OC at site C (downstream Umeå) compared to 2 400 pg g^{-1} OC at the site with second highest concentration. The concentration of PCDD/Fs downstream Umeå was more than doubled compared to the second highest site, while for PCBs the difference was very pronounced: 21 000 compared to 6 700 pg g^{-1} OC. The city of Umeå thus constitutes a hot spot for contaminants, especially PCBs and PCDD/Fs. Persson et al. (2008) found dioxins and other chlorinated organic contaminants in ground water from a sawmill site in Umeå, and this is a potential source for dioxins to the Umeå River. The data from this study do show that Umeå is a hot spot for contaminants, and calls for further investigations on identification and apportioning of source emissions, e.g. how important is the contaminated sawmill site compared to the contribution from the municipal sewage treatment plant.

The dissolved fraction is considered to be the bioavailable fraction for aquatic organisms. Therefore, it is interesting to investigate the distribution between dissolved and particulate phases for the various HOCs. There was a large variation in this distribution, but some general tendencies were seen. For example, HCB showed a higher fraction in the dissolved phase than PCBs, which in turn showed a higher dissolved fraction than the PCDD/Fs. This is in line with their partitioning behaviour. HCB has a lower octanol-water partition coefficient (K_{OW}), and is thus less hydrophobic than most of the PCBs and the PCDD/Fs. Furthermore, the results from this study showed that the furans (PCDFs) in general had a higher fraction in the dissolved phase than the dioxins (PCDDs). This trend is in accordance with findings by Persson et al. (2008), who observed a higher PCDF/PCDD ratio in the dissolved phase as compared to the colloidal fraction (>0.2 µm).

Another trend was that the dissolved fraction was lower in October than in May/July. On average, the dissolved fraction in May/July was almost twice as large as the dissolved fraction in October. For instance, 84% of the HCB pollution was present in the dissolved phase in May/July, and only 58% in October. PCBs exhibited an even more marked decrease: 58% in May/July compared to 22% in October. These observations suggest that a higher fraction of the pollutants are present as dissolved during the spring flood than during a typical snow free season flow.

Looking at the congener pattern of the PCDD/Fs, there were no distinct differences between the sampling sites, as shown by the pattern of six of the sites in the May/July sampling campaign (Figure 9.5-3). This implies that the source of contamination is similar for all sites. Some interesting features did appear for the October samples, but more samples need to be analysed before any conclusions can be drawn.
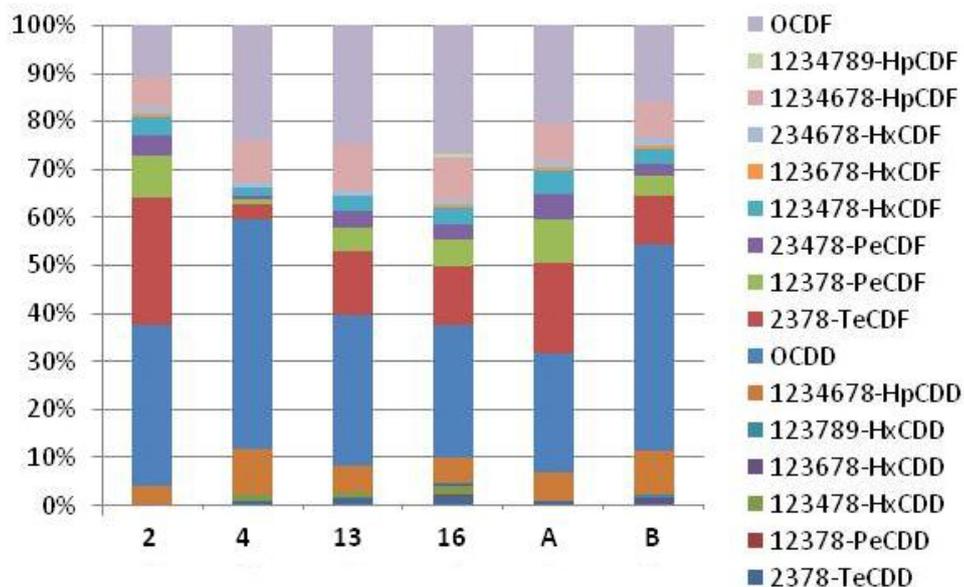
Figure 9.5-3. The contribution of different PCDD and PCDF congeners to the sum of PCDD/Fs at six sampling sites in May/July.

This study is ongoing, and the field measurement will continue for at least one more year. This will enable a better understanding on spatiotemporal patterns of HOCs in a boreal baseline environment. Sampling and analysis of HOCs are time consuming and very expensive, which limits the number of HOC samples. For metals, on the other hand, a larger and more long-term data set exists for the Krycklan area. When the HOC study is terminated, it will thus be interesting to compare the behaviour of these two substance groups. Substances that sorb primarily to DOC are likely to display a similar behaviour in DOC mediated transport and conclusions regarding the behaviour of one substance may be extended to other substances. A fundamental understanding of the interaction between terrestrial and aquatic systems will ultimately lead to reliable environmental fate models, thereby enabling predictions of effects of environmental changes, e.g. effects of climate change

9.5.4   Levels of hydrophobic compounds (PCDD/Fs, PCBs, HCB) in enhanced contamination level waters in Europe

In the following, levels of PCDD/Fs, PCBs and HCB in aquatic media in Europe with distinctly enhanced contamination are reported. The compilation is not exhaustive but provides some examples of well-known contaminated areas. This enables a comparison between different waters, including the waters from the Krycklan catchment presented in the previous section. The reported data is for water, suspended particulate matter (SPM) and sediment. Sediment concentrations were included since there is a lack of water concentration data.

9.5.4.1   PCDD/Fs
PCDD/F contamination can be caused by different activities, for instance the production of chlorinated chemicals, the use of substances contaminated with PCDD/Fs, and thermal processes such as waste incineration or metal industry activities (Weber et al., 2008). Since industries tend to be located close to waterways and a convenient way of disposing of waste was to discharge it into the water, many waters in Europe have been contaminated with PCDD/Fs.

One of the most severely PCDD/F contaminated rivers in Europe is the Kymijoki River in Finland. The contamination was caused by the production of a chlorophenol based wood preservative, known as Ky-5, where PCDD/Fs were present as impurities in the product (Salo et al., 2008). Sediment samples from a lake upstream the point source had substantially lower PCDD/F levels than downstream the point source, 435 ng I-TEQ kg^{-1} dry weight (dw) compared to 106 000 ng I-TEQ kg^{-1} dw (mean value for the most polluted stretch of Kymijoki). However, the area has an intensive pulp and paper mill industry, and areas upstream the wood preservative factory also have enhanced levels of PCDD/Fs compared to a rural lake in the vicinity (Salo et al., 2008). The most polluted sample, located just below the pollution source, contained 356 000 ng I-TEQ

kg^{-1} dw. The authors calculated the load from the river to the Baltic Sea based on concentrations in sediment traps along the river, and for the year 2001 an estimated amount of 44 g I-TEQ was transported to the Gulf of Finland. According to Salo et al. (2008), this amount corresponds to between 10 and 100% of the amount entering the Baltic Sea by air deposition as determined by different modelled estimates, and Kymijoki River thus constitutes a major source of PCDD/Fs to the Baltic Sea basin.

Another heavily polluted water system is the Grenlandfjords in south Norway. These fjords are marine, with an upper layer of fresh water from a river inflow. The area became polluted due to discharges from a magnesium production plant at the innermost fjord, the Frierfjord, between 1951 and 2002 (Knutzen et al., 2003, Ruus et al., 2006). The load of PCDD/Fs could have amounted to 3-5 kg TEQ yr^{-1} before the first treatment plant was installed in 1975 (Knutzen et al., 2003). High levels of PCDD/F have been reported, with values decreasing outwards from the Frierfjord (Knutzen & Oehme, 1989, Ruus et al., 2006). Levels of PCDD/Fs in surface sediment 1 km from the factory were 18 µg TEQ kg^{-1} dw. This decreased to 5.6 at a distance of 4 km from the factory, but 11.5 km downstream the level was still high, 1.6 µg TEQ kg^{-1} dw (Knutzen & Oehme, 1989).

Several studies on the Elbe River basin have looked at point sources of PCDD/F contamination (Stachel et al., 2004, Götz et al., 2007, Götz et al., 1994). The watercourse of Elbe stretches from the Czech Republic through Germany to the North Sea. One important area for PCDD/F contamination seems to be the Bitterfeld region, about 350-400 km upstream of Hamburg. Production of magnesium metal has taken place in Bitterfeld (Weber et al., 2008), and in sediment cores from the tributaries from Bitterfeld (such as Mulde River), a PCDD/F congener pattern typical for metallurgic processes has been found (Götz et al., 2007). Another heavily contaminated site in the Elbe catchment is the Spolana chemical factory in the Czech Republic. In 2002, this factory, as well as several sewage treatment plants along the river, was flooded. Stachel et al. (2004) determined the PCDD/F concentrations in SPM and sediment in connection with the flood to be 7-150 pg WHO-TEQ g^{-1} dw in SPM and 3-140 pg WHO-TEQ g^{-1} dw in sediment. The statistical analyses revealed a contamination source near the Spolana works during the flood, but the by far largest influence on contamination levels in the Elbe came from the Mulde River. The concentrations of PCDD/Fs in SPM at Spolana was 11 pg WHO-TEQ g^{-1} dw; upstream the Mulde tributary it was 4-15 pg WHO-TEQ g^{-1} dw; but at the mouth of Mulde it increased to 10-160 pg WHO-TEQ g^{-1} dw. The concentrations then dropped slowly downstream the mouth of Mulde, and 65 km downstream the levels peaked at 82-87 pg WHO-TEQ g^{-1} dw during the days with maximum water level (Stachel et al., 2004).

Another potential source along Elbe is the city of Hamburg. Götz et al. (1994) found a higher dissolved concentration downstream Hamburg than upstream, 17 and 4 fg I-TEQ L^{-1}, respectively. However, the concentration of particle-bound PCDD/Fs were substantially higher than the concentration of dissolved PCDD/Fs, and this concentration was actually lower downstream Hamburg than upstream, 41 ng and 73 ng I-TEQ kg^{-1} dw, respectively. Götz et al. thus observed higher levels of dioxins upstream Hamburg (3.1 pg I-TEQ L^{-1}) than downstream (1.2 pg I-TEQ L^{-1}), and explained this with a higher amount of SPM at the upstream location, as well as a higher content of organic carbon. The authors argued that the SPM at the downstream location could be a mix of more contaminated limnic particles with less contaminated marine material. The Elbe water discharge at the sampling time (August) was very low, around 200 m^3 s^{-1}, compared to an average freshwater discharge of approximately 877 m^3 s^{-1} (Götz et al., 1994). This demonstrates the difficulty in evaluating data, and the dependence of PCDD/F concentration on various factors such as quality and quantity of organic matter.

In Chapaevsk, southwest of Samara, Russia, high levels of PCDD/F contamination have been determined in various matrices (Revich et al., 2001). The source of contamination is believed to be the Middle Volga chemical plant, which has produced chlorinated chemicals since 1967. Soil within a 2 km distance from the plant contained on average 141.3 ng TEQ kg^{-1}. The concentration in drinking water was 102.4 and 74.1 pg TEQ L^{-1} in two samples from the city centre, and 28.45 pg TEQ L^{-1} in drinking water 6-8 km from the plant. According to the authors, these levels are the highest found in Russia. The drinking water source is groundwater, but it is not clear whether the levels in the drinking water are directly due to a contaminated water source or if the contamination has occurred in the distribution system due to broken pipes. Evidence for a link between this point source and levels in the Chapaevka river or further downstream in the Volga river has so far not been found.

9.5.4.2   PCBs and HCB

PCBs are present in the environment in higher concentrations than PCDD/Fs, which facilitates the chemical analysis. They were also discovered in the environment earlier than PCDD/Fs. There is a large number of data available on PCB levels in water, but a direct comparison between levels is often problematic due to the

inclusion of a different number of congeners in studies, and due to the fact that older studies report concentrations in Aroclor-equivalents (or other technical PCB mixtures), instead of on a congener basis. HCB is more water-soluble than most of the PCBs, and it has also been deliberately spread as a pesticide in the environment, unlike PCDD/Fs and PCBs.

Near Semič, Slovenia, PCBs have leached from waste dumped by a capacitor manufacturing plant and into the ground water, and have been found in surface water and sediment (Brumen 1984). It has entered the Lahinja river, and from there into the Kupa river (Šmit et al., 1987). Upstream of the Lahinja tributary Šmit et al. did not detect PCBs, while the water 200 km downstream the tributary contained 4-52 ng L^{-1} (as Aroclor 1260-equivalents). The concentration in suspended sediment decreased with increasing distance from the source area, from 190 µg kg^{-1} dw 10 km downstream the Lahinja river mouth to 50 µg kg^{-1} dw 200 km downstream, and a similar trend was observed for the bottom sediment (from 39 to 8 µg kg^{-1} dw). According to Picer & Holoubek (2003), 30-50 tons of PCBs have been removed from the karstic hollows and other places near the manufacturing plant, but large amounts are still believed to be present in the karstic ground.

Fernández et al. (1999) investigated the occurrence of PCBs in water (particulate + dissolved) and sediment of the Ebro during 1995/1996. The mean bulk water concentration of PCBs (13 congeners) was 76 ng L^{-1} (range 43-108 ng L^{-1}). There was no significant difference between the sampling sites along the river, and no point sources could be identified. Looking at the sediment samples, however, one sampling site had a significantly higher value (1770 µg kg^{-1}) than the other 12 sites. This site was located at Flix, which has a chemical industry. The authors point out that this source is not reflected in the water concentrations, where the highest values were found upstream. It is possible that the water samples would reflect a different situation if they were normalised to dry matter, or organic carbon, as the measurements in Krycklan during this project showed (Chapter 9.5.3).

Heinisch et al. (2006a, b) has compiled reviews of monitoring data for aquatic media, and provided time series as well as profiles of PCB and HCB contamination levels along European rivers. They point out Elbe as a river with an enhanced contamination of HCB. An important point source for Elbe is a landfill in Chabařovice, Czech Republic, where municipal waste as well as chemical wastes containing HCB from the HCB-producing company Spolchemie Ústí n/L has been deposited. Ground and drainage water from the landfill, as well as wastewater from Spolchemie, reaches the Elbe through the Bilina River. Upstream the tributary, HCB levels in sediment are below 50 µg kg^{-1} dw, but at the tributary the level increases enormously, to above 1300 µg kg^{-1} dw. Also PCBs are found at high concentrations at the Bilina tributary to Elbe, with sediment samples containing concentrations of 1290 µg ∑PCB (6 congeners) kg^{-1} dry matter in 1999, due to Spolchemie.

The inputs from rivers are most important for the coastal region, and the HOCs are often deposited in the deltas or prodeltas. In offshore areas, the atmospheric deposition tends to be more important (Tolosa et al., 1995). The load of particulate-bound PCBs from the Rhône into the Mediterranean Sea (for 1994/1995) was estimated to 304 kg yr^{-1}, and the input of HCB to 171 kg yr^{-1}, of which a large fraction (157 kg) was found to be particle-bound (Albaiges 2005). The Rhône is the Mediterranean river with the largest discharge, after the construction of the Aswan dam, which decreased the discharge of the Nile considerably. The high loads are not surprising, considering the large discharge and the highly industrialized character of the Rhône basin. Agrell et al. (2001) found median bulk water concentrations of PCBs in four rivers in the Baltic drainage area to be 0.21-1.44 ng L^{-1}; the lowest value was for the Umeå River concentration. In an international comparison, all four rivers have low levels of contamination and the median transport in kg month^{-1} was 1.26 for Wistula, 1.15 for Odra, 0.04 for Mörrum and 0.20 for Umeå, which is considerably lower than the load of the Rhône.

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9.6   D6: A model assessing the influence of the spring flood on delivering POPs to surface water by snowmelt, soil runoff and mobilisation of DOC and POC in a background scenario.

Deliverable leader: Sandra Meijer, Lancaster University.
Contains contributions from all PERSPEC partners

9.6.1   Background

In a background contamination area such as Krycklan, contaminants are delivered to the terrestrial environment entirely by atmospheric transport (see also section 9.2). Mobile dissolved organic carbon (DOC) in the soils is known to act as an important carrier for both metals and hydrophobic organic contaminants (HOCs) (see D3 and D4). Various loss processes such as volatilisation and degradation also have an impact of contaminant concentrations in soil. Volatilisation is expected to occur only in the top-most layer of the soil which is in contact with the atmosphere. However, processes such as bioturbation and diffusion can supply HOCs from lower layers to the surface. Degradation of HOCs is not well quantified, but is a potentially important loss process in soil as well as in air, snow and water for certain HOCs. However, most HOCs have long half-lives in the environment (see section 9.3). The main processes involved in the mobilisation of contaminants from catchment to surface water are summarised in the figure below.
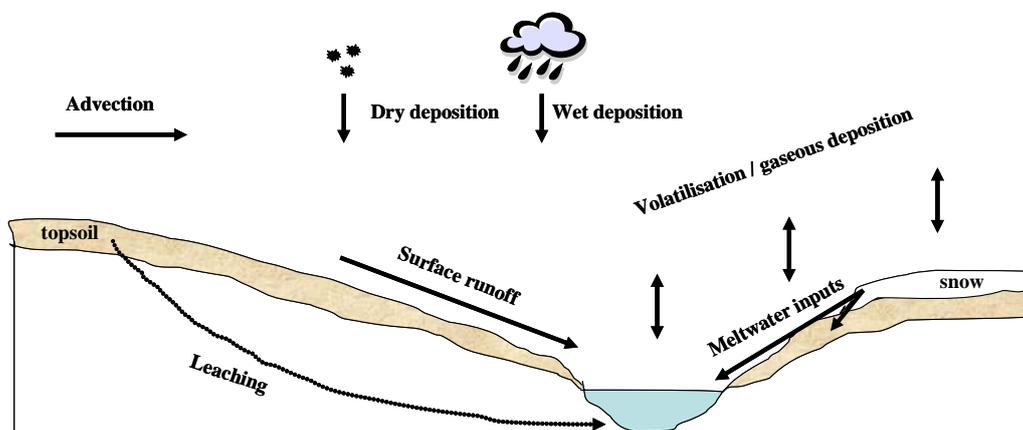
Figure 9.6-1. The main processes involved in the mobilisation of contaminants from catchment to surface water

The Krycklan catchment and its hydrology is described in detail in section 9.3 and 9.4, as well as in the literature (for ex. [*Agren, et al.*, 2007; *Laudon, et al.*, 2007]. In Krycklan as in most boreal environments, the spring flood is a drastic hydrological episode resulting in important biogeochemical changes of fundamental importance for the mobilisation and flux of contaminants. It has been shown that the seasonal hydrology has a pronounced impact on seasonal DOC exports from the catchment (see D3 and D4). Also, research has shown a difference in water runoff and DOC export between forested areas and mires within the catchment.

For example, in the spring and summer season, the organic rich riparian zone (RZ) is the last horizon intersected by the out flowing water before it reaches the stream, resulting in increased DOC export from forested catchments. In the winter season, the water table drops as all precipitation is held in the standing snow pack. In forested catchments, this means water flows mainly through the mineral soil, bypassing the RZ. As DOC levels are much lower in the mineral soil, DOC export for forested catchments is very low during this season. In mire catchments however, deeper layers are rich in DOC.

During the spring season, several additional processes come into play. Apart from runoff from the RZ, there is also overland flow of melt water adding HOCs to the stream. Not all the meltwater flows overland into the stream, a portion seeps into the soils making the water table rise and pushing out "old water". Several experiments were carried out which enabled researchers to quantify the fraction of "new" water (i.e. overland flow), and the fraction of "old" water [*Bishop, et al.*, 2004; *Laudon, et al.*, 2002; *Laudon, et al.*, 2004]. It was found that in catchments dominated by mire, the amount of new water was higher compared to forested catchments.

Considering the strong sorption of HOCs to organic matter and the influence of both seasonal hydrology and catchment type on DOC export, we will consider the following 6 scenarios in our calculations (see table 1 below).

Table 9.6-1.

	Forested catchment	Mire catchment
snow-free	Inputs: atmospheric deposition Export: DOC leaching from riparian soils	Inputs: atmospheric deposition Export: DOC leaching from upper peat layers
snow-covered	Inputs: to snow cover; no input directly to soil. Export: Leaching form deeper layers – mineral soil low in DOC	Inputs: to snow cover; no input directly to soil. Export: Leaching from deeper layers- high in DOC (same as upper peat layers?)
snow melt	Input: atmospheric deposition and infiltration of melt water Export: 77% old water (riparian zone) 23% overland flow	Input: atmospheric deposition and infiltration of melt water Export: 57% old water 43% overland flow

We will compare two first-order sub catchments, one forested (Västrabäcken - C2) and one dominated by mire (Kallkällsmyren - C4). Catchment 2 is 100% forested, with a 10 cm podzol layer overlaying mineral soils, and a riparian zone extending to about 70 cm depth near the stream and ranging up to 15 m away from the stream. Catchment 4 (Kallkällsmyren) is the subcatchment with the highest percentage of mire, i.e. 40%. However, the forest soils are not directly connected to the stream, i.e. any runoff will have passed through the mire area before reaching the stream. It is therefore expected that the forest soils have only limited impact on the DOC export from this catchment. These forest soils are mostly mineral (the podzol layer is not hydrologically connected to the stream) and there is no forest riparian zone. Catchment 4 can therefore be considered a typical mire-dominated catchment for our purposes.

The collected data from section 9.3 and section 9.4 will be used in model calculations to describe the fluxes of contaminants and the gain insight into the processes that regulate these fluxes within the studied catchment and water path.

In particular, the model calculations will be used to:

- Estimate total atmospheric inputs for each season

- Compare HOC exports for the different seasons and different catchment types (forested / mire).

- Compare to exports to total soil inventory

- Calculate relative contribution of snowmelt to total HOC exports

- Quantify the role of the spring flood in delivering HOCs to the Krycklan catchment

- Estimate the influence of enhanced soil contamination on export of HOCs to the stream

The calculations are implemented in an excel spreadsheet format, in such a way that new data and additional compounds can easily be added.

9.6.2   Modelling approach

The model world can be built by a single box or multiple boxes that are connected to each other, the system can be closed or open with in- and outflows. More complex models allow non-equilibrium states with net fluxes between environmental compartments and in the most complex models, changes over time are considered (dynamic models). A common feature for the transport of HOCs and many metals is that the mobility is largely related to the release and transport of organic carbon. To accurately describe the movement of HOCs through the different soil layers and their delivery to the stream, a fully dynamic fully mechanistic model would be necessary (see also D3). However, this is beyond the scope of this project. Therefore, the approach taken here is a simple input-output mass balance [*Gocht, et al.*, 2007].

Top soil layers which receive HOCs through atmospheric deposition are not hydrologically connected to the stream. Water infiltrates the soil causing downward movement of POC, DOC and associated HOCs. However, the high organic matter soil acts as a retarding medium, so HOCs move downward very slowly. This was shown in a recent study by Chatzikosma et al., in which polychlorinated biphenyl (PCB) transport in the vadose zone was simulated [*Chatzikosma and Voudrias*, 2007]. They considered a sandy soil column with organic carbon content of 0.5-1%, and groundwater level at 3.5 m depth. After one year, dissolved PCBs had moved to 15 cm depth, and to 100 cm depth in 30 years. If no organic carbon was specified in the soil at all, then PCBs reached groundwater (3.5 m depth) within the year. This highlights the role of organic carbon as a retarding medium. However, if taking into account DOC-associated transport, PCBs travelled about 35 cm further in the year, i.e. to 50 cm depth. The soils in the Krycklan catchment consist either of mire (highly organic soils up to several meters deep), or forested soils made up of an organic rich podzol layer overlaying mineral soil. The organic layer extends to between 10cm (away from the stream) and 70cm (riparian zone near-stream) depth, with very high organic carbon content (up to 45% OC corresponding to 90% organic matter). In the light of these findings, we don't expect deposited chemical to move downward beyond 5-10 cm within one year. It is therefore highly unlikely that HOCs deposited in a certain year will reach the soil layers that are hydrologically connected to the stream, so we can assume that atmospheric deposition does not significantly alter the concentration of the soil layers from which HOCs are exported during the course of a year. Overland flow can supply DOC- and POC-bound HOCs to the stream from the upper soil layers, although this is likely to happen only during snow melt and certain high-precipitation (rainstorm) events.

In summary, we can assume that atmospheric inputs and DOC-mediated export of HOCs are decoupled in the time frame of our model calculations, i.e. one year. The HOCs found in the lower layers of the soil will have reached these layers through a number of different possible processes over the time course of historical HOC use, i.e. since the 1940s. These include downward leaching in dissolved form, or associated with DOC and POC, bioturbation (not so important in podzols), and through gradual build-up of the soil by mineralisation of the organic layer to form mineral soils, as well as diffusion in the water and air phases of

the soil. The time scales of these processes and their relative importance are highly uncertain however. A fully dynamic model would be necessary to investigate the time scales involved, as these are not captured by steady-state calculations. This is however beyond the scope of this project.

The mass balance approach consists of calculations to estimate inputs to the top 10 cm soil layer on the one hand, and exports from the hydrologically connected soil layers in the catchment on the other hand. As movement of HOCs through the soil is expected to be slow and degradation is ignored for now, we can assume the average soil concentration in a certain layer to be constant on the time scale of investigation, i.e. one year. For simplicity purposes we assume that the soil concentrations in the different horizons are constant with depth as well as with distance from the stream. Also, as a result of the high soil-water partition coefficients, the low particle export and the large size of the soil compartment, we will assume that in the one-year time frame, the export of HOCs from the soil to the stream does not significantly deplete the reservoir of HOCs in the soil. This will be checked by estimating the total reservoir of HOCs in the soil (if bulk density, compartment volume and soil concentration are known) and comparing this to the amount of HOCs exported in the year.

Input and output fluxes will be calculated as follows

$$F_{input} = D \tag{1}$$

Where D = atmospheric deposition (ng/m^2 yr)

$$F_{output} = \frac{C_w \times Q}{A} \tag{2}$$

Where

C_w = concentration of HOC in water [ng/m^3]

Q = water discharge [m^3/yr]

A = catchment area [m^2]

For a specific soil layer or horizon, the storage per area S [mg/m^2] can be calculated as

$$S = C_s \times \rho \times d \tag{3}$$

where

C_s = concentration in a specific horizon [mg/kg]

ρ = dry bulk density of horizon [kg/m^3]

d = thickness of soil horizon [m]

The total inventory (I) can then be calculated as the sum of the storages in different soil layers times the catchment area.

9.6.3   Calculation of fluxes

The values of the partition coefficients and energies of phase transition used in these calculations are given in table 8. All partition coefficients are temperature corrected using the van 't Hoff equation:

$$\ln K(T) = \ln K(T_0) - \frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$(4)$$

9.6.3.1   Input fluxes

Measured bulk deposition fluxes are available for dioxins (Wiberg, unpublished data) and these are used directly. For the other chemicals, input fluxes are calculated as described below.

Inputs of HOCs to the catchment are via atmospheric deposition only and include dry particle deposition, wet gaseous and particle deposition (snow or rain), and net gaseous absorption (i.e. absorption minus volatilisation) through air-soil exchange.

Measured air concentrations are usually reported as total (gas + particle) concentration. In order to calculate separately the contributions of gaseous and particle-bound deposition, we estimate the fraction of chemical in the air sorbed on particles as follows:

$$\phi = \frac{K_p \times TSP}{1 + K_p \times TSP}$$

$$(5)$$

Where TSP is the total suspended particles [µg m^{-3}] and K_p is the gas-particle partitioning coefficient [m^3 µg^{-1}].

Note that Cair,p is the particle-bound concentration *per volume of air* [ng m^{-3}]. The concentration on particles in air, Cp [ng µg^{-1}], is given as:

$$C_p = \frac{C_{air,p}}{TSP} \qquad \text{or} \qquad C_{air,p} = C_p \times TSP$$

$$(6)$$

Kp can be calculated according to [*Harner and Bidleman*, 1998]:

$$\log K_p = \log K_{oa} + \log f_{om} - 11.91$$

$$(7)$$

The fraction organic matter (f_{om}) on aerosols needed to calculate K_P was estimated at 0.20 (assuming a fraction organic carbon (f_{oc}) of 0.15, and the organic matter consisting of 74% carbon). Note that K_P and K_{oa} are temperature dependent.

As measurements of TSP at Krycklan are not (yet) available, an estimated value of 16 [μg m^{-3}] for TSP was taken from [*Fernandez, et al.*, 2002], which was measured in a remote environment.

Dry deposition

The dry deposition flux can be calculated as:

$$F_{dry,p} = V_D \times C_{air,p} \tag{8}$$

Where V_D is the dry deposition velocity and Cair,p is the particle-bound concentration *per volume of air* [ng m^{-3}].

Other studies report values of between 0.1 and 0.8 cm/s, which is between 85 and 690 m/d with the higher values usually measured in more urban environments. We have chosen a relatively low value of 250 m/d.

Wet deposition (rain)

The rain deposition fluxes for the dissolved and particulate-bound fractions of the chemical ($F_{rain,g}$ and $F_{rain,p}$, respectively [ng m^{-2} d^{-1}]) can be calculated using dimensionless washout ratios (W)

$$F_{rain,g} = W_{rain,g} \times G_R \times C_{air,g} \tag{9}$$

$$F_{rain,p} = W_{rain,p} \times G_R \times C_{air,p} \tag{10}$$

Where, W is the washout ratio, G_R is the precipitation rate [m d^{-1}] and C_{air} is the concentration in air [ng per m^3 of air]. The subscripts g and p stand for gas and particle-bound, respectively.

The washout ratios can be experimentally determined as the concentration in rain [ng m^{-3}] divided by the concentration in air [ng m^{-3}].

$$W_{rain} = \frac{C_{rain}}{C_{air}} \tag{11}$$

The different washout ratios are related by:

$$W_{rain,t} = W_{rain,g} \times (1 - \phi) + W_{rain,p} \times \phi \tag{12}$$

Where Φ is the fraction of chemical in the air sorbed on particles.

However, due to the lack of experimental data on washout ratios, a number of predictive relationships have been developed. Here, we use the equations cited in [*Lei and Wania*, 2004]:

The gaseous rain washout ratio equals $K_{rain/air}$, the partition coefficient between rain and air, which can be calculated as:

$$W_{rain,g} = K_{rain/air} = K_{WA} + 3K_{IA}/r \qquad (13)$$

Where K_{WA} is the partition coefficient between water and air [mol of chemical per m^3 of water / mol of chemical per m^3 of air], quantifying the dissolution of the chemical in the liquid water phase, and K_{IA} is the interfacial-air partition coefficient [mol of chemical per m^2 of surface / mol of chemical per m^3 of air], quantifying the sorption to the droplet surface. The radius r of the water droplet was assumed to be 1 mm.

$$K_{WA} = \frac{RT}{H} \qquad (14)$$

where H [J mol^{-1}] is the Henry's Law constant and R is the gas constant [J mol^{-1} K^{-1}]

$$\log K_{IA}(15^\circ C) = 3.60\Sigma\alpha_2^H + 5.11\Sigma\beta_2^H + 0.635\log L^{16} - 8.47 \qquad (15)$$

Values for the phys/chem properties used in equation 15 are found in [*Lei and Wania*, 2004].

For the rain washout ratio of particle-bound compounds, a constant value of 10^5 was chosen [*Lei and Wania*, 2004].

Wet deposition (snow)

Snow deposition fluxes of gaseous and particle-bound compounds ($F_{snow,g}$ and $F_{snow,p}$, respectively [ng m^{-2} d^{-1}]), can be calculated using washout ratios (W) analogous to the rain deposition:

$$F_{snow,g} = W_{snow,g} \times G_R \times C_{air,g} \qquad (16)$$

$$F_{snow,p} = W_{snow,p} \times G_R \times C_{air,p} \qquad (17)$$

where $W_{snow,g}$ is the snow washout ratio for gaseous compounds and $W_{snow,p}$ is the snow washout ratio for particle-bound compounds.

The snow washout ratio for gaseous compounds is equal to $K_{snow/air}$ (the partition coefficient between snow and air) and can be estimated from:

$$W_{snow,g} = K_{snow/air} = K_{SA} \times SA_S \times \rho \qquad (18)$$

Where K_{SA} is the sorption coefficient onto the snow surface [mol of chemical per m^2 of surface / mol of chemical per m^3 of air], SA_S is the specific surface area of snow (0.1 [m^2 g^{-1}]) and ρ is the density of water (10^6 [g m^{-3}]).

K_{SA} values were measured for a range of compounds at -6.8C (266.2K) and are given in [*Lei and Wania*, 2004].

For the snow washout ratio of particle-bound compounds, a constant value of 10^5 was chosen, equal to the rain washout ratio of particle-bound compounds.

We assume here that all snow inputs occur during the winter season and that snow inputs occur exclusively to the snowpack and therefore not directly to the soil.

The total input to the snow pack ($I_{tot,snowpack}$ [g] is therefore

$$I_{tot,snowpack} = (F_{dry,p} + F_{snow,g} + F_{snow,p}) \times days \times area \qquad (19)$$

Where days represent the length of the snow-covered season and area is the area of the subcatchment in question.

The maximum theoretical snow pack concentration (* to indicate value before considering any post-depositional losses) can be calculated as

$$C^*_{meltwater} = I_{tot,snowpack} / V_{melt} \qquad (20)$$

Where Vmelt is the meltwater equivalent of the snowpack (calculated based on precipitation amount during snow-covered season).

Recent measurements have shown that the concentration of PCBs and OC-pesticides decreases rapidly following fresh snow fall. This is mainly due to the increase in density of the snow. Herbert et al. [*Herbert, et al.*, 2005] experimentally derived an equation to describe the loss of chemical from the snow pack as a function of changes in snow density. Φs is the fraction left in the snow pack and can be calculated as

$$\phi_s = 0.6923 e^{-6.2609\Delta\rho} \qquad (21)$$

Where $\Delta\rho$ is the change in snow density over the entire snow covered period (until just before melting). We assume that the density of snow decreased from 0.05 (fresh snow) to 0.5 [kg L^{-1}] over the snow-covered period, before melting set in, i.e. $\Delta\rho$ equals 0.45. These are typical measured values [*Herbert, et al.*, 2005].

The final concentration of chemical in the meltwater is therefore

$$C_{meltwater} = C^*_{meltwater} \times \phi_S \qquad (22)$$

The data set on which eq 21 is based did not allow to statistically discriminate between compounds and therefore eq 21 is valid for all HOCs. In reality it is highly likely that Φs will be different for different compounds, with a greater fraction left in the snow pack for the less volatile compounds. At present however, the data is not available to make this distinction.

Air-soil exchange (dry gaseous deposition and volatilisation)

The air-soil exchange fluxes are calculated here using the fugacity approach. Fugacity represents the partial pressure of chemical in a particular medium and controls the movement of chemical between media. Fugacity can also be seen as "escaping tendency" and depends on the concentration of the chemical in the different compartments as well as temperature and the properties of the chemical and the surface compartment [*Mackay*, 1991]. Fugacity (f [Pa]) is related to concentration (C [mol m^{-3}]) through the "fugacity capacity" or Z-value (Z [mol m^{-3} Pa^{-1}]), which can be calculated from the compound physical/chemical properties and properties of the environmental compartment in question.

$$C = Z \times f \tag{23}$$

Chemicals strive to establish equilibrium i.e. equal fugacity between two phases (e.g. soil and air). A quick assessment of the soil-air equilibrium status of HOCs at a specific site can be performed by calculating fugacity fractions, provided soil and air concentrations are available.

$$ff = f_{soil} / (f_{soil} + f_{air}) \tag{24}$$

A fugacity fraction of 0.5 indicates that the air and the soil are at equilibrium, values <0.5 indicate net movement from the air to the soil (net gaseous absorption) and values >0.5 indicate net movement from the soil to the air (net volatilisation).

Fugacity capacities for air (Z_a) and soil (Z_s) are calculated as follows:

$$Z_a = 1/RT \tag{25}$$

$$Z_s = f_{OC} K_{OC} \rho Z_w \tag{26}$$

$$Z_w = 1/H \tag{27}$$

Where R is the ideal gas constant (Pa m^3 mol^{-1} K^{-1}), T is the absolute temperature (K), f_{OC} is the fraction organic carbon in the soil, ρ is the soil density (kg L^{-1}). K_{OC} is the organic carbon-water partition coefficient (L kg^{-1}), Z_w is the fugacity capacity for water (mol m^{-3} Pa^{-1}) and H is the Henry's Law constant (Pa m^{-3} mol^{-1}).

The organic carbon-water partition coefficient is defined as [*Seth, et al.*, 1999]

$$K_{OC} = 0.35 K_{OW} \tag{28}$$

Where K_{OW} is the octanol-water partition coefficient (note K_{OW} is dimensionless, therefore the factor 0.35 has units of [L kg^{-1}]).

Using the calculated fugacities, the net diffusive flux N (mol h^{-1}) from soil to air can be determined through:

$$N = D_v (f_s - f_a) \tag{29}$$

Where D_v (mol Pa^{-1} h^{-1}) is the overall D-value for transport across the soil/air interface [*Backe, et al.*, 2004]. D-values are transport parameters, similar to rate constants. For example, fast processes have large D-values [*Mackay*, 1991].

D_v is calculated through

$$1/D_v = 1/D_e + (1/(D_a + D_w + D_s)) \tag{30}$$

Where D_e is the D-value for transport across the soil-air boundary layer, D_a is the D-value for diffusion in the soil air, D_w is the D-value for transport in the soil water and D_s is the D-value for vertical bioturbation of soil solids [*Backe, et al.*, 2004]. Details on how to calculate these D-values can be found in [*Mackay*, 1991] and [*Cousins, et al.*, 1999]. The D-value for bioturbation was adjusted here for the special case of Krycklan, as earthworm activity is much lower in the organic soils found in Krycklan than in an average soil (top 10cm turned over in 20 years instead of in 5 years). The incorporation depth in the soil was assumed to be 10 cm. An arbitrary area of 1 m^2 was used, which means that the flux N has units of mol m^{-2} h^{-1}. This can then easily be converted into units of ng m^{-2} yr^{-1} Note that negative fluxes mean there is net deposition to the soil.

Physical-chemical properties used in the input flux calculations are given in table 8. Meteorological data, soil properties and concentration of HOCs in air and soil are given in table 2, 4 and 6 respectively.

9.6.3.2   Output fluxes

The output fluxes or export of HOCs from the catchment soils to the stream will be calculated from the concentration of the chemical in the soil water and the amount of water exported (see eq 2).

The concentration of chemical in soil water will be estimated using the three-phase partitioning model (e.g. [*Hwang, et al.*, 1998; *Mitra and Dickhut*, 1999]). As most of the DOC and associated chemical is exported to the stream from layers that are saturated (either permanently e.g. groundwater or transiently, e.g. during periods of high flow), we will assume for these calculations that the soil is saturated, in other words the porosity of the soil equals the water content and air content is set to zero. Thus we can consider three-phase partitioning in saturated soils analogous to sediments (see figure 2). This requires the assumption that soil particles can be viewed as suspended particles. This is not entirely realistic as soils consist of large particles and aggregates in which diffusion is slower, so instantaneous equilibrium between soil particles and the dissolved phase cannot be assumed. However we feel that for the purpose of these initial calculations this assumption is acceptable.
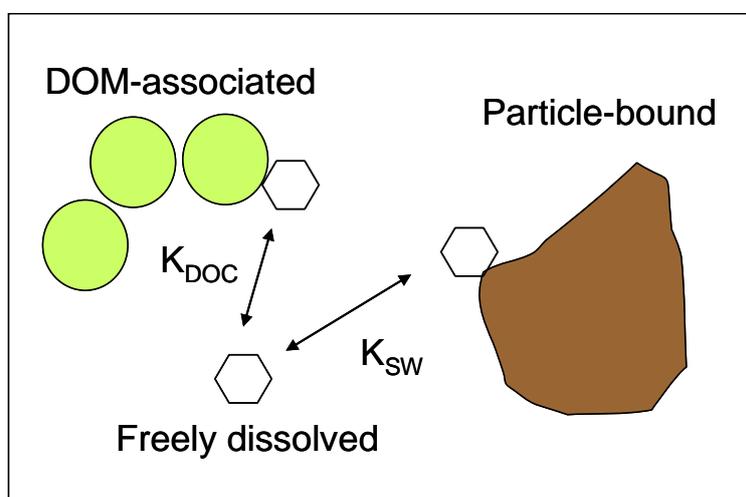
Figure 9.6-2. Three-phase partitioning model

The total chemical concentration in bulk saturated soil is given as:

$$C_{bs}^t = C_{bs}^p + C_{bs}^d \qquad\qquad (31)$$

Where:

C_{bs}^t is total concentration of chemical in the bulk soil [kg/L bulk soil]

C_{bs}^p is concentration of chemical in bulk soil bound to soil particles [kg/L bulk soil]

C_{bs}^d is dissolved concentration of chemical in the bulk soil [kg/L bulk soil]

The dissolved concentration of chemical in the soil water is made up of freely dissolved chemical and DOC-complexed chemical

$$C_{bs}^d = C_{bs}^{fd} + C_{bs}^{DOC} \qquad\qquad (32)$$

Combining eqs 31 and 32 gives:

$$C_{bs}^{t} = C_{bs}^{p} + C_{bs}^{fd} + C_{bs}^{DOC}$$
(33)

The concentration of chemical on the soil solids can be related to the freely dissolved concentration as:

$$C_{bs}^{p} = r_{sw} \times K_{sw} \times C_{bs}^{fd}$$
(34)

Rsw is the solid-to-water phase ratio [kg solid mass / m^3 water volume] and can be calculated as

$$r_{sw} = \rho \times \frac{1-\phi}{\phi}$$
(35)

Where:

ρ is the density of solid matrix [kg/m^3] and ϕ is the porosity [m^3 of fluid-filled pore space / m^3 of bulk space]. Typical values for porosity, dry bulk density and particle density were taken from a range of sources including site-specific measurements and the general literature. We assume that there is no air, so volumetric water content is equal to the porosity.

K_{sw} is the soil-water distribution coefficient [L kg^{-1} soil solids] and is calculated as

$$K_{sw} = f_{OC} \times K_{OC}$$
(36)

Where

K_{OC} is the organic carbon-water partition coefficient [L kg^{-1} OC] and f_{OC} is the fraction of organic carbon on the soil solids.

The concentration of DOC-bound chemical can be related to the freely dissolved concentration as:

$$C_{bs}^{DOC} = [DOC] \times K_{DOC} \times C_{bs}^{fd}$$
(37)

K_{DOC} is the dissolved organic carbon-water partition coefficient [L kg^{-1} DOC]. Burkhard et al. [*Burkhard*, 2000] developed the following predictive relationship for naturally occurring organic carbon:

$$K_{DOC} = 0.08 \times K_{OW}$$
(38)

Combining eqs 33, 34 and 37 gives:

$$C_{bs}^{t} = r_{sw} \times K_{sw} \times C_{bs}^{fd} + C_{bs}^{fd} + [DOC] \times K_{DOC} \times C_{bs}^{fd}$$

or

$$C_{bs}^{t} = C_{bs}^{fd} \times (r_{sw} K_{sw} + 1 + [DOC] K_{DOC})$$
(39)

The particulate and dissolved (both freely and DOC-bound) fractions in bulk soil are therefore given as

$$C_{bs}^{p} = f_{p} \times C_{bs}^{t} \tag{40}$$

$$C_{bs}^{fd} = f_{d}^{f} \times C_{bs}^{t} \tag{41}$$

$$C_{bs}^{DOC} = f_{d}^{DOC} \times C_{bs}^{t} \tag{42}$$

Where f_{p} is the fraction bound to particles, f_{d}^{f} is the freely dissolved fraction and f_{d}^{DOC} is the DOC-bound fraction

$$f_{p} = \frac{r_{sw}K_{sw}}{r_{sw}K_{sw} + 1 + [DOC]K_{DOC}} \tag{43}$$

$$f_{d}^{f} = \frac{1}{r_{sw}K_{sw} + 1 + [DOC]K_{DOC}} \tag{44}$$

$$f_{d}^{DOC} = \frac{[DOC]K_{DOC}}{r_{sw}K_{sw} + 1 + [DOC]K_{DOC}} \tag{45}$$

with

$$f_{p} + f_{d}^{f} + f_{d}^{DOC} = 1 \tag{46}$$

The concentration of chemical per solid mass is

$$C_{p} = \frac{C_{bs}^{p}}{(1-\phi)\rho} \tag{47}$$

The concentration of chemical per fluid volume is

$$C_{w} = \frac{C_{bs}^{d}}{\phi} \tag{48}$$

The concentration of HOCs in the soil water was calculated for the different layers (RZ and mineral layer for C2; the whole mire for C4).

The export of HOCs during the different seasons was subsequently estimated using eq 2 and using the following assumptions

C4 summer and winter: export from the whole mire

C2 snow-free season (summer): export from riparian zone

C2 snow-covered season (winter): export from mineral layer

Snow-melt season (spring):   C2:   77% old water (riparian zone)

                              23% overland flow of meltwater

                      C4:   57% old water

                              43% overland flow of meltwater

Soil properties, soil concentration of HOCs and physical-chemical properties used in the output flux calculations, are given in tables 4-7. A constant soil temperature of 277K was assumed to apply to all layers year-round. We assume soil water DOC content is uniform in space and time within a certain soil layer.

It has been shown previously that TOC in Krycklan as well as in other boreal environments is present almost exclusively as the dissolved fraction (DOC), and the particulate form is usually below 5%, even during the most high flow situations [*Ågren et al.*, 2007a; *Ivarsson and Jansson*, 1995; *Laudon and Bishop*, 1999] . In order to check the possible contribution of particulate organic carbon (POC) with respect to HOCs exports, we assume here that POC makes up 5% of TOC in both the stream water and the soil water.

9.6.3.3   Enhanced contamination scenario

Calculations are also performed with respect to an enhanced contamination scenario, which assumes application of contaminated sludge to the forested areas of Krycklan. Although this practice is not applied at Krycklan, it has been at other background sites in the past. We use a typical sludge application of 15 tonnes per hectare, and concentrations of target contaminants are given in table 7. The sludge concentration data are taken from a draft report on sludge monitoring that will be published by the Swedish EPA and from an environmental monitoring report from a Swedish STP (unpublished data).

In the model calculations performed in this study, we have been assuming that contaminants are exported only from the lower soil layers that are hydrologically connected to the stream. A sludge application to the soil surface would therefore not have any effect on export for that year under the current assumptions. However, the current assumptions omit to take into account surface runoff (overland flow) during autumn high precipitation events, which would be a dominant route for export of surface applied contaminated sludge to the stream. For the purpose of the enhanced contamination scenario, we will include overland flow in our model calculations for the forested catchment (C2) during the snow-free season (summer / autumn).

We assume for the purpose of these calculations that the top 10 cm of soil is affected by the application of sludge. As runoff will be more significant near the stream than uphill, we assume top 10 cm soil properties equal to upper riparian. An application rate of 15 tonnes per hectare and an incorporation depth of 10 cm yield and application of 0.015g sludge per cm3 of bulk soil or 5% of the overall mass of soil. The organic carbon content of the sludge was measured to be about 25%. Considering the application rate, the overall organic carbon content of the soil will not change significantly. Therefore, all soil parameters and soil water parameters are assumed to stay the same.

The fraction of exported water reaching the stream through surface runoff during the snow-free season is not known. Surface runoff during this season occurs only during high-precipitation events such as rain storms. If we assume that a daily precipitation of 10mm or more constitutes heavy rain, then the meteorological data for Krycklan show that between 50 and 60 percent of precipitation during the snow free season falls as heavy rain (depending on the year). Due to lack of specific data for the snow-free season, we assume here that the percentage of runoff which occurs as overland flow in the forested catchment is the same during the snow-free season as during snow melt, i.e. 23% (= "new water" during snowmelt). This would be about half of the precipitation falling as heavy rain, which seems like a reasonable assumption.

9.6.4   Model parameters and physical-chemical properties used

Met data used are given in table 2. Met data were obtained from the Krycklan Catchment Study, and are given as a 3-year average encompassing the years 2003-2005.

Table 9.6-2. Meteorological data (3-year average).

	snow-free	snow-covered	snow-melt
G_R (mm/day)	2.379	1.154	1.059
T (degrees C)	9.26	-6.43	5.03
amount of days	160	139	66

Water and DOC export data used are given in table 3. Measurements of TOC in stream water have been carried out over many years at a number of sites throughout the Krycklan catchment (see D4). Continuous monitoring of water discharge has allowed the calculation of organic carbon export for individual subcatchments. Values in table 3 are given as a 3-year average encompassing the years 2003-2005.

Table 9.6-3. Water and DOC export data from Krycklan.

site	ha		spring	summer	winter
C 2	14	water export (m3)	14543	18554	3185
		spec carbon exp. (kg/ha)	238.7	343.4	34.2
C 4	19	water export (m3)	20468	26113	4482
		spec carbon exp. (kg/ha)	473.1	1052.8	140.3

Soil properties are given in table 4. soil properties were compiled from actual measurements for C2 and C4, complemented with general literature data for similar environments in cases where measurements were unavailable.

DOC has been measured in soil water on the S-transect at different depths and different distances from the stream [*Cory, et al.*, 2007]. It has been shown that the stream water DOC content is mainly influenced by the last soil horizon intersected, which is usually the organic rich soils from the riparian zone [*Agren, et al.*, 2007], except in winter under low flow conditions when the deeper mineral layers are drained. Indeed, suction lysimeter data from S04 (riparian zone) show that the depth integrated value for soil water TOC in the summer season is equal to the measured stream water DOC [*Cory, et al.*, 2007].

DOC content in soil water was therefore estimated based on stream water measurements assuming soil water DOC content of the layer drained during that season is similar to the stream water DOC content. This is an acceptable assumption due to the fact that the two catchments under investigation are first order, so no contributions to surface water concentration from other streams are assumed to apply. Soil water DOC was not calculated for the podzol layer as this layer is not hydrologically connected to the stream.

Table 9.6-4. Soil properties.

		C2			C4
		RZ	podzol	mineral	peat
soil foc	-	0.06	0.2	0.008	0.49
particle density	g/cm^3	1.4	1.4	2.4	1.4
soil dry bulk density	g/cm^3	0.30	0.18	1.2	0.1
soil porosity	-	0.79	0.87	0.5	0.93
soil water content*	-	0.55	0.38	0.3	0.47
soil water TOC	mg/L	18.5	-	10.7	35.8

* unsaturated soil

Based on the information available for catchment 2 (see for example D7), we will assume in our model calculations an organic layer of 10 cm, and a mineral layer of 90 cm, as it has been shown that the water only moves in the top meter of soil [*Cory, et al.*, 2007]. The riparian zone extends to about 70 cm depth near the stream and ranges up to 15 m away from the stream. Knowing that the length of the stream in catchment 2 is 937 m, the following compartment volumes were calculated for C2:

Table 9.6-5.

	m^3	% of total
RZ	16398	12
podzol	8755	6
mineral	109243	81

In the mire catchment, only one horizon up to 1m depth will be considered, with 90% organic matter and density and porosity values representative of typical peaty soils.

Concentrations of HOCs in air and soil are given in table 6. Air concentrations were estimated based on regional values reported by EMEP and IVL (refs). Soil HOC concentration and fraction organic carbon were measured in catchment 2 at different depths and at different distances from the stream by Wiberg et al (unpublished data). In catchment 4, HOC concentrations and fraction organic carbon were measured at different location in the mire, at different depths. Based on those measurements, we calculated mean HOC concentrations and mean fraction organic carbon in the upper RZ, the RZ, the podzol layer, the mineral layer (all catchment 2) and the mire soil (catchment 4).

Table 9.6-6. Concentrations of HOCs in air and soil.

		PCB 28	PCB 180	HCB	2378 TCDF	23478 PCDF	OCDD
C_{air} (pg/m^3) [1]		1.72	0.148	50.0	0.0038	0.0033	0.102
C_{soil} (ng/kg dw)	RZ [2]	22.0	45.1	251	0.75	0.25	7.5
	podzol [3]	58.0	170.0	1100	3.5	1.6	65
	mineral [4]	4.7	4.0	11.6	0.068	0.05	0.903
	peat [5]	45.7	91.6	165	1.47	0.49	13.3

1. Estimated based on EMEP monitoring data for Swedish and finish background sites
2. Mean of all layers S4; 3. top layer S12; 4 mean of all layers S12; 5. mean of all samples C4

Table 9.6-7. Concentrations of HOCs per mass of sludge (ng/kg dw).

PCB 28	PCB 180	HCB	2378TCDF	23478PCDF	OCDD
14000	5900	82750	2.36	1.84	594

Table 9.6-8. Physical-chemical properties.

		PCB 28	PCB 180	HCB	2378 TCDF	23478 PCDF	OCDD
Partition coefficients							
K_{OA} [1] (25ºC)	-	$7.24\ 10^7$	$1.48\ 10^{10}$	$1.32\ 10^7$			
H [1] (25ºC)	Pa m^3/mol	29.1	7.66	76.6	1.46	0.505	0.684
K_{IA} [2] (15ºC)	m	$3.91\ 10^{-3}$	$8.85\ 10^{-2}$	$2.44\ 10^{-3}$			
K_{SA} [2] (snow-air) (-6.8ºC)	m	0.10	3.98	0.09			
K_{OW} [1] (25ºC)	-	$4.57\ 10^5$	$1.41\ 10^7$	$4.07\ 10^5$	$1.26\ 10^6$	$3.16\ 10^6$	$1.58\ 10^8$
Energies of phase transition							
delta U_{OA} [1]	J/mol	$-7.84\ 10^4$	$-9.52\ 10^4$	$-7.59\ 10^4$			
delta U_{AW} [1]	J/mol	$5.18\ 10^4$	$6.90\ 10^4$	$5.19\ 10^4$	$7.44\ 10^4$	$8.75\ 10^4$	$1.15\ 10^5$
delta H_{IA} [2]	J/mol	$-7.99\ 10^4$	$-9.57\ 10^4$	$-9.65\ 10^4$			
delta U_{OW} [1]	J/mol	$-2.66\ 10^4$	$-2.61\ 10^4$	$-2.40\ 10^4$	$-1.82\ 10^4$	$-1.70\ 10^4$	$2.99\ 10^4$

1. Schenker et al. 2005 for PCBs and HCB. Mackay for PCDD/Fs
2. Lei and Wania 2004 for PCBs. Values for HCB were estimated based on . Lei and Wania 2004. PCDD/F values were estimated based on Beyer et al.

9.6.5   Model uncertainties and sources of error

The model calculations presented here can only be regarded as estimates, due to the following reasons:

- Environmental concentrations are assumed constant in time and space for the purpose of the model. It is well-known that large variability exists in measured environmental concentrations, up to several orders of magnitude
- We assume continuous average rain or snow, and constant air concentrations. It has been shown that air concentrations tend to decrease during a precipitation event, and are higher during periods of no precipitation (Hertwich et al., 2001)).
- We assume that the temperature is always below zero in the winter season (i.e. precipitation is snow), and always above zero in spring and summer/autumn (i.e. precipitation is rain). However, in autumn, winter and spring, "cold-rain" events also occur, which – as mentioned in chapter 9.2.3 - are highly efficient in removing HOCs from the atmosphere (both vapour and particulate bound chemicals) (Lei and Wania 2004)
- Eq 21 in D6, used to estimate losses from the snow-pack to the atmosphere upon compaction, doesn't differentiate between chemicals with different phys-chem properties. Therefore losses for the less volatile compounds (PCB180, PCDD/Fs) are probably overestimated, i.e. melt water concentrations will be underestimated.
- Measured input values were used wherever possible. However, no deposition measurements were available for PCBs HCB, therefore these had to be calculated. This causes a discrepancy between PCBs/HCB on the one hand, and PCDD/Fs on the other hand, for which measured values were used. In the case of deposition, it has often been shown that calculated values tend to be higher than measured values. Either calculation overestimate deposition, or measurement could underestimate deposition as losses could occur from the sampling medium during extended sampling periods, which would not necessarily occur if the chemical was deposited to the soil instead.
- The air-surface exchange calculations were done according to the method by Mackay et al. (Mackay 1991). The original calculations specify a bioturbation mass transfer coefficient which is typical for grassland. It has been shown previously that bioturbation greatly influences the air-surface exchange of HOCs, by providing a means of vertical transport of contaminants in the soil (Cousins, Mackay et al. 1999; Sweetman, Cousins et al. 2002): Earthworms species typically found in the litter layer of forest soils are known to turn over the soil at a much slower rate than earthworms typically found in

grasslands. Therefore, we have adjusted the MTC for bioturbation from 10 cm turned over once every 5 years to once every 20 years. However, it is possible that this value is still too high.

- Air concentrations used for calculating PCB/HCB deposition and air-surface exchange are not from the site under study, but an average for northern background sites. Potentially slightly overestimated.
- The effect of the forest filter effect on deposition was not taken into account, therefore input to soil compartment probably underestimated.
- Overland flow during storm events in summer/autumn season is not taken into account. However, the top layer of soil is quite similar to the riparian soil in terms of HOC concentrations and soil properties. Therefore, we don't anticipate an important effect on exports via this route. An estimate of overland flow contributions from contaminated top soils (after sludge application, in the enhanced contamination scenario) was made in section 9.6.5.8., which showed a significantly increased export for PCB 28 and HCB.
- The assumption that soil particles can be viewed as suspended particles for three-phase partitioning calculations is not entirely realistic, as soils consist of large particles and aggregates in which diffusion is slower, so instantaneous equilibrium between soil particles and the dissolved phase cannot be assumed. By wrongly assuming instantaneous equilibrium, dissolved phase concentration could be overestimated or underestimated, depending on whether the dissolved phase concentration inside the aggregates was lower or higher than the fast flowing dissolved phase, respectively

In general, the lowest errors are expected in measured environmental parameters such as temperature, soil organic carbon content, DOC concentration, etc. Physical-chemical properties such as K_{ow} and K_{oa} usually have a large error associated with them, up to one order of magnitude. Direct measurements also have a relatively large error associated with them, although some measurements (e.g. deposition, aqueous concentration) would be expected to have larger errors than others (soil, air concentration) because of the difficulties associated with measuring hydrophobic chemicals in aqueous phases.

A thorough analysis of model uncertainty was not possible within the time-frame of this project, but is planned in a follow-up study.

9.6.6   Results

Preliminary results of the model calculations are presented below in the following subsections, which cover bulk deposition fluxes, the role of the melting snowpack and the change in the soil inventory with yearly inputs and outputs. It is important to stress that construction of a catchment model for HOCs is the key achievement of this chapter and that use and refinement of the model, along with sensitivity and uncertainty analyses, would be recommended for future work.

9.6.6.1   Comparison of bulk deposition between seasons

In remote catchments the input of HOCs is entirely mediated by atmospheric deposition. In table 9.6-9, we compare the seasonal and annual bulk deposition between different HOCs and for the different seasons.

Table 9.6-9. Seasonal (pg/m2/d) and annual (ng/m2/yr) bulk deposition*.

	PCB 28	PCB180	HCB	2378TCDF	23478PCDF	OCDD
snow-free	2.61	24.4	21.4	0.19	0.11	2.61
snow-melt	4.05	35.1	32.5	0.072	0.027	2.28
snow-covered	28.0	56.1	581	0.28	0.16	10.9
annual	5	17	89	0.080	0.044	2.302

* PCBs and HCB: calculated; PCDD/Fs: measured

Both the measured (PCDD/Fs) and the calculated (PCBs, HCB) values show significantly higher deposition in the winter (snow-covered) season. This is expected as snow is a highly efficient scavenger of HOCs from the atmosphere. The difference is most notable for the higher volatility compounds (PCB28 and HCB). It is

important to note however, that not all winter deposition is delivered to the soil, as it accumulates in the standing snowpack and a large percentage will volatilise before melt water can deliver the HOCs to the soil.

9.6.6.2   Soil/air equilibrium status in the summer season

The soil-air equilibrium status is calculated for the summer season only, as this is the season in which most air-soil exchange takes place. During winter, the soil is covered by snow and therefore no exchange takes place during this season. During the spring season, melting snow will impact on the air-soil exchange, making this the most difficult season to describe.

As only the top 10 cm or so are thought to exchange with the air, we calculate the air-soil equilibrium status for the upper 10 cm of forest soil (i.e. the podzol layer) in catchment 2. The net overall flux is calculated by subtracting the bulk deposition flux for the snow-free season (Table 9.6-9) from the net gaseous flux (Table 9.6-10).

Table 9.6-10. Soil-air equilibrium status in Catchment 2 for the summer season (fluxes in pg/m2 d).

	PCB 28	PCB180	HCB	2378 TCDF	23478 PCDF	OCDD
fugacity fraction[1]	0.681	0.300	0.814	0.0008	0.00004	0.000002
Net gaseous flux[2]	58.1	-7.53	2496	-334	-300	-9224
Net overall flux[2]	55.5	-31.9	2474	-335	-300	-9226

1. Values >0.5 signify net volatilisation, values <0.5 signify net gaseous deposition
2. Positive value means volatilisation, negative value means net deposition

The more volatile compounds PCB 28 and HCB show a higher volatilisation flux than bulk deposition flux (approx one order of magnitude difference). Net overall loss from the soil occurs for these compounds. The less volatile compounds PCB 180 and PCDD/Fs show net overall input to the soil, both by dry gaseous deposition and by bulk deposition.

9.6.6.3   Comparison of input fluxes with soil inventory

Here we compare the net overall flux (see Table 9.6-10) with the soil inventory (calculated as the sum of the storages (eq 3) in different soil layers times the catchment area) to estimate the long-term status of soil contamination. Table 9.6-10 showed that for the lighter compounds PCB 28 and HCB, there is a net loss from the soil, whereas for the heavier compounds there is a net input to the soil. When the net amount of chemical added to or lost from the soil in a year is compared to the soil inventory for the upper 10 cm, we find that it represents between 0.05 and 1.2% of the inventory, which implies there is no significant change in soil concentrations during the year. However, the amount of chemical leaching to lower layers and being lost through degradation, and the time scales involved in these processes, are not well quantified in general (and not considered in these calculations), so the long-term status of the upper soil layers remains unknown.

9.6.6.4 Seasonal output fluxes

The export of HOCs (ng/d) is compared for the different seasons in Table 9.6-11.

Table 9.6-11. Seasonal export of POPs (ng/d).

		PCB 28	PCB 180	HCB	2378TCDF	23478PCDF	OCDD
C2	summer	285	360	3517	7.6	2.2	59
	winter	45	19	124	0.47	0.25	4.1
	spring	466	625	6166	12	4	106
C4	summer	166	252	635	4.6	1.4	36
	winter	33	50	125	0.92	0.28	7.2
	spring	310	533	3372	6.3	2.3	90

Since HOC export is linked to both concentration and water discharge, we see the highest daily export of HOCs in spring in both catchments. This highlights the importance of the spring melt episode for contaminant mobilisation.

Interestingly, the daily export during the winter season is remarkably similar between the two catchments. Work by Agren et al (2007) and Laudon et al (2007) had shown that DOC export differs greatly between forested and mire catchments in winter, as lower soil layers are drained which are low in DOC in forested catchments, but high in DOC in mires. Concentrations of HOCs in soil water, according to the three-phase partitioning model, are dependent on soil concentration, soil foc and soil water DOC. The mineral soil water has lower DOC content, but mineral soil also has a lower foc which means HOCs are more easily released from these soils.

9.6.6.5 Relative importance of snow melt for delivering POPs to surface waters during spring melt season.

The snow-melt season (spring flood) is an important hydrological event in a remote boreal catchment such as Krycklan. Here we assess its importance in terms of contaminant mobilisation. Table 9.6-12 summarises the amount of chemical exported per area in spring by old and new water.

Table 9.6-12. HOCs exported per area (µg/km2) in spring by old and new water.

		PCB 28	PCB 180	HCB	2378TCDF	23478PCDF	OCDD
C2	old	196	248	2426	5.3	1.5	41
	new	24	48	481	0.23	0.14	9.1
C4	old	63	95	239	1.7	0.5	14
	new	45	90	933	0.45	0.26	18

For all compounds, we see that the amount of chemical exported per km2 by old water is higher in C2 than in C4 and on the other hand the amount of chemical exported per km2 by new water is higher in C4 than in C2. In other words new water (overland flow of snow melt water) is more important for HOC export in C4 than in C2.

It is clear that in C4, the spring flood has a marked influence on the exported contaminants, as overland flow accounts for 43% of exported water, but for several compounds (HCB, OCDD), this overland flow is responsible for more than 50% of the chemical exported in spring. An important note to make here is that the estimate of chemical left in the snowpack after it has melted is very conservative. Based on the relationship measured by Herbert et al., we calculate that 4% of the chemical remains in the snowpack after melting (see eq 21). This relationship does not discriminate between compounds of different volatility and it is highly likely that for the less volatile compounds a larger fraction than 4% is left in the snowpack. If for example we

assume a fraction of 10% instead of 4%, more than 75% of the total OCDD exported from C4 in spring would come from overland flow of melt water.

9.6.6.6   Comparison with surface water measurements

Estimated and measured surface water concentrations are given in table 9.6-13.

Table 9.6-13. Concentration in surface water – calculated versus measured (pg/m3).

		PCB 28	PCB 180	HCB	2378TCDF	23478PCDF	OCDD
C2	calculated	2113	2838	27981	53	16	480
	measured	477	117	2060	34	5	43
C4	calculated	998	1717	10875	20	7.4	290
	measured	1165	360	2740	3.7	0.93	56

Predicted surface water concentrations are generally within one or two orders of magnitude of measured concentrations. This is not unusual when using a model such as the one used here, since the model is an extreme simplification of the real world. In addition, surface water concentrations are notoriously difficult to analyse for HOCs, due to the extremely low water solubility of the chemicals in question. In general, predictions for C4 (within a factor 8) are better than preditions for C2 (up to a factor 24 for PCB 180). This might be because the mire catchment is more uniform in terms of soil properties.

9.6.6.7   Comparison of output fluxes with soil inventory
In the case of metals, it seems that the RZ accumulates metals which originate from the mineral soil, acting as a sort of retarding medium. It is uncertain whether this is the case for HOCs.

A quick calculation comparing the amount of HOCs exported from the mineral soil in a year, to the inventories of both the mineral layer and the RZ, shows that less than 0.1% of the inventory of the mineral layer is lost through export in a year. If we assume that all this compound accumulates in the RZ, then it would add less than 0.05% to the inventory of the riparian zone. The amount lost from the riparian zone through DOC- and POC-associated export again is well below 1% of the total inventory. It is clear from the above figures that the amount of chemical lost from the soil via runoff is not sufficient to significantly change the concentration of the chemical in the soil layer within the time-frame of a year.

9.6.6.8   Enhanced contamination scenario

Using the three-phase partitioning model, total (= freely dissolved + DOC-bound + particle-bound) water concentrations (Cw(t)) are calculated for the runoff (overland flow) from sludge-treated forest soils (upper 10 cm), and compared to total water concentrations from water flowing through the riparian soil (below 10 cm).

Table 9.6-14. Cw(t) (pg/L) and export (µg) via sludged soils runoff and riparian export.

	PCB 28	PCB 180	HCB	2378TCDF	23478PCDF	OCDD
$C_{w(t)}$ (pg/L)						
Riparian soil (old water)	2.41	3.01	29.8	0.080	0.018	0.492
Sludged soil runoff	360	94.7	2325	0.139	0.050	9.58
factor	149	32	78	2	3	19
Export (µg)						
Riparian soil (old water)	34.4	42.9	425	1.14	0.264	7.03
Sludged soil runoff	1535	404	9921	0.593	0.214	40.9
factor	45	9	23	0.5	0.8	6

Table 9.6-14 shows that for most HOCs, there would be an increase in export to the stream due to runoff from sludge-treated soils. However, this is not the case for 2378TDDF and 23478PCDF. This is due to the fact that the sludge concentrations for these compounds are very low, in fact lower than soil concentrations (compare Tables 9.6-6 and 9.6-7).. The greatest difference in sludge concentrations versus soil concentrations is seen for PCB 28 and HCB. Therefore applying sludge to the forest soil would greatly increase the export of these contaminants to the stream via overland flow during high-precipitation events.

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9.7   D7: A comparison of two approaches, PHAST and WITCH, for modelling the mobilisation of metals within and from catchments.

Deliverable leader: Stephan Koehler, Graz University of Technology
Contains contributions from all PERSPEC partners

9.7.1   Introduction to the mobilisation of metals- processes

The aim of this part of the WP will be to seek minimum model complexity to run process oriented models on a landscape scale. Model complexity can vary on vastly different scales in time and space and the selection of various approaches depends on the available resolution of the data and the degree to which the exact nature of the process needs to be quantified. In this research project we chose to select two different model approaches that allow highlighting the factor model complexity. In the first part I will give a brief overview of the major processes that mobilize metals from soils and shortly present existing approaches and models with varying complexity to highlight the difference of process understanding and input data needed to run the various modelling codes.

The mobilisation of metals from soils is driven by two main fluxes: metals that originate from the fluxes of *wet and dry deposition* and those that originate from the release of metals from the *soil and bedrock*. The apparent solubility of metals is in most cases very low as they tend to strongly adsorb to clays and hydroxides, to solid organic matter and some even form stable secondary mineral phases (CotterHowells, 1996; Gaillardet et al., 2005; Stille et al., 2003; Tyler and Olsson, 2001). The transport of metals under natural conditions in soils and groundwater is controlled by the presence of organic matter, iron and manganese colloids and may also be affected by changing redox conditions. The degree to which either of these processes dominates is different for different metals. Redox sensitive metals that change speciation as a function of prevailing redox conditions include Fe (Bjorkvald et al., 2008), Mn, U, Ce, Th (Tricca et al., 2001), Se, As (Burton et al., 2008), Hg and Cr while other elements such as Pb, Cd, Zn, Ba, Ni or Al are stable. The transport of these latter metals may however still be affected by the prevailing redox condition as that the redox value or pe has a strong influence on the presence or absence of iron, manganese or organic carbon colloids that are known to act as carriers for most metals (Benedetti et al., 1996; Dia et al., 2000; Weng et al., 2002; Johannesson et al., 2004; Pourret et al., 2007; Quinn et al., 2006; Sherman et al., 2008; Sonke, 2006; Tang and Johannesson, 2003; Tipping, 2005).

In systems with comparably low pH and reductive environments such as those studied here, the relative importance of organic matter is more pronounced than in systems that are oxidative and have higher pH (Pokrovsky and Schott, 2002). Very useful models that treat only so called batch systems allow estimating the importance of single chemical factors such as the concentration of organic matter on the speciation of metals. The more elaborated examples for mixed metal-organic acid solutions are WHAM ((Tipping, 1994)) and NICCA-DONNAN (Milne et al., 2003) and PHREEQC (Parkhurst, 1998).The successful modelling of transport of metals is thus depending to a large extent on the flux of organic matter from the soils to the streams. Naturally metals may be released from geogene sources through the disintegration of metal bearing minerals in the bedrock and subsequent soil formation. Especially for the release of trace metals such as lead or rare earth elements a quantitative understanding of the kinetics of the dissolution process is necessary (Guidry and Mackenzie, 2003; Harlavan and Yigal, 2002; Köhler et al., 2005; Öhlander et al., 1996). The following sketch (Fig. 1) describes an example of a series of interactions of chemical reactions that participate in controlling the mobility of Rare Earth Elements (REE) in soils. Similar series of reactions can be made up for other trace compounds such as lead (Pb), cadmium (Cd) or zinc (Zn).
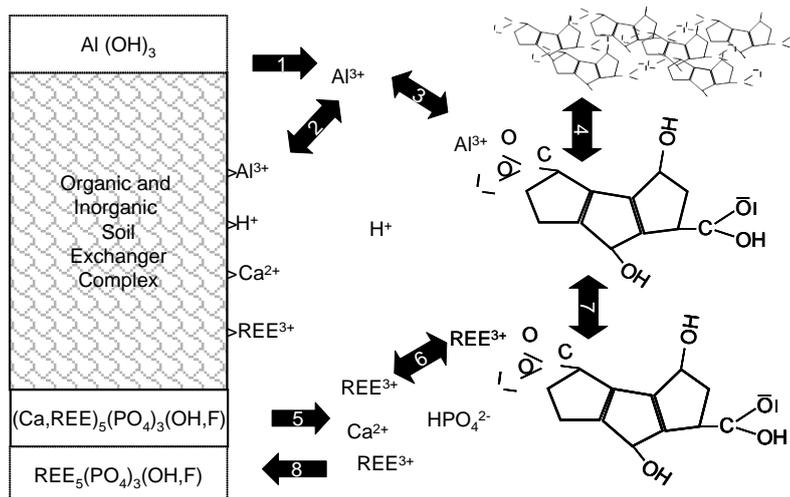
Figure 9.7-1. Example of a series of interactions of chemical reactions that participate in controlling the mobility of elements in soils. 1: Dissolution of aluminium bearing phase and release of Al^{3+} 2: Exchange equilibrium with the soil exchanger complex of soil water cations and Al^{3+} 3: Equilibrium with dissolved soil organic matter (SOM) and Al^{3+} 4: Precipitation of aluminium bearing SOM and Al^{3+} 5: Dissolution of trace mineral and liberation of rare earth elements (REE) 6: Equilibrium with dissolved soil organic matter (SOM) and REE 7: Competition reaction of REE with Al^{3+} 8: Precipitation of secondary trace element enriched mineral phase.

On the left side of figure 1, one potential phase boundary, that of the hypothetical mineral assemblage apatite, gibbsite, REE-phosphate and solid organic matter, is displayed. In this microcosm, and setting aside any concurrent biological reactions for the moment, eight reactions may occur simultaneously.

9.7.2   Short overview of modelling concepts

9.7.2.1   The catchment approach

The quantitative mobilisation of cations and anions from soils to the streams and lakes further downstream have been modelled since the 1980s. Especially during the most intensive phase of the acid rain studies in the 1990s a larger number of dynamic or static biogeochemical models were developed (Cosby et al., 1995; Warfvinge and Sverdrup, 1992) and applied to different sites (Sverdrup et al., 1995b) (Sverdrup et al., 1995c) (Jonsson et al., 1995) (Kram et al., 2001) (Malek et al., 2005) (Laudon et al., 2005) (Erlandsson et al., 2008). Two classic models in this context are the MAGIC (Cosby et al., 1995) and PROFILE (Warfvinge and Sverdrup, 1992) model that allow to calculate the geochemical reactions in soil profiles as a result of varying deposition and plant growth. These models quantify the reactions occurring during the transfer of rainwater through the soil complex into the stream and incorporate to a varying degree of complexity a number of soil chemical and biological reactions as a function of time and water flux between different soil horizons. From a soil chemical and biological viewpoint most models incorporate deposition, ion-exchange, cation uptake by plants, and weathering reactions. The complexity of the models differs as a function of their purpose, aim of process understanding and their spatial and temporal resolution and whether they consider stead-state or dynamic processes. In earlier years the models that were originally developed with the aim of specifically describing the flux of elements through the soil compartment and a large effort was put into describing the element fluxes within different soil compartments. A general equation of the different net element fluxes (Ni) incorporates in general the following separate fluxes:

$$N_i = W_i + P_i + A_i - R_i - M_i - B_i - S_i \qquad \text{(eq.1)}$$

With N_i = Net accumulation or depletion, W_i = weathering , D_i = deposition A_i = anthropogenic input, R_i = chemical erosion, M_i = mechanical erosion, B_i = biomass uptake and S_i = storage in the watershed.

Most of these fluxes are relatively easy to measure within a given landscape system.
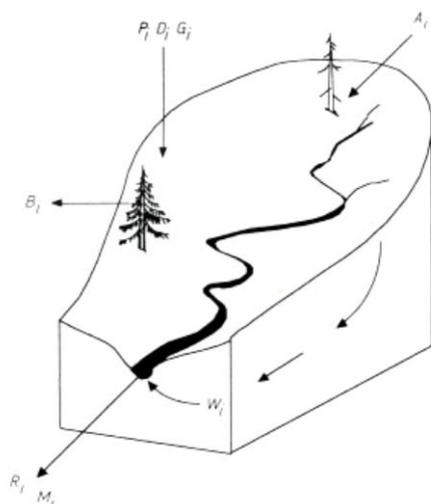
Figure 9.7-2. Simplified sketch of the catchment approach that takes into account a number of element fluxes at the boundary of soil-air and soil-water to estimate the areal output of elements from a known and well delimited surface.
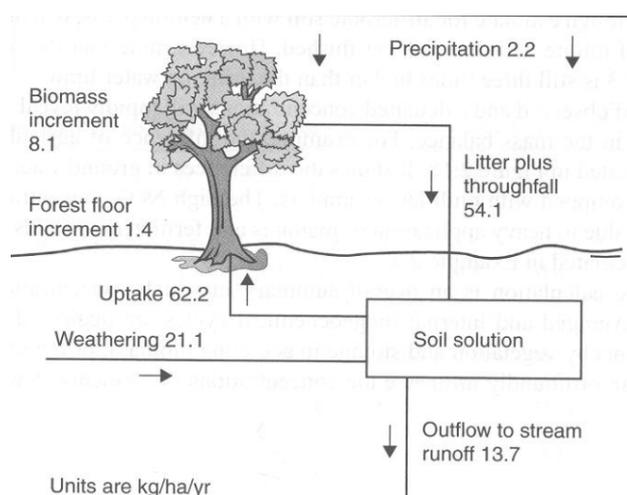

Figure 9.7-3. Example of different element fluxes from plant, air and soil compartments in the Hubbard Brook watershed.

A much smaller number of models also incorporate biological feedback mechanisms such as the build-up and degradation of living and dead organic matter as a function of nutrient availability SAFE (Sverdrup et al., 1995a) and climatic soil variables. Fully dynamic models also allow for feedback mechanisms between the geochemical cycling of various elements as in the WITCH (Godderis et al., 2006) model, between carbon and nitrogen (Svensson et al., 2008) or even between the water regime, temperature and plant growth as is the case in PnET-BGC/CHESS (Kram et al., 1999). In these models separate processes control the build-up and breakdown of dead and living organic matter in different compartments of the soil. In these models the energy and mass transfer is fully coupled and separate equations for the heat and water transport as a function of the state of the soil, i.e. temporary water content and allow driving the model with simple climate variable such as temporal variations in air temperature, radiation and precipitation. Another large difference exists between the various spatial resolutions that are used. One distinguishes 1-D, 2-D or 3-D models with ideally mixed boxes or partially mixed boxes from 1-D, 2-D or 3-D that consist of finite elements (Fig. 4).
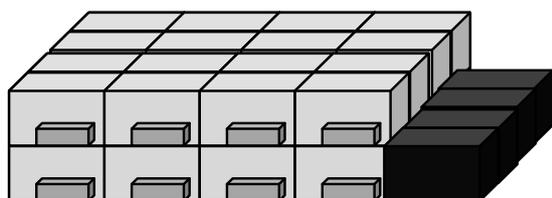
Figure 9.7-4. Example of a finite element based model that includes a large number of boxes in which separate reactions occur and between which water is moving to the stream from left to right.
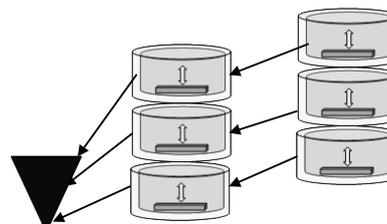
Figure 9.7-5. Example of a box based approach that includes a smaller number of boxes in which separate reactions occur and between which water is moving to the stream from right to left.

A final distinction may be made between those models that allow the user to enter for example a larger number of chemical or biological reactions or select the mode of water flow and water uptake and those models that are rigid in their model structure. These latter approaches only allow for changing the values of certain driving variables while the former may be applied at different levels of sophistication. The advantage in this approach lies on the possibility of excluding processes that are not known, very difficult to calibrate or apparently not important for the specified flux of a specific element. This difference is a key factor that needs to be considered when choosing various models.

9.7.2.2   Riparian zones as chemical buffer

In the context of this project we want to test whether the use of two different approaches for modelling soil chemical reactions coupled to water flux may be used to quantify the importance of the riparian zone as a chemical buffer for trace metals. An analogue can be the study of a soil profile or a 2-dimensional transect in the flow-line of a water molecule from the soil to the stream. In this type of a setup one samples the soil

water composition using soil lysimeters over time during and after rain events or during and after dry periods to study how the soil solutions responds to a physical or chemical perturbation. This type of setup will help to establish mass balances for elements and weathering. A transect that is displayed below was established in 1995 and has been sampled since.
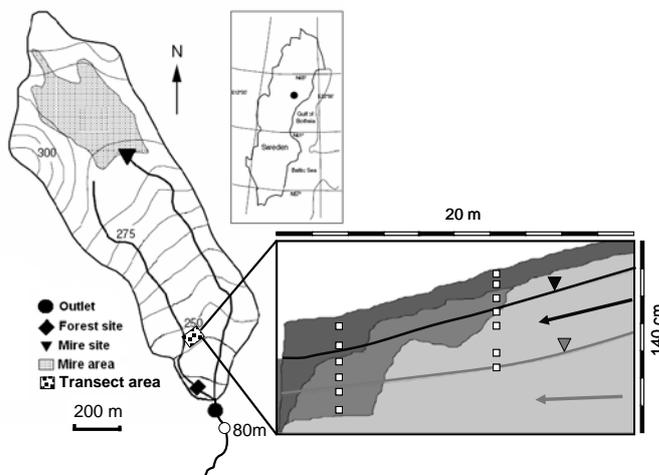

Figure 9.7-6. Location of a catchment within Sweden and map with indication of a transect area and sampling sites The inlet displays the transect section, lowest (grey line) and highest groundwater level (black line), sampling depths and location of the soil lysimeters in S4 and S12 at 4 and 12m from the stream (□) while the site S22 further up at 22m is not displayed. The dark grey, grey and light grey areas display the extent of peat, organic soil and mineral soil respectively and the arrows indicate the flow of soil water to the stream channel displayed to the left of the inlet.

9.7.2.3   Modelling the flux of Organic Carbon

The quantification of export of organic matter from catchments is one of the key parameters for describing the export of metals but also control other biogeochemical reactions in the soil. Changes in DOC concentrations in surface water as those observed in recent years (Monteith et al., 2007; Worrall and Burt, 2004) may have profound consequences on the surface water biota in streams and lakes. For this purpose various codes that model the temporal variation of TOC in streams shave been developed in recent years. The biogeochemical model CHUM (Tipping, 1996)is using WHAM as a subroutine to calculate the speciation of soil solutions before performing the transport calculations. This model was used successfully to model the export of metals from catchments in England (Tipping et al., 2005; Tipping et al., 2006). Despite a large number of calibration parameters this model approach is very promising. The dynamics of organic carbon is modelled in higher detailed in Dy-DOC (Michalzik et al., 2003) which is a dynamic model describing the C fixation reactions occurring within soil plots. A simpler model that was developed to describe TOC dynamics on a landscape scale is INCA-C (Futter et al., 2007). This model describes the variation of stream water TOC with a coupled hydrological and simplified biochemical approach. The large advantage of this model is the easy implementation even in larger landscapes and the small amount to calibration parameters. We are currently also working with developing a model that produces the temporal variation of stream water TOC using a convolution model and regression model approach that are shortly presented below.

9.7.3   Comparison WITCH and PHAST

9.7.3.1   The witch model

The WITCH code is a geochemical model that allows calculating soil solution composition and mass balance calculations of elements in different soil compartments based on a series of parallel reactions of dissolution, plant uptake and precipitation. The code is originally driven by an external climate model (ASPECTS) that produces the necessary flux data for water moving between compartments, flux of elements between the soil and the plant and state variables such as pCO_2, water content and temperature. The model may also be run separately if this necessary data is provided either via measurements or other codes. The geochemical part of the model that describes the dissolution kinetics and ion-exchange

reactions relies on thermodynamically mineralogical data and experimental data on the dissolution kinetics of different soil minerals.
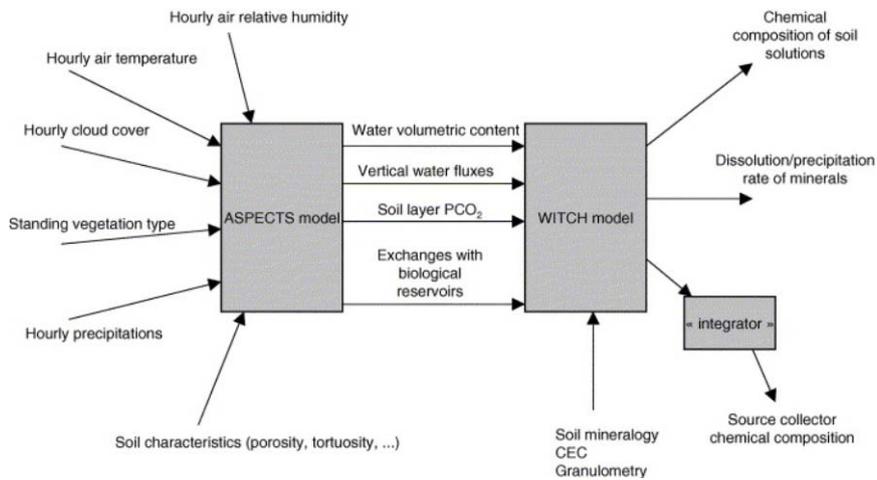

Figure 9.7-7. Model structure of the WITCH model (GODDERIS et al., 2006)

This code is a boxed-type model and requires the user to define the dimensions of different boxes within the model that may be ascribed to known parts of the area to be modelled such as characteristic soil layers or source areas such as upslope recharge or downslope discharge areas. In the case of the study of riparian soils we chose to represent the riparian soil into two compartments, one representative of the upslope Podsol type area and another representative of the downslope organic peat rich area. The water is routed through the different layers allowing water to enter the middle layer in situations of high flow as is shown below.
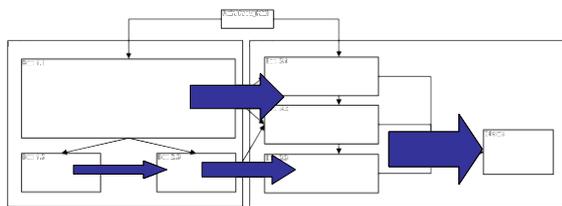

Figure 9.7-8. Sketch of the proposed box-model with the stream box to the right and two compartments to the left that represent an upslope and a downslope soil.
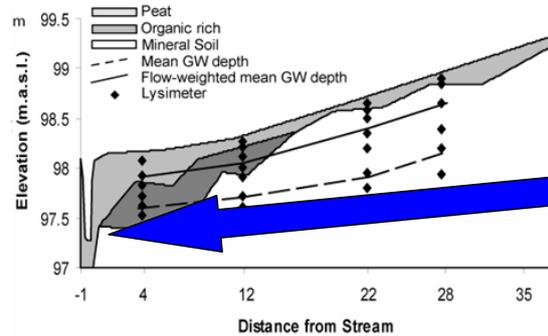

Figure 9.7-9. Sketch of the studied transect and sampling sites at various depths. Left incision is the stream channel and water moves from upslope right to downslide left.

9.7.3.1.1 Necessary input data

A large amount of time was invested in assembling the necessary input data for both model approaches. The necessary data are discussed in the following sections.

9.7.3.1.1.1 Characterising the soil

Basic soil physical parameters include the porosity and soil depth in the different boxes. All of this information is available from earlier measurements. For the WITCH approach it is necessary to estimate average values that are representative of the chosen sub-compartments presented above. These compartments are not physical entities but represent the average value of the zones that are included in respective box.

9.7.3.1.1.2 Modelling the water flux in the soil

For the modelling of the water fluxes it is necessary to estimate the incoming and outgoing water fluxes from each compartment.

Table 9.7-1.

Parameter name	IN	IN	OUT	OUT
Water content	-	-	-	-
Water flux	vertical	horizontal	vertical	Horizontal
Units	[mm]	[mm]	[mm]	[mm]

9.7.3.1.1.3 Modelling the reactions in the soil

A general equation for the net reaction of a dissolving mineral can take the following form:

$$r_{net} = k_+ s\, f_{(j,k,l)}\, e^{-\frac{EA}{RT}} \left(1 - e^{-\frac{A}{RT}}\right) \qquad \text{(eq.2)}$$

This rate equation is composed of five terms which are related to (1) an intrinsic mineral specific constant k_+ that may be related to the type and structure of the mineral, (2) the reactive surface area s where the breaking of the bonds at steady-state occur, (3) an interaction term $f_{(j,k,l)}$ that describes possible chemical reactions of the solutes with the mineral surface such as adsorption or ion-exchange here exemplified for three potential interactions j, k and l, (4) a term that accounts for the change of rate with temperature due to a mechanism specific activation energy and (5) a term that quantifies the distance to chemical equilibrium. When the factor (5) in eq. 3 is close to 1 these rates are called "far from equilibrium rates".

The dissolution kinetics of minerals depends on the amount of exposed reactive surface area (s). In reality reactive surface area is determined by factors such as crystal morphology and the relative percentage of exposed crystallographic surfaces that usually vary in reactivity. In practice this reactive surface area is often very difficult to quantify and as a convention often geometric or surface areas from gas adsorption experiments using the method of Brunauer, Emmett and Teller (BET) are used for this purpose. Surface areas may be either obtained from inert gas adsorption onto known amounts of solid or estimated from geometric considerations on size and geometry of the average particle. All kinetic parameters in equation 2 are available in the WITCH database and there is no need to recalibrate those factors.

Table 9.7-2.

Parameter name	Mineral type	Mineral abundance	Surface area
Unit	[ ]	[Vol %]	[$m^2\ g^{-1}$]

In the witch code ion exchange reactions is modelled using the Gapon approach that follows the following mathematical relationship:

$$K_G = \frac{(Ca_{1/2}-x)\ (Na^+)}{(Ca^{2+})^{1/2}\ (Na-x)} \qquad \text{(eq. 3)}$$

Where Me-X is the fraction of metal (M) bound to a hypothetical soil surface (X) and $(M_i)^{1/i}$ the activity in the free solution.

Table 9.7-3.

Parameter name	Cation enhance capacity	Gappon coefficient
Unit	[meq g^{-1}]	[ ]

The data for the various Gappon coefficents were taken from the calibration made at another site.

Plant uptake in the various boxes needs to be quantified for each cation in each layer as a function of time. A reasonably good data set is available from an inventory made in the 1980s.

Table 9.7-4.

Parameter name	Cation uptake
Unit	[meq day^{-1}]

The concentration of organic carbon in the WITCH model is not modelled but needs to be specified by the user. This is a strong weakness of the program in areas where organic matter plays a key role in transporting metals as is the case of our study.

9.7.3.2   The PHAST model

When working on a landscape scale with varying vegetation, bedrock and hydrogeology multibox models such as PHAST that have a built-in chemical programming functions (i.e. PHREEQC (Parkhurst, 1998) are more flexible. They allow hydrology to be connected to both thermodynamic and empirical kinetic rate laws (non-equilibrium). This permits a more flexible model structure and varying depth in model complexity. In the Krycklan sites, the release of many trace metals is like that of dissolved organic carbon (DOC) driven by hydrological events (Bishop et al., 2004) (Laudon et al., 2004) (Köhler et al., 2008). These dynamics have been studied in depth during the last years.
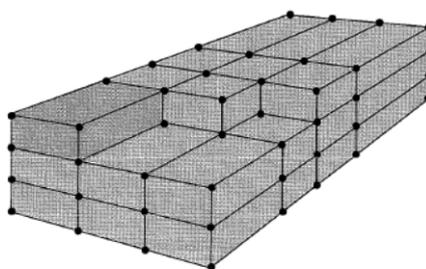

Figure 9.7-10. Grid base of the PHAST program.

The PHAST codes is a grid based program that uses a finite element approach. The basic principles include a conservation of extensive variables in an open system including mass, solute mass, solute moles, electrons, redox state, mechanisms of transport for Flow in porous media including advection-dispersion and diffusion. Reactions include mass action equilibrium and kinetically driven reactions. The code can be run in four modes: steady-state ground-water flow, transient ground-water flow, steady-state ground-water flow and transient reactive transport or transient ground-water flow and transient reactive transport. The model needs to be defined up by the user and this also includes the definition of the geometry of the systems and associated parameters of the aquifer.

Table 9.7-5.

Parameter name	Porosity	Kf sat.	Thickness
unit	[]	[m s^{-1}]	[m]

As discussed in previous parts of this report the hydrological processes in the riparian zone exert a large control on the stream water chemistry. It is of uttermost importance that the model can reproduce the observed groundwater fluctuations as the chemical signature between soil horizons only 20 cm apart differ drastically. Initially the catchment needed to be downscaled to a manageable transect. Using the available information on the catchment area (13ha), catchment boundaries (ca 100m to the right water divide) and the transect data (sampling at 4, 12 and 22m from the stream) we downscaled it to a 70m*2m*5m box.
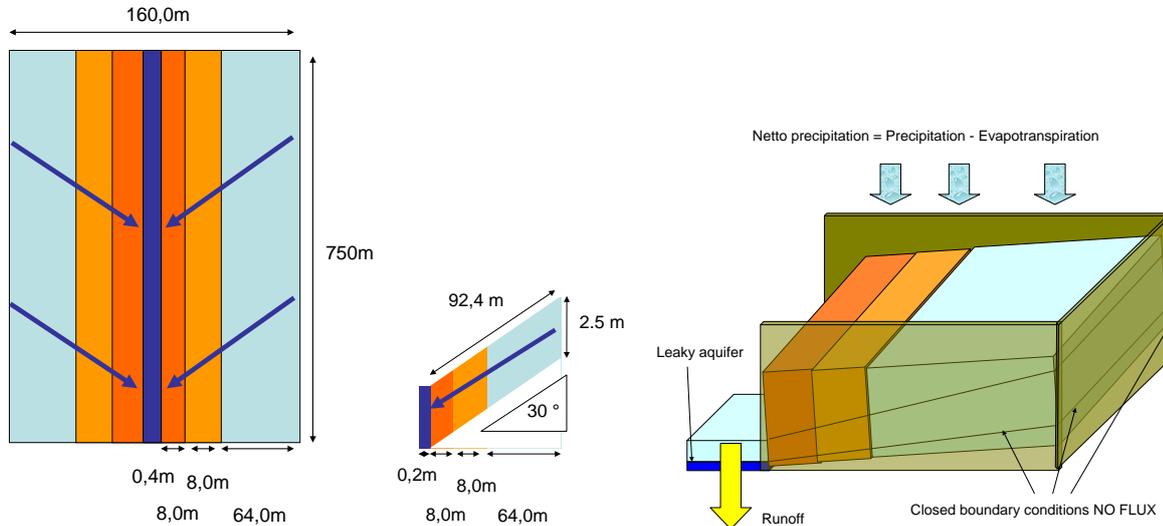

Figure 9.7-11. Downscaling of the catchment presented in Fig. 6. from left to right: scaling to a rectangular, extraction of a flow line and identification of the flow barriers to the right.

9.7.4 Analysis, Calibration, Evaluation, Modelling enhances scenarios and Improvement of Models

When trying to reproduce the chemical signature of the stream it is necessary to identify a) critical meteorological driving parameters, b) key variables such as DOC, pH and capacity terms such as ion-exchange, and c) important thermodynamic or kinetic reactions. Potential chemical reactions that have been identified are ion-exchange, dissolution kinetics, equilibrium precipitation, precipitation or organic matter. Input data that has already been presented in the WITCH section and is therefore not be repeated here.

9.7.4.1 Analysis: example Al and Pb mobilisation

As explained in detail in a section above, organic matter is a key factor for describing the mobilisation of metals in the study catchment. The correlation between stream water Al and stream water TOC and stream water lead and stream water TOC respectively and the temporal variation of all three parameters is shown below.
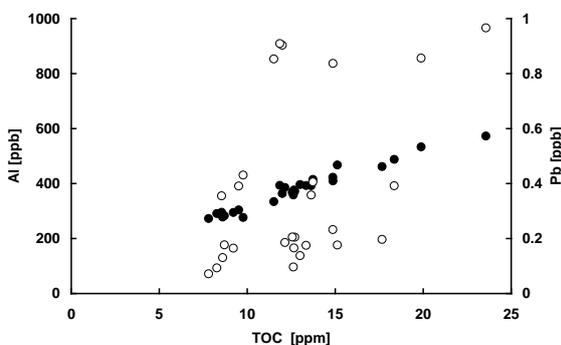

Figure 9.7-12. Temporal variation of Al [ppb] ●, TOC [ppm], Pb ○ [ppb] and flow Q ♦ [mm] during 2003.
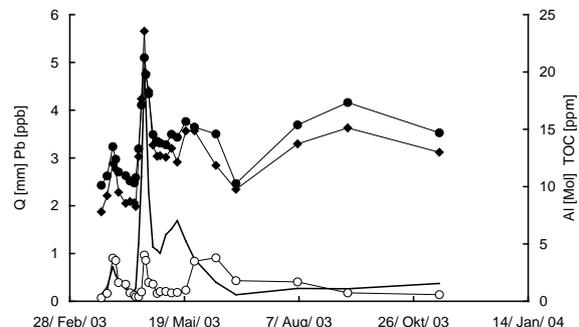
Figure 9.7-13. Correlation of stream concentrations of TOC and aluminium ● [Al] and lead ○ [Pb]

9.7.4.2   Modelling TOC and modelling the TOC using only flow

From the previous section it is evident that a quantitative modelling of the organic carbon concentration in the stream is a prerequisite to understand the dynamics of aluminium and partly even those of lead. This is why we have chosen to analyze our soil and stream data to put together a simple model that would reproduce the temporal variation of stream water TOC using available meteorological data such as air temperature and water flow. Both of these factors are major driving variables in the WITCH and the PHAST model.

9.7.4.2.1 The Regression Model

Temperature and runoff are known to be related to stream TOC concentrations. One key observation made in a recent study of this catchment (Köhler et al., 2008) was the appearance of significant inter-annual patterns in TOC concentration related to soil temperature, although this became clear only after distinguishing wet from dry years. Only during the wet years when sufficient rainwater has been stored in the soil groundwater levels are constantly higher and rain or melt water flows through the organic rich topsoils that show the highest soil solution TOC in response to variations in soil temperature. Measured groundwater levels in the riparian soil are proportional to the logarithm of Q (Bishop et al., 2004) and, thus this parameter was included as a proxy for groundwater levels. To summarize the three parameters T_{soil}, Q and lnQ were chosen as potential variables for predicting instantaneous stream TOC [mg/l] using a multi-linear relationship (Eq. 1). TOC_0 [mg/l] is the base TOC concentration, T_{soil} [°C] is the modelled soil temperature calculated from daily air temperature as described in (Köhler et al., 2008) and calibrated as described in that study to reproduce the measured temperatures at a depth of 30cm in a soil profile 4m from the stream and Q [mm/d] is the specific runoff measured at the outlet of the Nyänget catchment.

$$TOC(t) = TOC_{(0)} + aT_{soil}(t) + bQ(t) + c\ln\left(Q_{(ti)}\right) \qquad\qquad (eq.4)$$

While daily soil temperature fluctuations are always below 0.6°C (Köhler et al., 2008), large changes in Q may occur within hours of a rainfall or snowmelt event. The wetting of soil and subsequent release of TOC might be lagged in time. This is why we systematically tested whether a lagged signal in ln(Q) could improve the fit between modelled and measured stream water TOC. Also, in an effort to minimize the number of parameters, we tested whether the omission of different terms of equation 1 would significantly affect the model estimates. While the fitting factor c in equation 1 does show a systematic pattern throughout the year, no attempt was made to model the months separately. In this way the numbers of adjustable model parameters were limited to 4. This approach will be referred to as regression model in the following.

9.7.4.2.2 Convolution model

As an alternative to the statistical approach of a regression analysis of the data (Regression Model) we tested a convolution model where stream TOC was computed as a flow-weighted mean of the average observed $TOC_{(j)}$ [mg/l] at various soil depths (j) in the riparian soil based on the concept presented by (Bishop et al., 2004). We used the flow-groundwater depth relationship established for the hillslope (e.g. (Bishop and Dambrine, 1995); (Nyberg et al., 2001), (Laudon et al., 2004)) to calculate the amount of water that flows laterally through each layer of the riparian zone, q_j [mm/d], and then computed the flow-weighted means (eq. 2):

$$TOC_{(t)} = \frac{\sum_{i=0}^{100cm} TOC_j * q_j(t)}{Q_{tot}(t)} \qquad\qquad (eq.5)$$

The spatial resolution for the computations in eq. 2 was set to 5cm. This is half the spatial resolution that is available for the soil TOC data, which were sampled every 10cm. Consequently average values for TOC between the sampled depths were calculated to attain a 5 cm resolution. Below the deepest lysimeter that was used for soil solution TOC sampling (65cm) we assumed average TOC values of 6, 3 and 2 mg/l at -75 , -85 and -95cm depth respectively following the observed decrease of TOC with depth from the layers above. In the following this model is referred to as the convolution model.
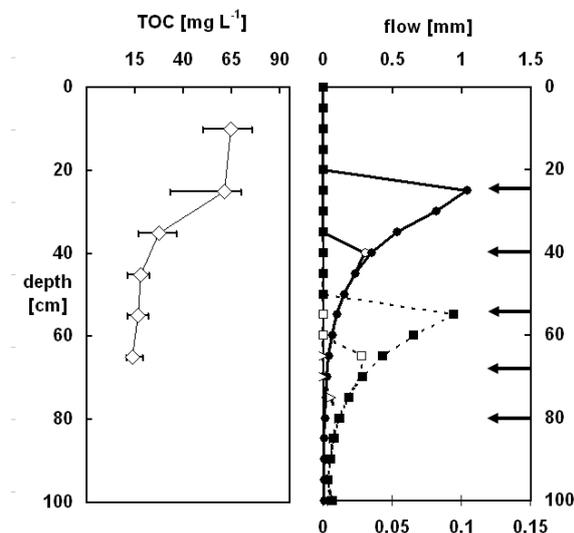

Figure 9.7-14. **Left**: Measured average TOC concentration and variation in the soil solutions during 1996-2004 as a function of depth in the riparian soil (upper and lower 90 and 10% percentile). **Right**: Distribution of water flux at various soil levels in the riparian soil at 5 different flow scenarios Q5 (white triangles, lower scale), Q25 (white squares, lower scale) Q50 (black squares, lower scale) Q75 (white circles, upper scale) and Q95 (black circles, upper scale) that refer to the text. The groundwater depth of the highest flux at each situation is highlighted with an arrow.
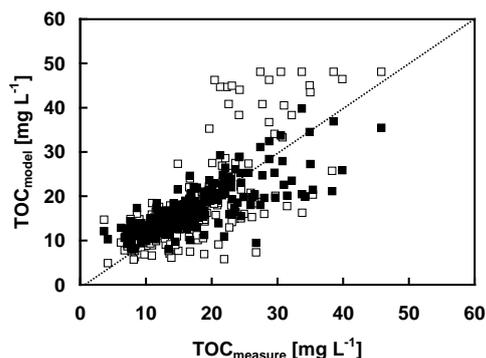
Figure 9.7-15. Comparison between instantaneous measured and instantaneous modelled TOC using model I (black diamonds) and model I (white diamonds) during season 3.

Especially the regression model reproduces the temporal variation of stream water TOC and may be implemented into the PHAST and WITCH model. An evaluation of the performance during dry and wet years is displayed in the attachment.

9.7.4.3   Calibration
During the calibration phase of the models certain mineralogical and geochemical parameters needed to be identified.

9.7.4.3.1 Solubility of minerals for both approaches.

From the mineralogical analysis we have identified the key minerals hornblende, plagioclase and k-feldspar that should contribute as major phases to the element fluxes of the major rock forming cations Ca, Na, K and Si. The soil chemical data available were used to compute saturation indices for a series of major rock forming minerals to test which mineral phases may be assumed to be in equilibrium and which change over time. This allows excluding a series of minerals in the precipitation routine and speeds up the computation time
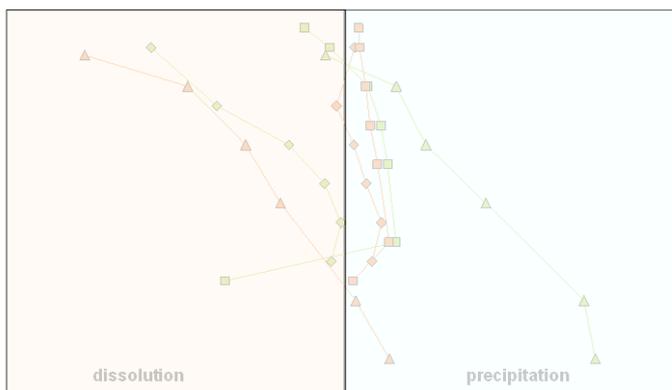
Figure 9.7-16Saturation index for proto-imogolite and ferrihydrate (diamonds refer to the soil plots S4, squares to S12 and triangles to S22).

9.7.4.3.2 Speciation of aluminium

For the element Al that was identified as a component that should be modelled initially we made a large number of calculations and retreated some field data to determine which processes control the solubility and mobility of this cation. Later this approach may be used for other metals too.
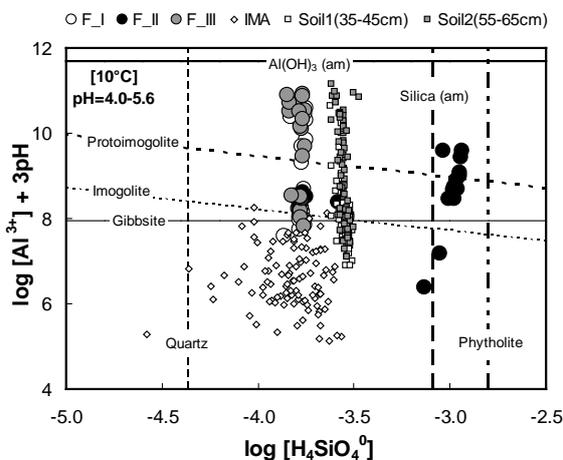

Figure 9.7-17. Log stability diagram with the stability fields of the major aluminium and silicate inorganic solid phases present in soils and that of phytolithe. The white, grey and black circles represent the calculated positions using the calibrated version of WHAM VI of the first, second and third instream manipulation experiment respectively. The soil solution data have been split into two depth groups, 35-45cm (□) and 55-65cm ( ). The remaining symbols (◊) display the long term IMA data of the stream outlet site.
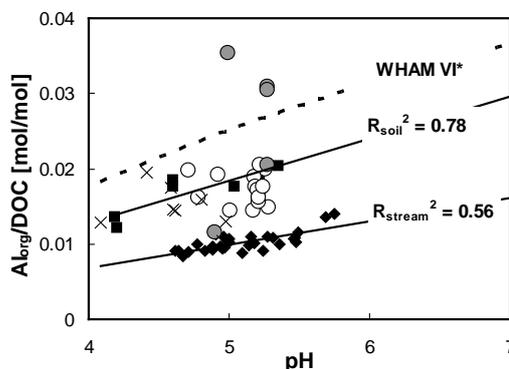
Figure 9.7-18. Fraction of organic Al per DOC as a function of pH for the available soil solution data ( ), the samples taken at the forest site ( ), those from the first ( ) and third ( ) manipulation experiment and the data from the Hubbard brook research site ( ). The hyphenated line displays the average modelled fraction of organically bound aluminium per TOC using the calibrated version of WHAM VI at a constant Al/TOC ratio of Al/TOC = 0.035 observed in the soil solution data.

Our calculations indicate that Al in the soil and stream is controlled by organic matter and confirms what was reported earlier. These findings also strengthen our decision to identify models that may explain temporal variations of stream water TOC. In the following we also identified a new useful capacity term, $Ba-Cl_2$ extractable Al, for describing the control of Al in the soil water.

9.7.4.3.4 Water flux in the PHAST code.

A large number of groundwater-discharge measurements and a good set of soil physical data permitted to establish a transect with a set of physical parameters close to those measured in the field. The result of an intensive calibration exercise resulted in a representation of the transect as displayed below (Fig. 19). This figure that displays the real geometry of the transect and the highest and lowest GW level together with the modelled variations of a stead state GW level as a function of varying precipitation input is displayed below.
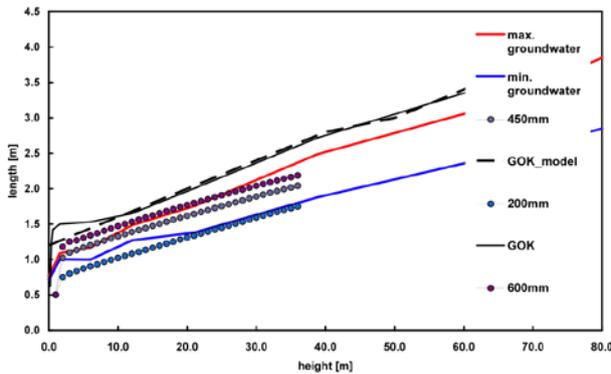

Figure 9.7-19. Comparison between measured and modelled groundwater distance at three different steady-state rainfall scenarios.
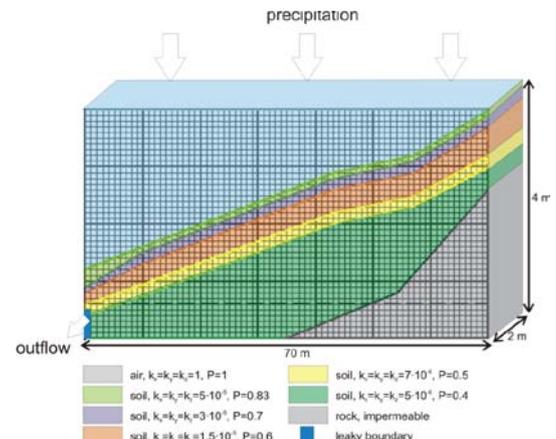

Figure 9.7-20. Representation of the idealized model in PHAST with the topographic height (line below the light blue area), the stream (dark blue) and several layers of varying hydraulic conductivity (green, violet, orange, yellow and green and bedrock in grey.

9.7.4.3.5 Temperature and water flux in the WITCH approach

9.7.4.3.5.1 Continuous soil temperature data

One key input parameter in both models is the soil temperature. Measured soil temperature was available during parts of the measurement period but not continuously. In order to establish full time series of soil temperature at all depths and all sites (n=15) we established a procedure how to calculate soil temperature from air temperature using measured air temperature that is available since 1981. This method allows us to extrapolate our modelling regime even outside the measurement period between 1995-2007 back in time.
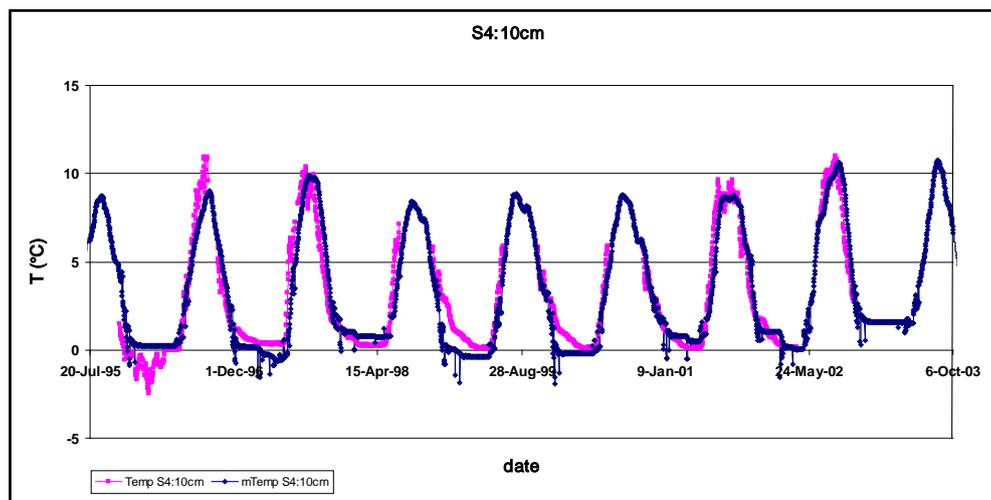

Figure 9.7-21. Modelled temperature and measure temperature for S4 in 10cm depth (January 1995 to October 2003)

<u>9.7.4.3.5.2 Continuous water content</u>

In the WITCH approach continuous data on the flux of water and respective water content is a needed input data. Available data for calibrating these values are the measured and modelled groundwater depth in the riparian soils and the measured water content at different depths within the different layers of the soils. In the PHAST approach no function for evaporation is included which necessities transforming precipitation data into potential runoff. For this purpose we used a conceptual runoff model, namely the HBV model (Bergström, 1976, {Lindström, 1997 #2842}) similar to the approach presented by (Lindstrom et al., 2002). In the HBV model simple routines, such as the degree-day equation for snow melt, are used to simulate runoff on a daily time step. Descriptions of the model can be found, for instance, in (Bergström, 1992a; e.g. Bergström, 1992b; Lindström et al., 1997; Seibert, 1997) ..Before simulation of runoff for changed conditions the HBV model was calibrated for current conditions. A Monte Carlo approach was used where the 100 best parameter sets, according the model efficiency (Nash and Sutcliffe, 1970) , were selected from 1 000 000 model runs with randomly generated parameter values. More details of the procedure can be found in (Seibert, 2002). This model routes the rain water or melt water that is produced with a melting function through two soil layers to reproduce measured runoff. The water content in the soil may be compared to the measured water content to verify the data as shown below.
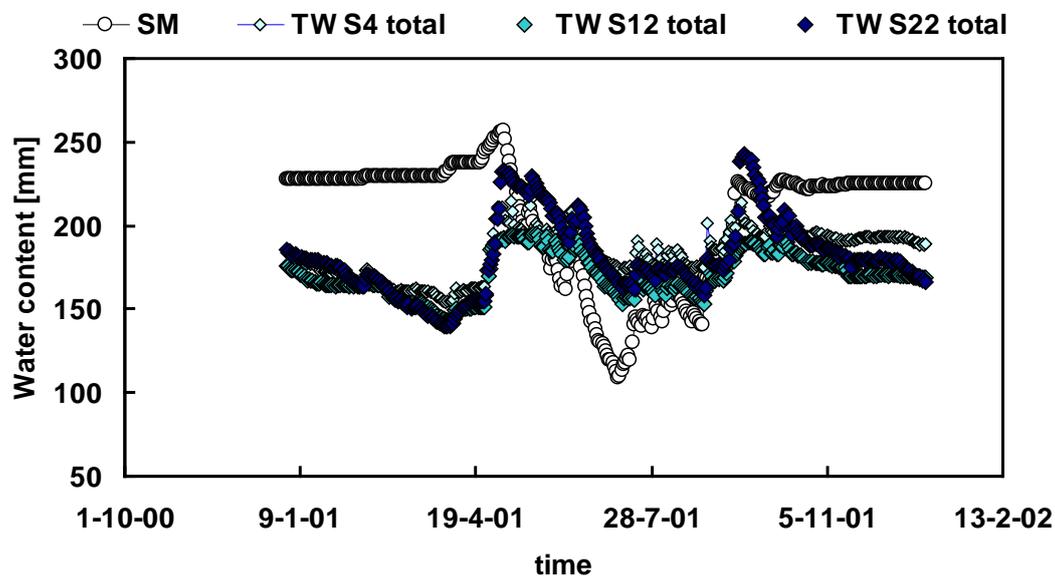

Figure 9.7-22. Comparison of the total modelled water content in the soil using HBV and that calculated from the soil moisture measurements at the three sites S4, S12 and S22 in mm water column

While the general behaviour of the modelled water content is in accordance during large part of the year, there is a need for refining or correcting the modelled values before the PHAST and WITCH model can be run.

9.7.5   Other approaches

In many areas of Europe with warmer climate other model approaches that include the soil compartment where unsaturated flow occurs need to be incorporated. There is a large number of available programs on the market some of which are free of access others commercial programs. The program MIN3P has been used in several studies (Mayer et al., 2002) This code models reactive transport in variably saturated media and includes a large number of features for the inclusion of chemical interactions with the solid phase such as surface speciation, ion-exchange, gas-phase equilibrium and redox reactions. Both kinetic reactions and equilibrium with non-aqueous phase liquids (NAPLs) and diffusive transport in the gas-phase may be incorporated. This model was recently applied to model the redox reactions occurring during the transport of redox active substance in groundwater (Amos et al., 2004).

The model HP1 which is a coupled model between Hydrus and PHREEQC is also a good candidate for modelling geochemical reactions in soils. The HYDRUS program is a finite element model for simulating the two- and three-dimensional movement of water, heat, and multiple solutes in variably saturated media. It

includes the possibility to include plant-soil interactions. Physical non-equilibrium solute transport can be accounted for by assuming a two-region, dual porosity type formulation which partition the liquid phase into mobile and immobile regions. It is also possible to simulate the transport of viruses, colloids, and/or bacteria. The model allows for a very flexible definition of flow pathways and heterogeneity of the soil compartments. The program also allows optimization of parameters from measured field observations using a technique for inverse estimation and a statistical analysis of the parameter uncertainty. Recently a new module simulating the biochemical transformation and degradation processes in subsurface-flow constructed wetlands was developed for two-dimensional applications of HYDRUS (Simunek et al., 2008). This module considers the biochemical degradation and transformation processes for three fractions of organic matter (readily- and slowly-biodegradable, and inert), four nitrogen compounds (ammonium, nitrite, nitrate, and dinitrogen), inorganic phosphorus, and heterotrophic and autotrophic micro-organisms, and dissolved oxygen. This model has now been enlarged to also include 2-D and 3-D scenarios and is commercially available at: http://www.pc-progress.cz/Fr_Hydrus.htm.

Finally another physically based model for the transport of water through the saturated and unsaturated zone is the model COUP. This model has been developed with the aim to be able to model the physical and biological reactions within a soil profile. The model simulates soil water and heat processes in many types of soils; bare soils or soils covered by vegetation. The basic structure of the model is a depth profile of the soil. Processes such as snow-melt, interception of precipitation and evapotranspiration are examples of important interfaces between soil and atmosphere. Two coupled differential equations for water and heat flow represent the central part of the model. These equations are solved with an explicit numerical method. This model has been recently applied to model the C and N dynamics is a northern forest (Svensson et al., 2008) and this model software available for free at: http://www.lwr.kth.se/vara%20datorprogram/CoupModel/index.htm. Chemical reactions may be implemented using a submodel of Minteq (Allison et al., 1991) that is now limited to 20 different elements or more specialised models such as Tracey (Gärdenäs et al., 2008) when radionuclides are concerned.

9.7.6   Summary, advantages and disadvantages in the two approaches presented here and outlook

The presented convolution and regression models may be used to estimate the fluxes of elements that are bound very strongly to organic matter such as Al and Hg. The implementation of an empiric equation into the PHAST code is a logical next step in this process. From there on different hypotheses about different pools of organic carbon in the soil may be tested against measured data.

The chosen approach has a certain number of advantages and disadvantages. One large disadvantage is the necessity of supplying a large number of calibration data for driving the major physical processes in the soil such as the water content, the water fluxes and the changes in temperature and pCO_2. In fully coupled models these parameters are derived through physical laws such as heat and mass transfer and specialised functions that drive the activity of the soil biota. Nevertheless many of the parameters necessary to calibrate such coupled models are not available at the spatial and temporal resolution needed to drive complete biogeochemical reactions in a hillslope. While much progress has been made in recent years to include detailed speciation of metals including the surface complexation to oxides and hydroxides the exact nature of many processes are not known. Again all those features require large calibration data sets that are metal specific. The inclusion of all of these options sharply increases computation time and data handling of variables. The advantage of using the coupled PHAST-PHREEQC approach is that all of the above named processes may be included stepwise into the PHAST code if the data reveal that the existing functionality does not reproduce the measured data. The possibility of explicitly including isotopes such lead (^{204}Pb), sulphur (^{34}S), carbon (^{13}C) or oxygen (^{18}O) into the PHREEQC part of the model allows calibrating the model data with the available data. None of the other models discussed in section 5 allow this option. Especially in the selected riparian zone where the flow situation differs largely from that of a simple soil profile, a number of simplifications allow to focus the most important transport phenomena. This approach allows testing different hypothesis about the major control of mobilisation of metals from different types of catchments. Setting up well defined hillslopes and riparian zones is straightforward in PHAST which makes the tool useful and user-friendly for judging the effect of land use, vegetation and climate change on the mobilisation of metals.

9.7.7   Attachments:

water flux through the soil 12m from the stream
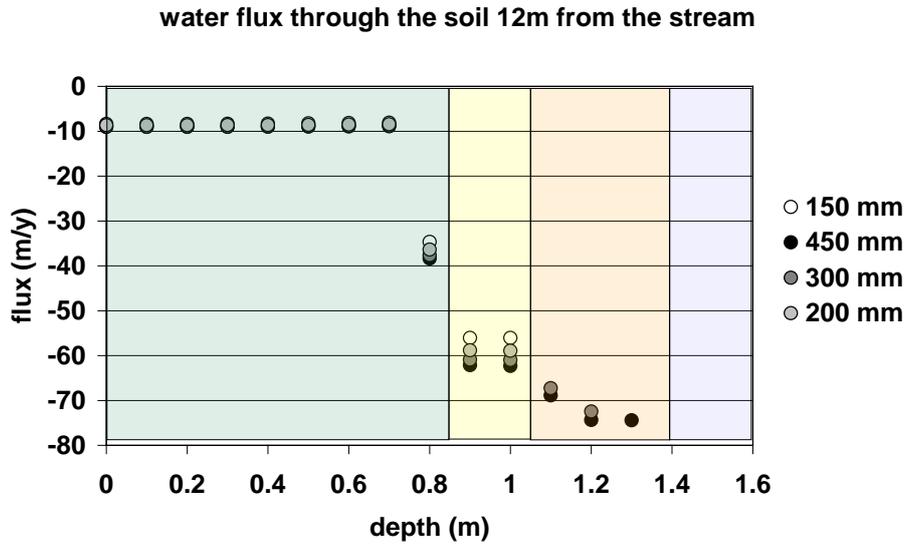
Figure 9.7-23. Plot of the vertical fluxes [m/year] through different soil layers in the PHAST model as a function of soil depth at the site S12 and different steady-state rainfall ranging from 150 to 600mm. The calibrated model reproduces the feacture of wetting up the upper layers at intensive rainfall as displayed in Fig. 19.
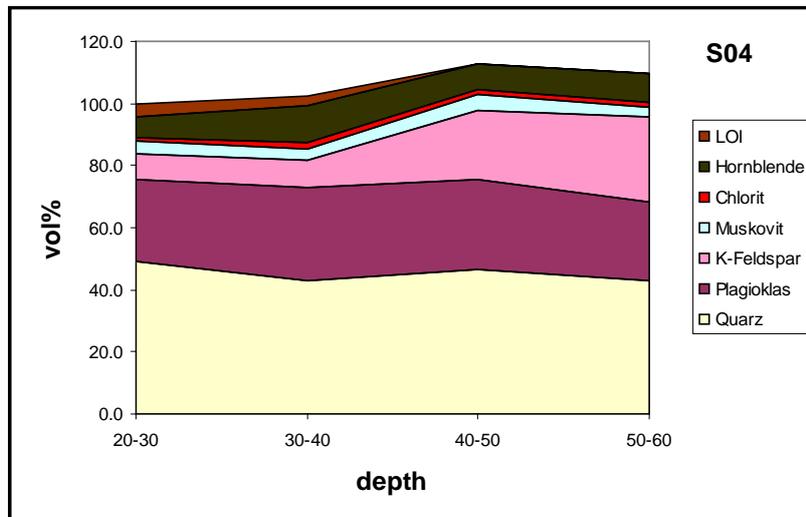
Figure 9.7-24. Volumetric fraction of various major mineral identified in the SO4 transect determined by XRD. Comparably fast weathering minerals are Hornblende and plagioclase.
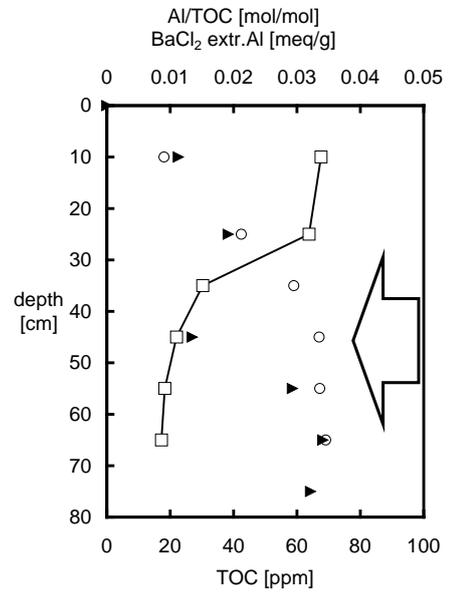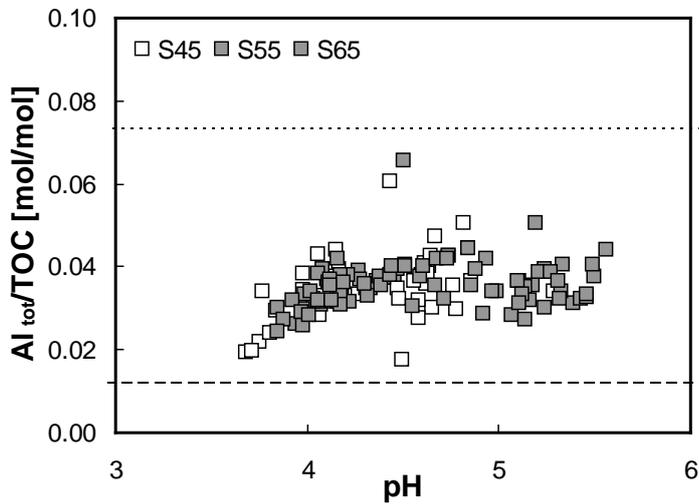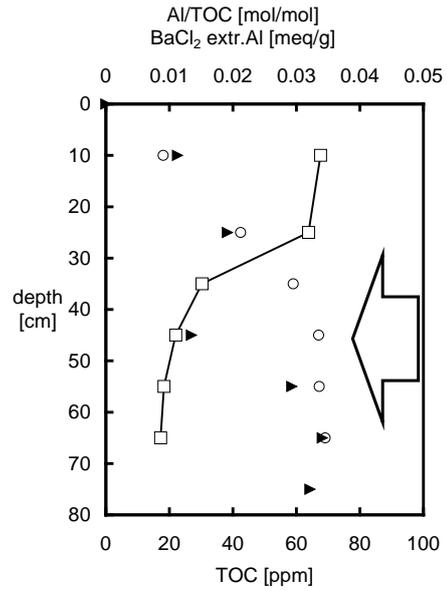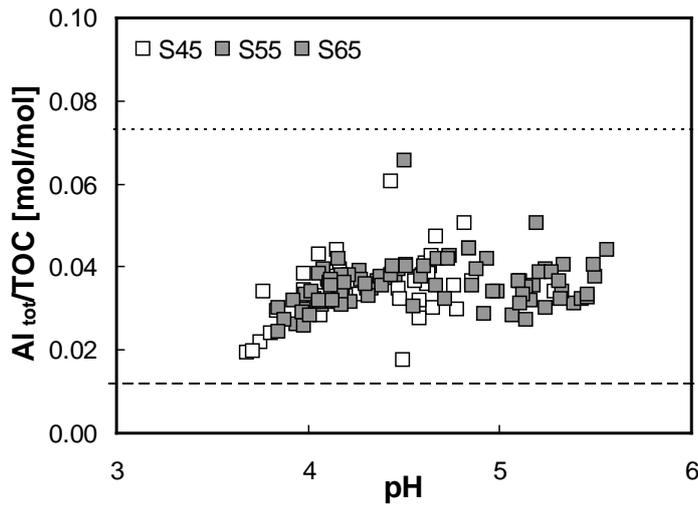
Figure 9.7-25. Observed ratio of total aluminium per total organic carbon in the soil solutions at selected depths 45, 55 and 65cm from the riparian transect during the observation period 1996-2005. The upper hyphenated line represents the Al/TOC ratio from which on Al and TOC removal were observed during the soil solution laboratory manipulation experiment while the lower line is the value that is observed in the adjacent stream at the forest site).

Figure 9.7-26. Long-term TOC [ppm] (□) and average Al/TOC [mol/mol] (○) ratio observed in the soil solutions and the amount of 0.5 N BaCl$_2$ extractable aluminium per dry weight [meq/g] in the riparian soil S4 as a function of depth (▲).

Figure 9.7-27. Temporal variation in TOC using the regression model (bold line), convolution model (hyphenated) and instantaneous measured TOC (black circles) for four characteristic years during the period 1993 through 2003.

Table 9.7-6. Calculated saturation indexes for several minerals (dark grey $SI < 0$, light grey: $SI > 0$, white: $-1 \leq SI \leq 1$).

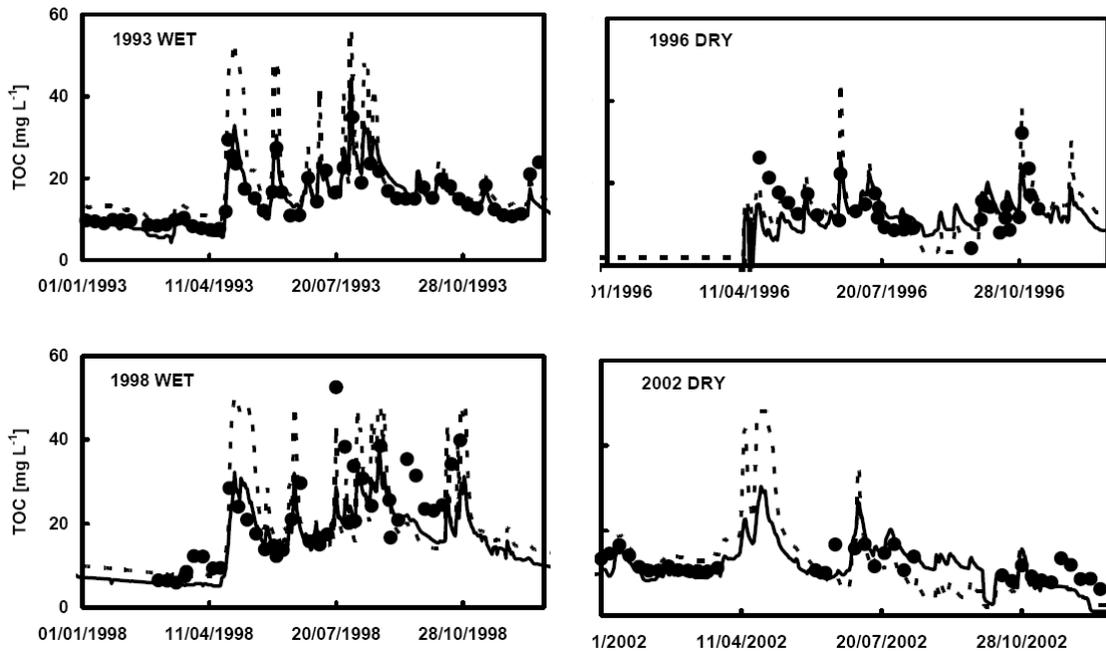| depth	Albite	Plagioclase	Microcline	Orthoclase	Gibbsite$_{amorphous}$	Chlorite	Anorthite	Proto-Imogolite	Imogolite	Halloysite
S4-10cm	-20.26	-10.10	-6.25	-6.50	-4.81	-49.61	-17.82	-5.71	-3.24	17.18
S4-25cm	-18.33	-8.49	-5.44	-5.69	-3.59	-50.14	-16.27	-3.76	-1.29	19.27
S4-35cm	-17.97	-6.47	-3.68	-3.93	-2.85	-43.14	-13.26	-1.63	0.84	21.40
S4-45cm	-17.81	-5.48	-2.92	-3.17	-2.32	-39.83	-11.75	-0.57	1.90	22.45
S4-55cm	-18.00	-4.91	-2.43	-2.68	-2.07	-37.18	-10.87	-0.09	2.38	22.93
S4-65cm	-17.80	-5.26	-2.70	-2.95	-2.23	-39.05	-11.41	-0.37	2.10	22.66
S12-5cm	-18.96	-5.94	-3.37	-3.63	-2.56	-38.82	-12.22	-1.16	1.31	21.76
S12-10cm	-18.90	-5.12	-2.80	-3.06	-2.19	-36.06	-11.03	-0.42	2.05	22.51
S12-20cm	-18.61	-3.83	-1.89	-2.15	-1.64	-32.88	-8.91	0.71	3.18	23.65
S12-30cm	-18.85	-3.33	-1.12	-1.37	-1.45	-29.50	-8.46	1.10	3.57	24.06
S12-40cm	-19.08	-3.24	-0.91	-1.16	-1.34	-29.34	-8.32	1.29	3.76	24.23
S12-60cm	-17.73	-3.27	-0.57	-0.83	-1.22	-29.75	-9.03	1.54	4.01	24.47
S12-70cm	-19.77	-8.30	-4.83	-5.08	-3.72	-45.39	-15.75	-3.53	-1.06	19.35
S22-12cm	-14.80	-44.94	-19.37	-4.29	-4.06	-3.01	23.20	-0.54	2.92	-29.79
S22-20cm	-10.02	-29.20	-21.00	-2.08	-1.84	-0.92	27.62	1.55	-0.60	-25.72
S22-35cm	-7.70	-21.41	-21.75	-1.12	-0.89	-0.04	29.40	2.43	6.77	-18.86
S22-50cm	-6.27	-21.29	-20.36	-0.46	-0.23	1.73	31.81	4.20	4.21	-20.03
S22-75cm	-3.01	-16.51	-19.10	1.27	1.51	4.64	36.46	7.11	5.14	-17.39
S22-90cm	-1.67	-11.47	-19.26	2.68	2.91	4.97	38.10	7.44	6.20	-14.56

	Fe(OH)3	Gibbsit	Na-Montmorillonite	K-Montmorillonite	Illite	Mg-Montmorillonite	Cordierite anhydride	Muscovite	Kaolinite	Ca-Montmorillonite
S4-10cm	0.32	-1.67	-1.17	-1.90	8.06	-0.65	65.01	18.36	12.09	-0.50
S4-25cm	-0.22	-0.76	0.88	-0.13	10.45	1.23	68.57	20.98	14.18	1.35
S4-35cm	0.29	0.31	3.09	2.20	13.32	3.48	74.77	24.87	16.31	3.59
S4-45cm	0.66	0.84	4.16	3.29	14.69	4.57	77.77	26.70	17.36	4.68
S4-55cm	1.11	1.08	4.73	3.91	15.38	5.17	79.59	27.68	17.84	5.28
S4-65cm	0.83	0.93	4.39	3.56	14.99	4.82	78.43	27.11	17.57	4.94
S12-5cm	0.43	0.59	3.50	2.65	13.81	3.96	76.98	25.74	16.67	4.05
S12-10cm	0.46	0.95	4.34	3.48	14.80	4.80	79.29	27.04	17.42	4.90
S12-20cm	0.65	1.51	5.52	4.70	16.33	5.98	82.40	29.07	18.56	6.17
S12-30cm	0.78	1.70	6.19	5.45	17.08	6.65	84.42	30.23	18.97	6.75
S12-40cm	1.00	1.81	6.30	5.60	17.34	6.75	84.75	30.65	19.15	6.84
S12-60cm	1.34	1.93	6.53	5.83	17.71	6.88	84.99	31.23	19.39	6.84
S12-70cm	0.26	-0.58	1.01	0.22	10.81	1.45	70.50	21.95	14.27	1.49
S22-12cm	-7.67	-0.35	2.06	11.72	19.93	0.95	71.65	14.84	2.16	1.63
S22-20cm	-4.62	0.75	4.83	14.69	21.91	3.75	81.09	16.83	4.94	4.35
S22-35cm	-2.91	1.17	6.40	16.06	22.84	5.22	85.70	17.76	6.51	5.95
S22-50cm	-1.88	2.04	7.76	18.07	24.63	6.55	88.60	19.54	7.87	7.32
S22-75cm	0.35	3.50	10.39	21.68	27.54	9.20	95.19	22.46	10.49	9.93
S22-90cm	1.34	3.61	11.41	22.75	27.97	10.41	97.94	22.88	11.52	10.93

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9.8   D8: A comparison of key parameters driving the HOC and metal models and evaluation of the obtained results in light of the knowledge acquired in WP 2 (Compilation of current knowledge).

Contains contributions from all PERSPEC partners

From the compilation of knowledge performed in section 9.2 – 9.5 it is apparent that a quantitative modelling of the organic carbon concentration in the stream is a prerequisite to understand the dynamics of contaminants in Krycklan and in downstream surface waters. However, a number of additional parameters also need to be addressed, including critical meteorological driving parameters, supplementary key variables (for example pH and capacity terms such as ion-exchange), and important thermodynamic or kinetic reactions. Furthermore, as the hydrological processes in the riparian zone exert a large control on the stream water chemistry it is of uttermost importance that the models can reproduce or incorporate the observed groundwater fluctuations as the chemical signature between different soil horizons differ drastically. The models presented in this report tackled these difficulties somewhat differently. The models used for assessing the mobilisation of metals within and from catchments (section 9.7) pursued different ways of modelling basic parameters such as temperature, water content in different compartments, and DOC in soil and stream water, as an initial step towards more complex models. In contrast, the HOC models (section 9.6) used already available meteorological data, soil properties, water and DOC export, concentrations of HOCs, etc, in a simplified input-output mass balance model based around a three-phase partitioning approach. While the different strategies used in the modelling of metals and HOCs are, given available data, both valid and in parts very successful, it is evident that further basic research is essential in order to be able to feed future models with much needed input data as well as with detailed descriptions of the mechanism or processes active at the soil / DOC – water interface. This will minimise the number of wide-ranging assumptions and general parameters used within the models and as a result more complex modelling approaches may be approached and evaluated.

9.9   Dissemination

The following disseminations activities were an integral part of the PERSPEC project.

Internet based dissemination

Project information and news were uploaded to the EUGRIS homepage (www.eugris.info)

A PERSPEC home page, featuring project details and dissemination activities, was launched at the beginning of the project (http://project.chem.umu.se/perspec/). The home page also includes a PERSPEC file repository, hence facilitating internal dissemination and collaboration

Kick-off meeting in Vindeln / Umeå, Sweden, 25-26 October 2007

PERSPEC members and external researchers were invited to visit the Krycklan catchment, which is the basis for the PERSPEC project, followed by several short talks focusing on past and future research at the Krycklan catchment. The talks included an introduction to the Era-net SNOWMAN as well as the PERSPEC project. A tentative program can be downloaded from: http://project.chem.umu.se/perspec/?Dissemination.

Workshop in Lancaster, UK, 2-4 June 2008

PERSPEC members and external researchers were invited to a workshop focusing on catchment related issues, including hydrology, biogeochemistry, diffuse pollution, soil erosion, monitoring, and modelling. The talks included an introduction to the Era-net SNOWMAN, the PERSPEC project, and preliminary results from the PERSPEC project. A tentative workshop program can be downloaded from: http://project.chem.umu.se/perspec/?Dissemination.

Participation at conferences

The PERSPEC project presented a poster at the NORDROCS conference (24-25 September 2008, Helsinki, Finland) and will present a poster at the SETAC Europe 19th Annual Meeting (31 May - 4 June 2009, Göteborg, Sweden).

The PERSPEC project and results obtained as a result of the PERSPEC project were presented at the 5th Annual Krycklan Symposium (October 6-8, 2008, Umeå, Sweden).

Interesting contacts made

Several contacts have been established as a result of the PERSPEC project. These contacts include agencies, research institutions, and SMEs from a number of EU member states, including the UK, Germany, France, Hungary, Sweden, and Austria. This has in turn resulted in PERSPEC being part of several research applications, including one EU FP7 application, one EU Structural Fund objective 2 application, and one BONUS application.

10   Anticipated use and application of results

The PERSPEC project, the findings presented in this report, and detailed results from the PERSPEC project planned to be published in scientific journals are expected to be valuable contributions in a number of instances, as discussed below.

10.1   Policy makers

The PERSPEC project, the findings presented in this report, and the data from the PERSPEC project planned to be published in scientific journals are well suited to be used as basic data for future decision-making. The PERSPEC project has highlighted the need for improved understanding of the fate of both natural solutes and anthropogenic contaminants. Combined with an assessment of current baseline ecological status these are necessary steps in order to safeguard the wellbeing of our aquatic ecosystem. This is of special urgency in boreal regions in northern latitude. These areas are experiencing a disproportionate accumulation of anthropogenic contaminants as they are atmospherically transported from more densely populated regions with the prevailing weather systems. This northern zone is also a region where climate change scenarios predict the largest changes in temperature and precipitation in the future, which will affect both the accumulation and mobility patterns of contaminants in the region. Furthermore, the PERSPEC project has, using a catchment scale approach, assessed the impact of atmospherically derived diffuse pollution for headwaters in correlation to point sources. This is expected to be of importance in the context of understanding chemical loading downstream and the baseline contribution of atmospherically-derived chemicals to Environmental Quality standards within the European Water Framework Directive (WFD). It should also be noted that some of the results from the PERSPEC project likely might be applied to the high altitude alpine regions of central Europe that have a climate that may lead to enhanced atmospheric deposition in areas which are important from a water supply perspective. Finally, a full understanding of baseline contribution and the soil to water processes controlling the transport of priority substances at catchment scale, as well as the connection to such factors as atmospheric deposition, hydrological events, soil matrix characteristics, DOC, pH, and temperature, is a prerequisite for assessing the variation of priority substances in water streams and river basins on a seasonal and regional scale. Such basic understanding is also needed in order to estimate the impact of diffuse sources in comparison to point sources on water quality, and to make valid recommendations for regional and national threshold values.

10.2   Future research

The findings from the PERSPEC project are applicable to a wide variety of north European catchments systems. However, the PERSPEC project has identified a number of challenging tasks that needs to be addressed by further research. This includes basic research, encompassing the whole range of metals and HOC measured in the catchment, in order to be able to feed models with much needed input data as well as with detailed descriptions of the mechanism and processes active at the soil / DOC – water interface. This will minimise the number of wide-ranging assumptions and general parameters used within the models. For this to be successful, one needs to evaluate the obtained models using a well defined systems such as the Krycklan catchment where soils and surface water are well characterised and appropriate field data is readily available. The possibility of applying the models based on Krycklan and other catchments to contaminated sites, both point sources and larger land areas, should also be evaluated. The PERSPEC project has clearly shown that although metals, trace elements and HOCs are governed by significantly different chemical properties, they are subject to the same soil - water controlled processes, which have a considerable impact on their environmental fate. Hence it is evident that future research efforts will benefit from an interdisciplinary approach incorporating hydrology, soil science, and organic and inorganic environmental chemistry, as well as other scientific disciplines. A fundamental understanding of the interaction between terrestrial and aquatic systems will ultimately lead to reliable environmental fate models, thereby enabling predictions of effects of environmental changes, e.g. effects of climate change on atmospheric inputs and aqueous exports.

10.3   Environmental monitoring

The PERSPEC project has clearly shown that both metals and HOCs are subject to a number of processes resulting in great seasonality in levels and export of contaminants. This has direct consequences for environmental monitoring programs. One such example is the monitoring of water quality recommended by the European water framework directive (WFD). As it stands, this directive recommends monthly sampling as a way of monitoring water quality with the possibility to adjust recommended threshold values according to national conditions. As should be evident from the data presented within this report, monthly levels of priory substances may display large variation, which in turn is connected to a number of ambient factors detailed in this report. The data presented in this report also highlights the need for coherent methodologies for sampling, chemical analysis and data reporting. As the transfer of some metals and HOCs from soils to water is primarily mediated by DOC and small particles (colloids), this is especially important when it comes to distinguish between particulate and dissolved phases, and the methodologies used to separate the dissolved phase from the particulate phase. Furthermore, determining the flux of contaminants and DOC may also be a much needed, and sometimes necessary, complement to studies on concentration of contaminants in surface waters.

11   Realised or planned publication of project results

A number of papers including data obtained as a direct or indirect result of the PERSPEC project are planned. These papers will focus on detailed HOC data from the Krycklan catchment area, on the models presented in chapter 9.6, and, given time for further refinement, the models presented in 9.7.

Due to the nature of scientific work and the process of publishing in scientific journals, the date of publication cannot be given.

12   Conclusion and recommendations

The major conclusion and recommendations from the PERSPEC project may be summarised as:

- A full understanding of baseline contribution and the soil to water processes controlling the transport of priority substances at catchment scale, as well as the connection to such factors as atmospheric deposition, hydrological events, soil matrix characteristics, DOC, pH, and temperature, is a prerequisite for assessing the variation of priority substances in water streams, river basins, or on a seasonal and regional scale. Such basic knowledge is also needed in order to estimate the impact of diffuse sources in comparison to point sources on water quality, and to make valid recommendations for regional and national threshold values

- Climate change scenarios including changes in temperature and precipitation will affect both the accumulation and mobility patterns of contaminants in northern latitude boreal regions.

- Headwater atmospherically derived diffuse pollution has an impact in addition to downstream point sources.

- The great seasonality in levels and export of contaminants, and the contaminants partitioning between particles (colloids) and the dissolved phase, may have direct consequences for environmental monitoring programs.

- There is urgent need for improved understanding of the fate of both natural solutes and anthropogenic contaminants. Basic data as well as detailed descriptions of the mechanism and processes active during atmospheric deposition, the transfer of contaminants from snow to soil, and at the soil / DOC – water interface is needed for refining current models on levels and export of metals and HOCs from catchments.

- Although metals, trace elements and HOCs are governed by significantly different chemical properties, they are subject to the same soil - water controlled processes, which have a considerable impact on their environmental fate. Hence it is recommended that future research efforts incorporate hydrology, soil science, and organic and inorganic environmental chemistry, as well as other scientific disciplines.

- It is recommended that the interdisciplinary approach used in the PERSPEC project is applied to other sites or areas of interest. These areas may be polluted sites or larger land areas with diffuse pollution as a major source of contaminants. Other examples of interests are the alpine regions of northern Sweden or the high altitude alpine regions of central Europe. The alpine regions of northern Sweden are of interest as they provide an extreme climate endpoint as a complement to the Krycklan data. The alpine regions of central Europe are of special interest as the regional climate may lead to enhanced atmospheric deposition in areas that are important from a water supply perspective.

13   List of abbreviations

ANC	Acid neutralisation capacity
B[*a*]P	Benzo[*a*]pyrene
B[*ghi*]P	Benzo[*ghi*]perylene
B[*k*]F	Benzo[*k*]fluoranthene
CO_2	Carbon dioxide
DOC	Dissolved organic carbon
Fla	Fluoranthene
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexanes
HOCs	Hydrophobic organic contaminants
KCS	Krycklan Catchment Study
K_D	Partitioning coefficient
K_{ow}	Octanol-water partitioning coefficient
LOI	Loss on ignition
LRAT	long range air transport
OC	Organic carbon
OM	Organic matter
PAHs	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyl
PCDDs	Polychlorinated dibenzo-*p*-dioxins
PCDFs	Polychlorinated dibenzofurans
PERSPEC	Perspectives on mobilisation of prioritised contaminants in soil
PHAST	Metal multibox model
Phen	Phenanthrene
POC	Particulate organic carbon
POPs	Persistent organic pollutants
Pyr	Pyrene
RZ	Riparian zone

SNOWMAN   Sustainable management of soil and groundwater under the pressure of soil pollution and soil contamination

SOM   Soil organic matter

SPM   Suspended particulate matter

SVOCs   Semi-volatile organic compounds

TOC   Total organic carbon

WITCH   Metal geochemical based model