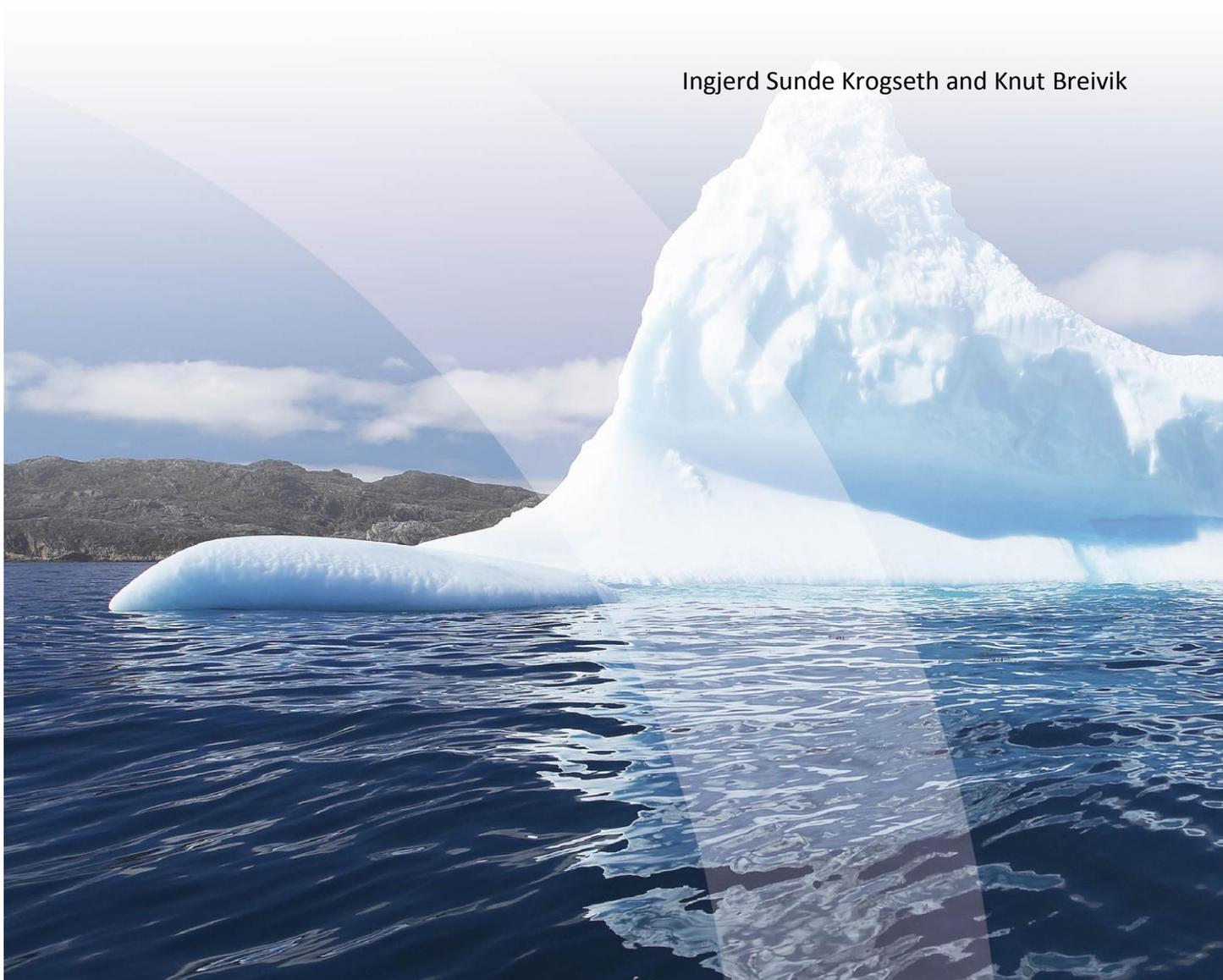


Multimedia models and observations in concert

A powerful tool to understand and manage organic contaminants

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Scientific report

Preface

This report summarizes selected results from a research project, funded by the Research Council of Norway from 2010-2014 through the programme Miljø 2015 (196191/S30). The overall goal of the project was to better understand relationships between emissions of organic contaminants of emerging concern and levels in the environment and food-chains of the Nordic region through integrated monitoring and modeling studies. The potential of using models and observations “in concert” was explored as a tool for improved chemical understanding and management specifically within the Nordic region, reflecting actual environmental and climatic conditions. Four case studies were selected (i) cyclic volatile methyl siloxanes (cVMSs) in the Inner Oslofjord, (ii) cVMSs in the Norwegian Arctic, (iii) short-chain chlorinated paraffins (SCCPs) in the Nordic environment and (iv) risk-based model screening of chemicals in commerce in the Nordic countries. Most contaminants of interest to this project are multimedia chemicals, i.e. they partition extensively between different media like air, water, and organic matter. Therefore, we also provide a brief introduction to the key multimedia modelling tools which were used. NILU has extensive experience with such models after continuously working with further development and evaluation of such modelling tools for two decades. These tools target the environmental fate and behaviour of contaminants under relevant environmental and climatic conditions, and it is our hope that they may assist Nordic environmental authorities interested in understanding and managing organic contaminants.

We want to thank the Research Council of Norway for funding this project. We also would like to express our gratitude to our international collaborators from University of Toronto Scarborough, Canada (*Frank Wania, Jon A. Arnot, Ying D. Lei, Xianming Zhang*), Stockholm University, Sweden (*Michael S. McLachlan, Amelie Kierkegaard*), University of Leicester, UK (*Mick J. Whelan*), Aarhus University, Denmark (*Kaj M. Hansen*) and colleagues at NILU (*Martin Schlabach, Anders Borgen*) for their valuable contributions brought into this project.

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List of abbreviations

α -HCH = α -hexachlorocyclohexane
cVMS = cyclic volatile methyl siloxane
D3 = hexamethylcyclotrisiloxane
D4 = octamethylcyclotetrasiloxane
D5 = decamethylcyclopentasiloxane
D6 = dodecamethylcyclohexasiloxane
DEHM = Danish Eulerian Hemispheric Model
EAF = exposure assessment factor
EUSES = European System for Evaluation of Substances
HAF = hazard assessment factor
 K_{AW} = air-water partition coefficient
 K_{OA} = octanol-air partition coefficient
 K_{OW} = octanol-water partition coefficient
NILU = Norwegian Institute for Air Research (Norwegian: Norsk institutt for luftforskning)
PCB = polychlorinated biphenyl
POP = persistent organic pollutant (Norwegian: persistente organiske miljøgifter)
RAF = risk assessment factor
RAIDAR = risk assessment, identification, and ranking
SCCP = short chain chlorinated paraffin
SPIN = substances in preparations in the Nordic countries
VMS = volatile methyl siloxane
WWTPs = wastewater treatment plants

Norsk sammendrag

Denne rapporten oppsummerer resultater fra et forskningsprosjekt finansiert av Norges Forskningsråd under Miljø2015 programmet (196191/S30). Det overordnede målet var å forbedre forståelsen av sammenhenger mellom utslipp og eksponering av nye organiske miljøgifter i Norden gjennom studier som kombinerer målinger av nivåer i miljøet med modellering. Det ble fokusert på fire enkelttilfeller (i) sykliske flyktige metylsiloksaner i Oslofjorden, (ii) sykliske flyktige metylsiloksaner på Svalbard, (iii) kortkjedede klorparaffiner i nordisk miljø og (iii) risikobasert screening av kommersielle kjemikalier i Norden. Denne rapporten presenterer utvalgte resultater fra prosjektet, med hovedvekt på bruken av modeller og resultatene fra disse.

De fleste persistente organiske miljøgifter (POPs), og andre kjemikalier med POP-liknende egenskaper, er såkalte multimedia-kjemikalier. Det betyr at de finnes i og på tvers av ulike deler (media/matriser) av miljøet, som luft, vann, sediment, og jord. For å forstå hva som skjer med disse stoffene når de slippes ut til det ytre miljø, er det derfor nødvendig å ta hensyn til den totale fordelingen i det ytre miljø. En multimediatilnærming er derfor ofte mer rasjonelt enn rene fokus på miljøskjebne i for eksempel luft eller vann alene. Dette er det felles grunnlaget for såkalte fugasitetsbaserte multimedia-modeller som har vært brukt i dette prosjektet. Denne rapporten belyser innledningsvis hvorfor en slik multimediatilnærming er nødvendig samt gir eksempler på hva disse modellene kan brukes til. Det legges spesielt fokus på hvordan de kan brukes i kombinasjon med målte data for å forstå sammenhenger mellom utslipp og konsentrasjoner av organiske miljøgifter i både det fysiske miljøet og i næringskjeder i Nordisk miljø.

Siloksaner i Indre Oslofjord

Siloksaner brukes i store mengder i kosmetikk og hudpleieprodukter, kan slippes ut til miljøet med avløpsvann, og tidligere studier har målt høye nivåer av siloksaner i torsk fra Indre Oslofjord. I dette prosjektet ble Oslofjord POP Modellen brukt i kombinasjon med den akvatiske delen av næringskjedemodellen ACC-HUMAN for å forsøke og gi en mekanistisk forklaring på de høye konsentrasjonene som har vært målt. Predikerte konsentrasjoner i rensed avløpsvann, vann, og sediment i Indre Oslofjord stemte relativt godt overens med konsentrasjoner som har vært målt, noe som støtter opp om modellsimuleringene. ACC-HUMAN predikerte synkende konsentrasjoner av siloksaner oppover i næringskjeden, noe som stemmer med målinger gjort i Oslofjorden, men som er i motsetning til studier gjort andre steder. Sammenlikningen mellom modell- og måleresultatene pekte på viktige usikkerheter og kunnskapshull, slik som størrelsen på utslipp av siloksaner og evnen som fisk har til å metabolisere de ulike siloksanene. I tillegg ga modellsimuleringene nyttig innsikt i den predikerte betydningen av ulike mekanismer for transport og «tap» av siloksaner, både i det fysiske miljøet og i næringskjeden.

Siloksaner i arktisk luft

De største utslippene av siloksaner til miljøet er direkte til luft, og atmosfæren er predikert til å være det største reservoaret for siloksaner i miljøet. I dette prosjektet ble konsentrasjonen av siloksaner målt i luft på Zeppelin-observatoriet på Svalbard i 2011, og resultatene ble sammenliknet med prediksjoner fra den

transportorienterte multimedia-modellen DEHM-POP. De to siloksanene D5 og D6 ble målt over deteksjonsgrenser, med høyest konsentrasjoner av D5. Konsentrasjonene av siloksaner var 100-1000 ganger høyere enn typiske konsentrasjoner av PCB (polyklorerte bifenyler) i luft på Zeppelin, og sammenliknbare med konsentrasjoner av siloksaner i luft som har vært målt i Sverige. Modellprediksjonene for D5 stemte godt overens med både de målte konsentrasjonene og sesongvariasjonene for D5, med høyere konsentrasjoner om vinteren enn om sommeren. Det gode samsvaret mellom modellen og målingene betyr at vi har en relativt god forståelse av hvordan D5 oppfører seg i atmosfæren. Tilstedeværelsen av D5 og D6 i luft på Zeppelin, særlig i kombinasjon med en modell som kan gi en mekanistisk forklaring på de målte konsentrasjonene av D5, bekrefter at disse siloksanene har evne til å transporteres over lange avstander i atmosfæren.

Kortkjededede klorparaffiner i nordisk miljø

Kortkjededede klorparaffiner er tekniske blandinger som er utfordrende både å måle og å modellere fordi de består av tusenvis av enkeltkomponenter. I dette prosjektet ble den integrerte miljøskjebne og næringskjedemodellen CoZMoMAN brukt for å predikere konsentrasjoner og sammensetningen av kortkjededede klorparaffiner i nordisk miljø. Resultatene ble sammenliknet med allerede eksisterende målinger av kortkjededede klorparaffiner i Norden. Et utslippsestimat på 15 tonn per år ga det beste samsvaret mellom predikerte og målte konsentrasjoner. Da var forholdet mellom prediksjonene og målingene innenfor en faktor 6 for både luft, jord, ferskvannssedimenter, torsk og human brystmelk. Dette betyr at vi har en relativt god forståelse av miljøskjebnen til de kortkjededede klorparaffinene og av sammenhengen mellom utslipp og human eksponering for disse stoffene. Det styrker også tilliten til CoZMoMAN modellen. Sammenlikningen mellom prediksjoner og målinger fremhevet også eksisterende usikkerheter og kunnskapshull, spesielt når det gjelder utslipp av og egenskapene til de enkelte komponentene av kortkjededede klorparaffiner. Det er stor variasjon i miljøegenskaper innad i gruppen, og det anbefales ikke å ignorere denne variasjonen ved å betrakte disse som «en» forbindelse.

Risikobasert modellscreening av kommersielle kjemikalier

I tillegg til studier som er rettet mot spesifikke kjemikalier eller grupper av kjemikalier, finnes det også modelleringstilnærminger som kan gå gjennom lange lister over kommersielle kjemikalier for å lete etter stoffer som kan ha POP-liknende egenskaper. Disse tilnærmingene er ofte basert på de iboende egenskapene til stoffene, det vil si at de ikke tar mengden av stoffet som produseres og slippes ut til miljøet med i beregningen. Prosjektet har gjort det mulig å bidra til ytterligere internasjonalt samarbeid gjennom to studier som er risikobaserte, det vil si at de tar hensyn til mengden av stoffene som slippes ut i miljøet. I det ene studiet ble det utviklet en metode som kan beregne utslipp til luft, vann, og jord for tusenvis av stoffer. Denne metoden ble brukt i kombinasjon med en integrert miljøskjebne og næringskjedemodell (RAIDAR) i det andre studiet til å predikere menneskelig eksponering for 12 000 kommersielle kjemikalier. Begge studiene la vekt på den store usikkerheten som fortsatt finnes i utslippsdata, og begrensningene som dette fører til for modellbaserte screeninger. Disse studiene kommer til å bli fulgt opp av et screening-studie som bruker mer eksakt informasjon om bruk av kjemikalier i de nordiske landene for å forsøke å redusere denne usikkerheten.

Oppsummering

NILU har siden midten av 1990-tallet arbeidet med utvikling og evaluering av multimediamodeller. Disse har potensiale til å styrke framtidige overvåknings- og screeningaktiviteter. I dag investeres det allerede store ressurser på å overvåke konsentrasjoner av POPs og på å screene for potensielle nye POPs i miljøet vårt. Denne rapporten understreker en betydelig merverdi ved å kombinere empiriske resultater fra overvåknings- og screeningprogrammer med bruk av multimediamodeller. Både modeller og målinger har sine fordeler og begrensninger, og eksemplene i dette prosjektet illustrerer ulike måter for hvordan modeller og målinger kan utfylle hverandre. Modellsimuleringer kan bidra til å optimalisere design for prøvetakingskampanjer og dermed maksimere utbyttet fra begrensede ressurser. Dette kan for eksempel gjøres ved å predikere hvilke media eller organismer som kan være de mest interessante, hvilke nivåer som kan forventes å finnes, eller til og med optimal prøvetakingssted og -tid. Modeller kan også brukes i etterkant til å gi mekanistiske forklaringer på observasjoner som har vært gjort, inkludert til å belyse kilde-reseptor forhold som vanskelig kan utledes på basis av observasjoner alene. Mekanistiske modeller samler den eksisterende forståelsen av relevante systemer og prosesser på ett sted. Dermed kan sammenlikninger mellom modeller og observasjoner bidra til å vurdere den forståelsen vi har og til å identifisere viktige kunnskapshull. For å tilrettelegge for slike sammenlikninger, er det imidlertid en fordel med strategisk prøvetaking som gjør de empiriske resultatene sammenliknbare med modellresultatene. Vi håper at modellverktøyene som har vært illustrert her kan være relevant og til hjelp, ikke bare for forskningsformål, men også for aktuelle miljømyndigheter i Norden med interesse for organiske miljøgifter.

Multimedia models and observations in concert – A powerful tool to understand and manage organic contaminants

1 Background and context

Different factors affect how organic contaminants once released into the environment distribute and accumulate, enter various food-chains, and potentially cause harmful effects in wildlife and humans over time. A sound chemical risk assessment requires the determination of the quantitative relationship between emissions and human exposure. Although there are many models developed for predicting chemical fate in the physical environment or for describing bioaccumulation in food-chains, most current modeling tools only address parts of this relationship. One important exception is EUSES (Vermeire et al., 1997, Vermeire et al., 2005), the European Union System for the Evaluation of Substances, which is a quantitative risk assessment modeling tool. EUSES is furthermore an integrated model, which links a multimedia fate and transport model to a bioaccumulation model, and can predict human exposure from emissions. It has, however, two major deficiencies. 1) It is a steady-state model, i.e. it is not suitable to evaluate the response of the physical environment and its food-chains to changes in emissions over time. More specifically, steady-state approaches may fail to properly describe the long-term behavior of more persistent organic contaminants in environmental media that respond slowly to emission changes (e.g. soil and long-lived animals including humans). For example, there are fundamental difficulties in defining steady-state emission scenarios for substances for which the rate of release may have fluctuated over several orders of magnitude during the time scales relevant for exposure assessment (Li, 1999). 2) Major elements of existing integrated models are based on empirical correlations instead of mechanistically based descriptions of environmental fate and bioaccumulation processes. As such, the range of applicability of the empirical models is likely quite limited (Undeman and McLachlan, 2011). Indeed, it was found that the empirically based bioaccumulation model in EUSES over- and/or underestimated concentrations of well-studied chemicals such as PCBs (polychlorinated biphenyls) in the agricultural food chain by up to a factor of 100 (Jager et al., 1998). Finally, findings from past evaluations carried out elsewhere are not necessarily immediately applicable in the context of chemical management in the Nordic region. Chemical use and emission patterns, as well as environmental and climatic conditions which largely dictates fate, hazard and risks, may be widely different here compared to other areas like continental Europe or North-America.

This report summarizes some of the main outcomes of a research project, funded by the Research Council of Norway from 2010-2014. The overall goal of the project was to better understand relationships between emissions of organic contaminants of emerging concern and levels in the environment and food-chains of the Nordic region through integrated monitoring and modeling studies. The potential of using

models and observations “in concert” was explored as a tool for improved chemical understanding and management specifically within the Nordic region, reflecting actual environmental and climatic conditions. Four case studies were selected (i) cyclic volatile methyl siloxanes (cVMSs) in the Inner Oslofjord, (ii) cVMSs in the Norwegian Arctic, (iii) short-chain chlorinated paraffins (SCCPs) in the Nordic environment and (iv) risk-based model screening of chemicals in commerce in the Nordic countries.

Included among the sub-goals of the project was the aim to evaluate the applicability of an integrated modeling and monitoring approach as a higher tier tool in future screenings of organic chemicals of emerging concern in the Nordic region. An introduction to the modelling tools that were evaluated and applied in this research project is therefore provided in some detail in Chapter 2 before the case-studies are discussed in Chapter 3 and our conclusions presented in Chapter 4.

We hope that the modelling tools and outcome could be of relevance to future Norwegian and Nordic screening efforts as well as relevant policy activities in the Nordic region related to organic contaminants.

2 Introduction to multimedia chemicals and models

2.1 Most POP-like organic contaminants are multimedia chemicals

For most classical air pollutants, exposure and environmental concentrations will typically decline with increasing distance from primary sources due to dilution, dispersion, degradation, and deposition. However, circumstances have been described where concentrations of some organic contaminants, notably some persistent organic pollutants (POPs) and POP-like chemicals, are found at surprisingly high concentrations even in remote areas, such as the Arctic (Wania, 1999b). For some contaminants, concentrations in environmental surface media are even found to increase with increasing distance from source regions (Wania, 1999b). A key “text book” example is concentrations of α -HCH (α -hexachlorocyclohexane) in seawater. They were observed to increase with increasing latitude from Equator towards the Arctic in spite of being furthest away from major emission regions in Southeast Asia and India (Wania and Mackay, 1996). Indeed, the observed behavior of many POPs and POP-like chemicals clearly illustrate that source-receptor relationships cannot be fully rationalized by transport and loss processes within a single media (air or water) alone (Johansson et al., 2013). A key feature shared by most chemicals with POP-characteristics is that they are so-called multimedia chemicals. This means that they partition extensively within and across environmental media and therefore they require a multimedia modelling approach.

In the following sections, we will first introduce the so-called chemical space plots to show from a mechanistic point of view why the environmental behavior of these chemicals needs to be approached from a multimedia perspective (2.2). Next, we provide a brief introduction to multimedia environmental models (2.3) along with an introduction to the models used herein (2.4).

2.2 Chemical space plots

For readers unfamiliar with the concept of “multimedia” chemicals and models, it is informative to start by demonstrating mechanistically why many POPs and POP-like chemicals are better addressed as multimedia, rather than single-media, chemicals. The multimedia behavior of POPs and POP-like chemicals is best illustrated using the chemical space plots (Figure 1). It should be noted that the models and methods discussed herein are not directly applicable to inorganic chemicals, ionic, or very labile compounds. These chemical space plots are immensely useful and have become increasingly popular for evaluating the expected environmental behavior of POPs and POP-like chemicals.

The chemicals are plotted in the chemical space based on their partition coefficients between octanol and water (K_{OW}), octanol and air (K_{OA}), and air and water (K_{AW}). These partition coefficients are key properties which guide how organic substances distribute in the environment. As each of these properties tend to vary over many orders of magnitude, log-scale is preferred (Figure 1). Chemical space plots are regular two-dimensional plots for which K_{OA} is plotted along the x-axis and K_{AW} is plotted along the y-axis. K_{OW} is represented by the diagonal lines, exemplified by $\log K_{OW}$'s of -1, 5, and 9 in Figure 1A. This is a result of the thermodynamic consistency between the three partition coefficients, as can be seen by the following relationships:

$$K_{OW} = K_{OA} * K_{AW}$$

$$\log K_{OW} = \log K_{OA} + \log K_{AW}$$

As a result, chemical space plots simultaneously display the solubility of a given substance in air, water, and octanol. A high solubility in air or water is intuitive and indicates a high water solubility and high volatility, respectively. A high solubility in octanol is used as a substitute for high affinity for organic matter (e.g. organic-rich soils, sediment, and particles) or high affinity for lipids (in the case of biota). For example, chemicals exceeding a $\log K_{OW}$ of about 5 are often assumed to be potentially bioaccumulative substances and are hence often of particular interest to environmental scientists and authorities.

In the chemical space plots, chemicals with a high solubility in air (as opposed to in water and octanol) will tend to belong to the upper left corner (e.g. CH_4 or methane in Figure 1C). Chemicals with a high water solubility (as opposed to in air and octanol) will fall into the lower left corner. Finally, the upper left corner is reserved for substances with a high affinity for organic matter and lipids because of a high solubility in octanol (compared to its solubility in air and water). When moving horizontally in this plot from left to right (increasing $\log K_{OA}$), the affinity of a substance towards octanol will increase at the expense of air, and hence the substance becomes less volatile. Indeed, chemicals that have a $\log K_{OA}$ higher than about 10, will in the atmosphere be expected to be found attached to air particles. Hence, these chemicals are also more readily deposited from air to surface media attached to particles than more volatile compounds. When moving vertically in the plot from bottom to top (increasing $\log K_{AW}$), the water solubility of a given substance will decrease, which increases the tendency of a chemical to escape from water to air by volatilization. Finally, when moving from the lower left corner to

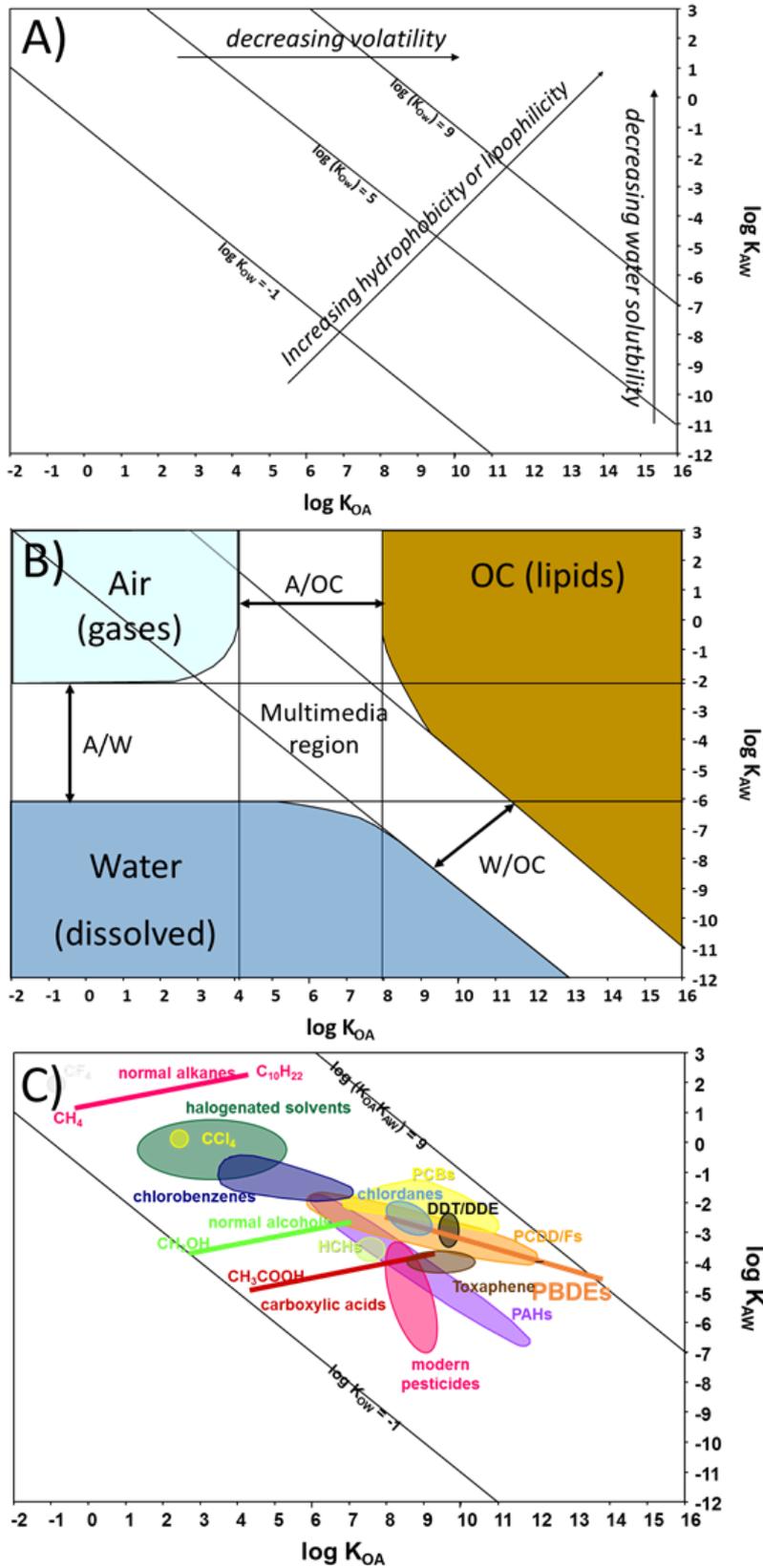


Figure 1: Chemical space plots displaying A) general outline (Gouin et al., 2000), B) main regions (single and multimedia), and C) approximate position of various

organic substances and substance groups, including POPs (the latter figure is courtesy of Frank Wania, University of Toronto). OC = organic carbon.

the upper right (increasing $\log K_{OW}$), the substances will experience an increasing lipophilicity (or hydrophobicity¹).

To further illustrate the concept of chemical space plots, we have made an alternative version in Figure 1B. Within Figure 1B, we highlight the approximate position of zones for chemicals with

- i) high air solubility (upper left corner),
- ii) high water solubility (lower left corner), and
- iii) high lipophilicity (upper right corner).

While the exact boundaries of these zones are not written in stone (Gouin et al., 2000), we will explain how these zones were derived. To do so, we have introduced two horizontal ($\log K_{AW}$), two vertical ($\log K_{OA}$) and two diagonal ($\log K_{OW}$) lines, or thresholds, for each partition coefficient.

To start with the horizontal lines ($\log K_{AW}$), the upper line is included to show that below a certain value for $\log K_{AW}$, dissolution from air into water will start to become significant. Likewise, above the lower horizontal line, evaporation from water into air will start to become significant. Based on this, there must be an intermediate region (“A/W”) for which chemicals are prone to exchange more readily between air and water. For the vertical lines ($\log K_{OA}$), there is a threshold when moving from left to right which indicates when chemicals will cease to be only in the gaseous state, and start to sorb to air particles or attach to vegetation (e.g. grass, leaves, and coniferous needles) or soil. Similarly, when moving from right to left, there is a threshold which indicates when chemicals will start to enter the gaseous state (from particles, vegetation, or soil). Again, chemicals located in the gap between these two vertical lines (“A/OC”) are chemicals more prone to air-particle or air-vegetation exchange.

Finally, two diagonal lines ($\log K_{OW}$) are included. If one moves from the upper right towards the lower left corner, the first diagonal line indicates when chemicals may be prone to leave organic phases and start to dissolve in water (e.g. leaching of contaminants from contaminated sediments). Likewise, moving in the opposite direction, the lower left diagonal line indicates when chemicals may cease to be truly dissolved in the water column and start to sorb onto suspended particles or sediments (or even bioconcentrate in aquatic organisms). Again, there is an intermediate zone occupied by chemicals which may exchange more readily between the water column and organic carbon (“W/OC”). Finally, there is a zone in the middle of the plot which is often referred to as the multimedia region. Chemicals within this area are those chemicals which may exchange readily between any three media (air, water, and organic phases), i.e. the multimedia chemicals, and indeed many POPs are located here (Figure 1C).

¹ Strictly speaking, K_{OW} is a measure of hydrophobicity rather than lipophilicity as most organic chemicals love lipids equally but hate water differently (Mackay, 2001). Chemicals positioned in the upper right corner and described as lipophilic herein thus combines a high affinity for lipids with a low affinity for water and air.

To summarize, from quantitative data for two out of three partition coefficients (as the third may be calculated from the other two), it is easy to plot a given substance in the chemical space. From this, some preliminary interpretations about its likely environmental behavior can be made. However, it is cautioned that most partition coefficients reported in the literature are standardized at 25 degrees Celsius. If one are interested in the position and fate of chemicals under more realistic environmental conditions (e.g. Nordic climatic conditions as in this project), there is a need to re-calculate these properties at the relevant temperatures. At lower temperatures, a given chemical will typically move towards the lower right corner because the volatility of organic chemicals decrease at lower temperatures. The practical implication is that chemicals will deposit to surface media like air and soil more easily at colder temperatures. This is at the core of the so-called “cold condensation” effect which is used to partly explain elevated concentrations of POPs in polar areas. Indeed, as mid-latitudes show significant seasonal differences in environmental temperatures between summer and winter, this also helps to explain seasonal cycles between evaporation and deposition which may develop - or the so-called “grasshopper effect”. All these processes are included in the mechanistic models that were used in this project to facilitate realistic simulations under Nordic environmental and climatic conditions.

Chemical space plots can also be used to understand other aspects of environmental behavior of organic contaminants, without doing any actual model simulations. This has been facilitated by earlier studies which have applied multimedia models to simulate any combination of partitioning properties representing the entire chemical space (Breivik and Wania, 2003, Meyer et al., 2005). For example, Wong and Wania used the chemical space to visualize the equilibrium and mobility potential of organic contaminants in soils (Wong and Wania, 2011). This could be used to assess the likely fate in soils for any property combination (e.g. is a chemical more prone to leave soils by volatilization, leaching or erosion?). Also, in a series of papers Wania and co-workers have used this technique to illustrate which property combinations that make a chemical more prone to accumulate in the Arctic physical environment (Wania, 2003, Wania, 2006) and even to bioaccumulate in indigenous people in the Arctic (Czub et al., 2008).

The key take-home message from the chemical space plots is that POPs and POP-like chemicals are rarely not either “air pollutants”, “water pollutants”, “soil pollutants”, nor “sediment pollutants” alone, but multimedia chemicals. This has significant implications not only for scientists interested in the environmental behavior and fate of these chemicals, but also for how such chemicals need to be managed. Single-media control strategies may be at great risk of missing out the larger picture in terms of how these chemicals actually cycle in the environment once they have been emitted.

2.3 Multimedia environmental fate models

2.3.1 Fugacity-based multimedia models

Reflecting the multimedia partitioning of many POPs and POP-like chemicals (deduced from K_{OA} , K_{AW} and/or K_{OW}), multimedia models have in common that they include multiple environmental compartments. They all tend to reflect the

paradigm that contaminant mass balances cannot be predicted and understood without including a description of the movement of air, water, and organic matter as either carriers and/or reservoirs for contaminants (Figure 2). It is beyond the scope of this report to review how these models were originally developed and the

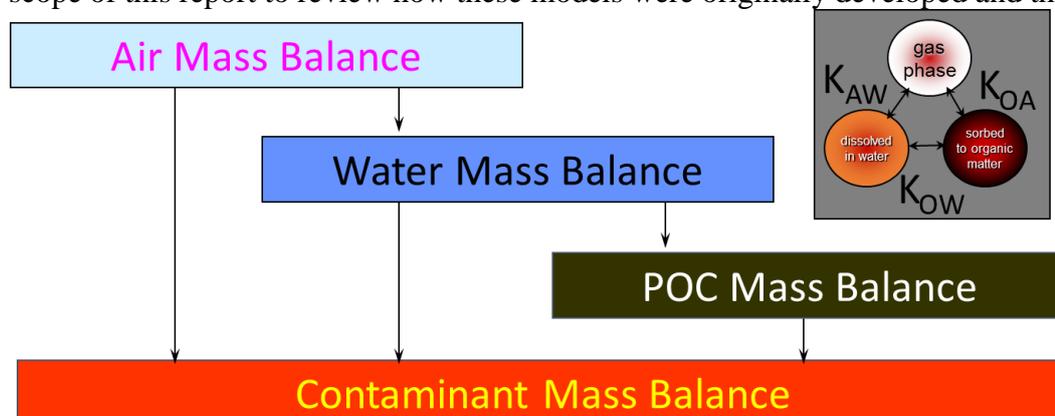


Figure 2: An understanding of the cycling of multimedia POPs and POP-like substances in the environment require an understanding of the movement of air, water and particulate organic carbon (POC) in the environment for which these contaminants partition or attach (modified after (Wania et al., 2000)).

detailed equations behind these models. However, the interested reader is encouraged to consult the landmark textbook by Mackay (Mackay, 2001) and/or reviews on multimedia modelling (Wania and Mackay, 1999, MacLeod et al., 2010) for a more extensive introduction to modelling theories and approaches.

Most environmental multimedia models are derived and formulated using fugacity notion (Mackay, 1979, Mackay, 2001). For readers unfamiliar with this concept, fugacity reflects the “escaping tendency” of a given chemical in a given media and has unit of pressure. Fugacity is also an important equilibrium criteria: Chemicals will tend to move from high to low fugacity and when the fugacity or “escaping tendency” of a chemical in two media in contact are identical, equilibrium is established and there is no net transfer of the chemical between the two media.

Fugacity (f) is linearly related to concentration (C) through the Z -value, so that C (mol m^{-3}) = f (Pa) * Z ($\text{mol m}^{-3} \text{Pa}^{-1}$). Z -values for each media are functions of the characteristics of the chemical (notably K_{OW} , K_{AW} , or K_{OA}), the characteristics of the media (e.g. organic matter content), and temperature. At lower temperatures, the Z -values will increase. This leads to increased capacity of a given media to store or retain chemicals, and may in turn lead to higher concentrations of the chemicals in this media. As already mentioned, this temperature dependence of partitioning is at the core of the cold condensation theory. In other words, POP-like chemicals are prone to accumulate in cold areas such as the Arctic because of higher Z -values in colder areas, and they strive towards an equilibrium distribution (equal fugacity) on a global scale (Wania, 2003).

2.3.2 Input requirements

Most multimedia models require three types of input parameters. These are input data used to describe (i) the characteristics of the chemical, (ii) the characteristics

of the environment (potentially including its food-chains), and (iii) the mode and rate of emissions. The predicted concentration in each medium will thus be controlled by the properties of the chemical, the emission patterns, and the characteristics of the environment into which it is released. Only a brief description is provided below. However, it is important to stress that elaboration of accurate input data typically involves large efforts and scientific rigor to facilitate both realistic and accurate predictions as well as transparency in model outcomes.

Chemical characteristics

Beyond two out of three partition coefficients (K_{OW} , K_{AW} , and/or K_{OA}), the temperature dependence of these partition coefficients will be required (enthalpies of phase transfer). Additionally, molecular weights (g mol^{-1}) are required to alternate between units. Also required are data on degradation half-lives in environmental media (typically air, water, soil, sediments, and vegetation) and their temperature dependencies, as well as biotransformation half-lives in organisms. While the particular input data may differ across models, we refer to the textbook by Mackay for an introduction to general data requirements (Mackay, 2001). For an exact and detailed account for specific models, the interested reader will have to consult the literature of each model.

Environmental and food-chain characteristics

In brief, these are the dimensions and properties of each environmental media. Also included are information on flows of environmental media and climatic conditions (temperatures, precipitation rates etc.) as well as boundary conditions (is there chemical exchange with the “outside” of the model?). In the case of bioaccumulation models, a description of organism characteristics and food-web characteristics will also be needed.

Mode and rate of emissions

For models which do not assume equilibrium, which applies to all models used within this project, there is a need to specify the rate and mode of release (emissions to air, water, soil etc). For models which additionally are dynamic (non-steady state), which again applies to all models in this project except for RAIDAR, there is also a need to specify emissions as a function of time. A key benefit of these dynamic non-equilibrium based models is that they are able to simulate the environmental response to changes in emissions (e.g. as a result of actual or potential control measures). Secondly, contemporary environmental burdens of POPs and POP-like chemicals may in part be due to primary emissions which occurred in the past. In this context, dynamic multimedia models are well suited to carry out simulations over time-scales that reflect the overall lifetime of these pollutants (years, decades, and even centuries).

2.3.3 Complementary multimedia approaches: Fugacity vs. transport-oriented

While fugacity-based multimedia models are at the core of this work, we would like to note that there are two “schools” of multimedia environmental modelling approaches: fugacity-based and transport-oriented models. The first is the fugacity-based multimedia models (also called box models) originating from the landmark

work by Mackay (Mackay, 1979). These tend to contain fairly simple mathematical descriptions of the natural environment and/or its food-chains. This is because they are designed to gain a qualitative and quantitative understanding of the behavior and fate of chemicals with a multimedia behavior. As discussed in detail by Wania (Wania, 1999a), these models typically subdivide the environment into an appropriate number of compartments (media, or boxes) which are all assumed to be homogenous and well mixed (e.g. homogeneous environmental characteristics and chemical concentrations within the whole water phase). These models then calculate the distribution across and within media (e.g. sorbed to suspended solids and dissolved in water). The models thus integrate information on multiple and interacting processes of partitioning, transport, and transformation into a comprehensive, yet readily understandable, picture of a chemicals fate in the environment. However, at least the early Mackay-type of models are characterized by a low spatial and temporal resolution. Citing Wania (Wania, 1999a) *“It is important to note that this low spatial and temporal resolution often is a deliberate restriction rather than a regrettable shortcoming. This is based on the belief that the predictive capability of numerical models of environmental POP behavior is not limited by the resolution of atmospheric transport processes, but rather by the uncertainties inherent in emission estimates, physical-chemical properties, degradation rates, and air-surface exchange descriptions of POPs. Adding complexity in the presence of such uncertainty does not improve a model.”* In other words, multimedia box modelling approaches aim to avoid over-parameterization with respect to available empirical input data by deliberately avoiding high spatial and temporal resolution. This is also beneficial, as it facilitates transparency in model outcomes and to relatively easily carry out model uncertainty and sensitivity analyses. This is far more difficult for highly resolved models.

Yet, there are complementary approaches from the other school of models which may be classified as “transport-oriented”. These transport-oriented models have typically evolved from the geophysical research community. Hence, they are based on models that contain more detailed and realistic descriptions of either atmospheric or oceanic transport. Typically, these models have a high temporal and spatial resolution and are much more computationally intensive than fugacity-based box models. The atmospheric transport-oriented models have proven immensely useful, e.g. to predict source-receptor relationships or long-range transport of classical air pollutants. However, they are not immediately applicable to multimedia chemicals because they often do not take into account that many POP-like chemicals can undergo reversible atmospheric deposition (i.e. the grasshopper effect). A similar reasoning applies for transport-oriented oceanic models which without significant modifications are ill-equipped to explicitly consider reversible exchange with both sediments and the atmosphere (Johansson et al., 2013).

However, over the last decade or so, many transport-oriented models have started to include intermedia exchange processes to facilitate simulations of multimedia chemicals (Hansen et al., 2004). At the same time, parts of the multimedia modelling community have moved towards including higher spatial and temporal resolution and enhanced realism in terms of transport processes (Toose et al., 2004), see Figure 3. As of today, the distinction between the Mackay-type multimedia models and the transport-oriented models is becoming increasingly blurred and somehow superficial as the two approaches tend to converge. Yet, the accuracy of

results of any modelling study is by the end of the day limited by the accuracy of input data, including their spatial and temporal variability.

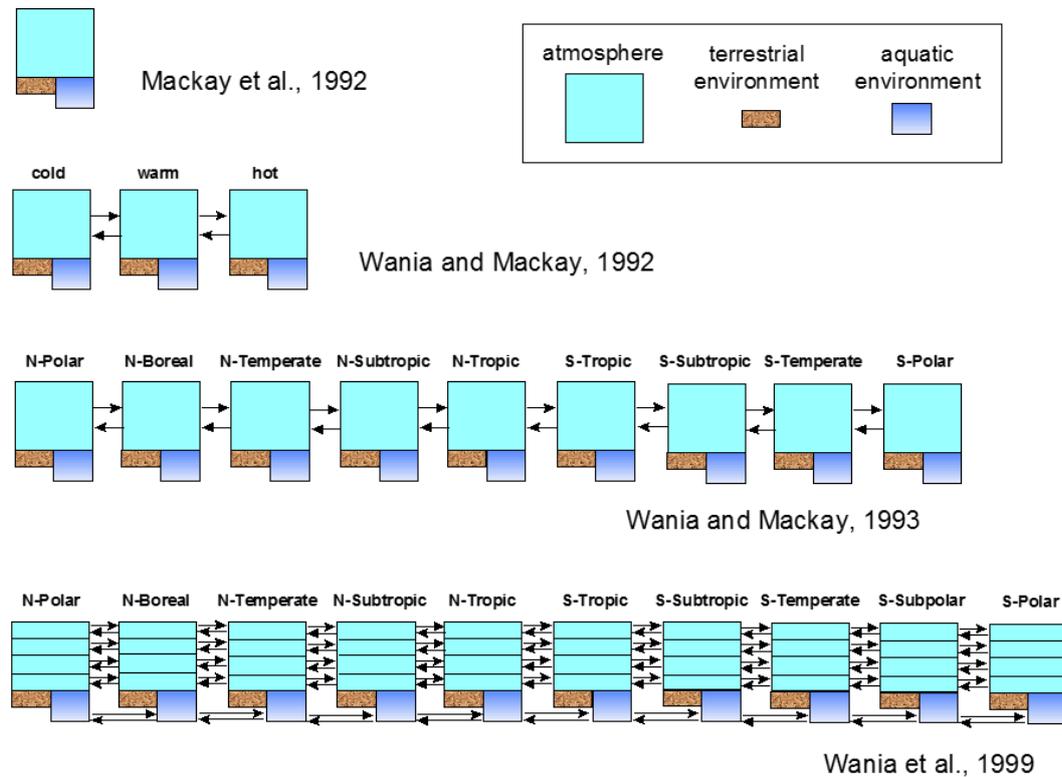


Figure 3: Evolution of the global distribution model for persistent organic pollutants by Wania and Mackay from a simple box model to a zonally averaged, two-dimensional multimedia model (Wania, 1999a).

For chemicals of emerging concern, which are almost by definition data-poor substances, a simple approach is often prudent. This is because it is often both difficult and expensive to measure concentrations of chemicals of emerging concern in the environment. This limits the potential for a comprehensive evaluation of these chemicals in time and space. This also illustrates why simple multimedia models may be particularly suitable for lesser studied pollutants. These models could help to complement the often fragmented measurement data that is available, and hence to provide a more holistic perspective than can be obtained on the basis of the empirical data alone. This perspective is at the core of this project and one of the key messages in this report.

2.4 Models used in this project

As indicated above, multimedia models tend not only to have different scientific origins but the main research questions which have fostered the development of each model may equally have varied widely. There is therefore no such thing as “one” supermodel available which is the right tool for any application. Rather, the different models selected for this project were those deemed best equipped to address our main research questions. These models are described below and include a site-specific dynamic fate and transport model for the Inner Oslofjord linked with the dynamic marine food-chain model in ACC-HUMAN, the dynamic integrated

CoZMoMAN model, the screening-level model RAIDAR, as well as the transport-oriented multimedia model DEHM-POP.

2.4.1 CoZMoMAN

CoZMoMAN (Breivik et al., 2010) was selected for the modelling work involving SCCPs in this project (Chapter 3.2) as well as the screening activities (Chapter 3.3). CoZMoMAN (Figure 4) is a linked version of the models CoZMoPOP 2 (Wania et al., 2006) and ACC-HUMAN (Czub and McLachlan, 2004). The physical fate module of CoZMoMAN calculates the long-term fate of organic contaminants in the drainage basin of a large lake (or in a coastal environment), and includes up to 19 compartments describing forest (deciduous and coniferous canopy), soils (forest soil, agricultural soil, uncultivated soil), a fresh water body (fresh water and two sediment compartments) and a user-defined number of fresh water or marine water units (e.g. representing the estuarine, coastal, open, and deep water compartments). The bioaccumulation module calculates human body burdens and lipid normalized tissue concentrations as a consequence of exposure through an aquatic and an agricultural food chain. Human exposure occurs through the dietary sources of fish, beef, and dairy products as well as drinking water and inhalation. An overall model evaluation for selected PCBs in the western part of the Baltic Sea drainage basin (Sweden including large areas of Norway, Denmark, and Finland) revealed that CoZMoMAN predicted PCB concentrations in 11 key model compartments (including air, water, soil, sediment, fish, dairy products, beef, and human breastmilk) to typically within a factor of 2-4 (Breivik et al., 2010).

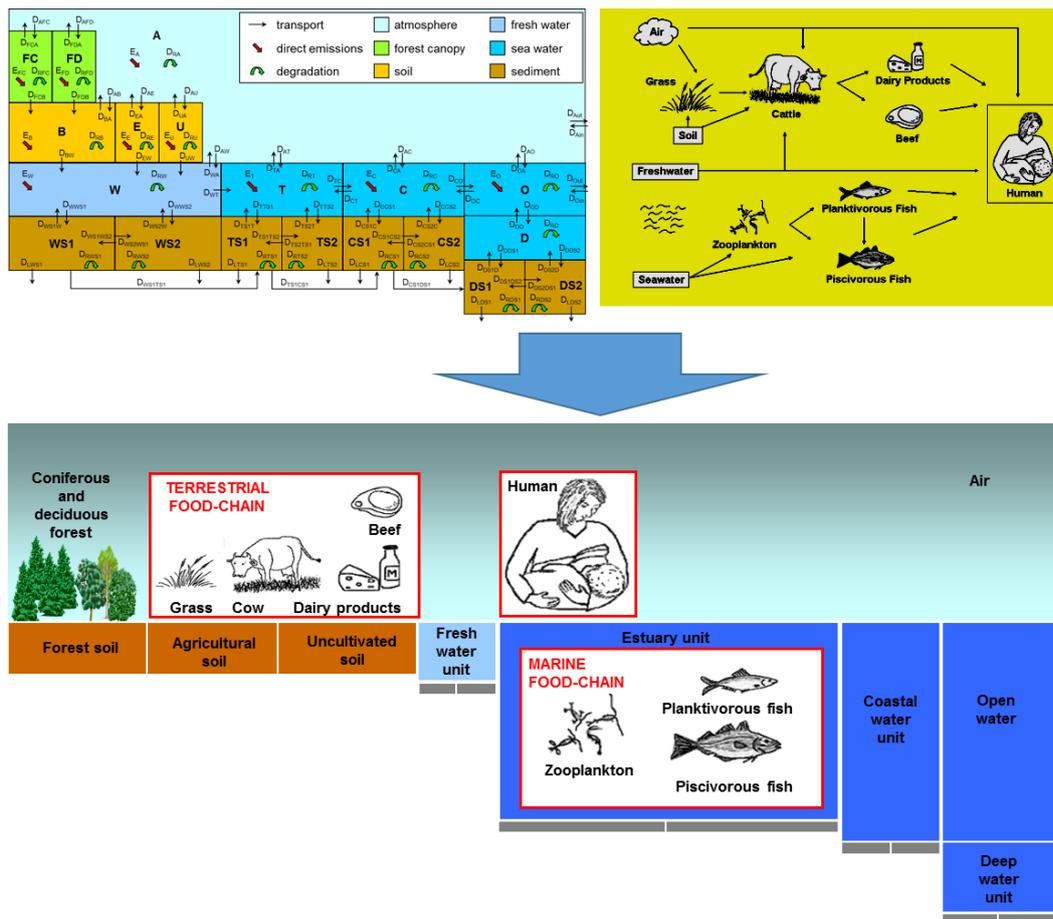


Figure 4: CoZMoMAN (Breivik et al., 2010) (bottom) is a linked integrated model, consisting of CoZMo-POP 2 (Wania et al., 2006) (upper left) and ACC-HUMAN (Czub and McLachlan, 2004) (upper right).

The potential of CoZMoMAN has afterwards been explored in a series of papers in *Environmental Health Perspectives*, directed towards a mechanistic understanding of human biomonitoring studies (Quinn et al., 2011, Quinn and Wania, 2012). It has been used to decipher the main controlling factors which dictates observed temporal trends of PCBs in a cohort of Norwegian men from 1979 to 2007 (Nøst et al., 2013). Also, an interesting outcome of the most recent work using CoZMoMAN is that the effectiveness of fish consumption advisories for long-lived organic contaminants, such as PCB-153, is questioned (Binnington et al., 2014).

The CoZMoMAN model, originally developed at NILU in collaboration with scientists at Stockholm University and University of Toronto, is available through internet free-of-charge and can be operated on any windows-based computer (<http://www.scar.utoronto.ca/~wania/downloads.html>).

2.4.2 The Oslofjord POP model and ACC-HUMAN

The Oslofjord POP model is a dynamic multimedia fate model with a limited spatial resolution and which is site-specific for the Inner Oslofjord (see Figure 5). The detailed equations contained within the model are described in a technical report (Breivik et al., 2003). It was originally developed and applied to simulate the fate of selected PCBs in the fjord during an earlier project funded by the Norwegian Research Council (1405320/720), with the main results described in Breivik et al. (Breivik et al., 2004). A key finding was that the atmosphere was predicted to

contribute far more extensively to the PCB-load of the Inner Oslofjord compared to leaching of PCBs from the contaminated sediments in the innermost harbor. The project illustrated how a successfully evaluated² model offered new insights on the more important sources controlling the overall fate of PCBs in this marine system. These insights could not have been rationalized without recognizing that PCBs are truly multimedia pollutants. An inevitable conclusion was that control strategies, if directed towards the most contaminated sediments in the harbor alone, would be expected to have a limited effect on future PCB recovery rates for the Inner Oslofjord (Breivik et al., 2004).

In the current project, the Oslofjord POP model was linked to the marine food-chain model of ACC-HUMAN originally developed by Stockholm University (see Chapter 2.4.1). These models were used in combination to explore whether the high concentrations of cVMSs which had been reported by NILU in an early screening project (Schlabach et al., 2007, Kaj et al., 2005) could be explained from a mechanistic point of view (Chapter 3.1.1). The ACC-HUMAN model is freely available online (<http://www.itm.su.se/page.php?pid=117>).

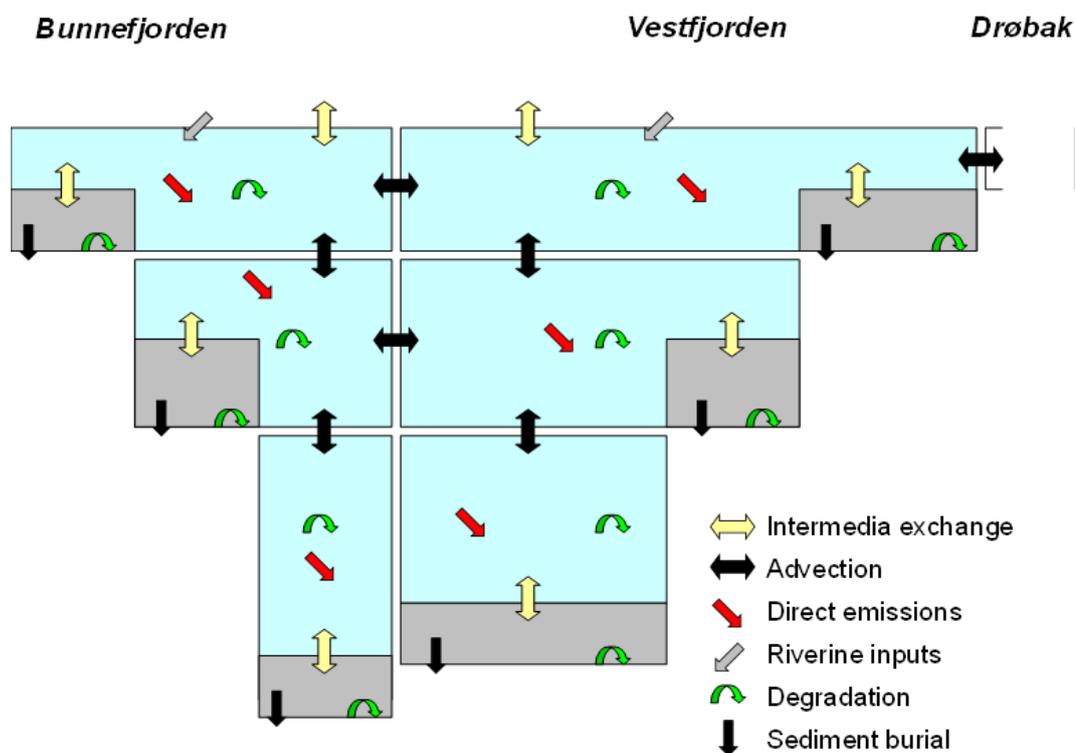


Figure 5: The Oslofjord POP model (Breivik et al., 2004).

² It is impossible to validate a model. However a model may (and indeed should) be evaluated with respect to its capability to reproduce the key features of the observed environmental behavior. In other words, to demonstrate that the model is capable of replicating measurements before making inferences about the fate which cannot be deduced from measurements alone.

2.4.3 RAIDAR

The RAIDAR (Risk Assessment, IDentification, And Ranking) model (Figure 6) was developed as a screening level tool to evaluate chemical fate and effects in the environment (Arnot et al., 2006, Arnot and Mackay, 2008). In contrast to CoZMoMAN and Oslofjord POP it is a steady-state model (i.e. it does not take temporal effects into account), and it is parameterized for an evaluative environment rather than a specifically defined regional model domain. The compartmental divisions for the physical environment are simpler than in CoZMoMAN, consisting of only four compartments (atmosphere, soil, water, sediments). On the other hand, RAIDAR includes more complex food-chains and includes aquatic, benthic, avian, terrestrial, and agricultural species as well as humans. In addition to predict environmental and biotic concentrations, it can also incorporate toxicological endpoints and work in a “reverse” direction. This way, it can calculate critical emission rates for the most sensitive endpoint organisms, and calculate exposure, hazard, and risk assessment factors (EAF, HAF, and RAF, respectively) (Arnot and Mackay, 2008). While EAF only incorporates considerations about persistence and bioaccumulation, HAF also includes toxicity, and RAF is the most complex that additionally includes quantity information.

RAIDAR has already been used in several small and large-scale screening studies of chemicals in commerce (Arnot and Mackay, 2008, Arnot et al., 2010, Gama et al., 2012, Gouin et al., 2012), and it was also used for the screening activities in this project (Chapter 3.3). The RAIDAR model can be downloaded free of charge from http://www.arnotresearch.com/index_download1.html#!/page_Downloads.

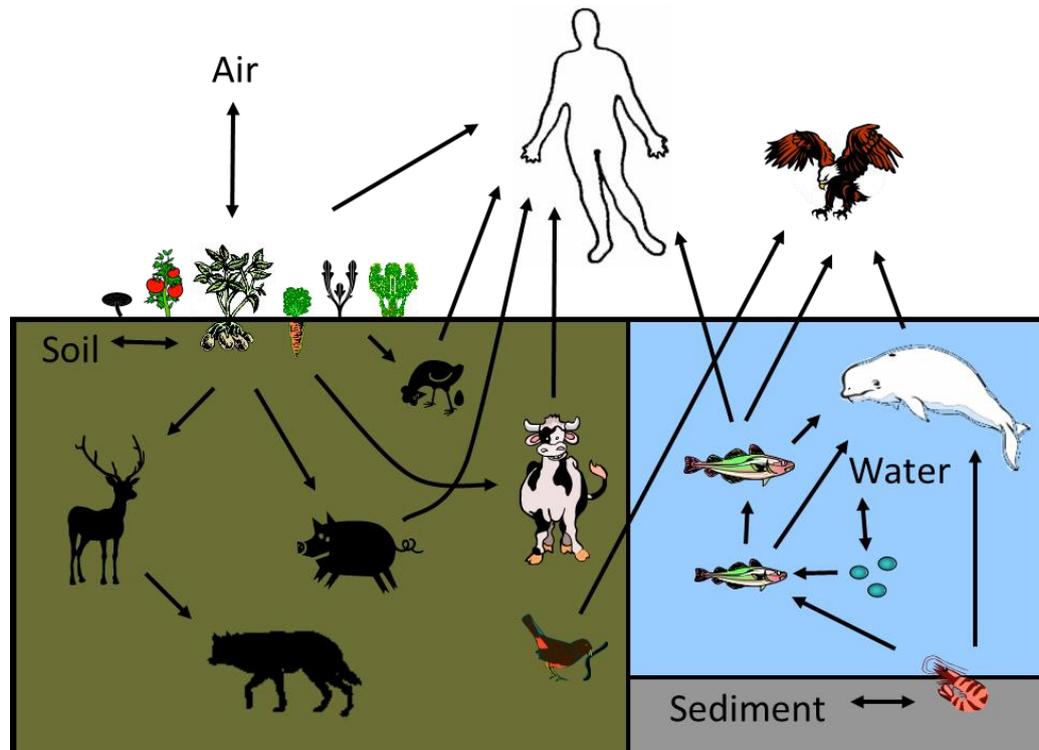


Figure 6: The RAIDAR model (Arnot et al., 2006, Arnot and Mackay, 2008).

2.4.4 DEHM-POP

As indicated earlier, multimedia models of the Mackay-type typically assume “average” weather and climatic conditions (constant drizzle, average wind speeds etc.). Thus, they were not developed to model actual meteorological variability from year to year, including specific long-range transport events. Because of this, there are fundamental difficulties in directly comparing predicted and measured air concentrations collected over short time-periods at a specific measurement point. For the research campaign carried out for cVMSs at Zeppelin, Svalbard, (Chapter 3.1.2) it was therefore deemed essential to explore the utility of a transport-oriented multimedia model. DEHM-POP (Danish Eulerian Hemispherical Model) is a highly temporally and spatially resolved 3-D atmospheric circulation model for the Northern Hemisphere³ (Figure 7). It has been extended to include atmospheric fate processes relevant for POPs, including exchange with various underlying surface media (Hansen et al., 2004, Hansen et al., 2008).

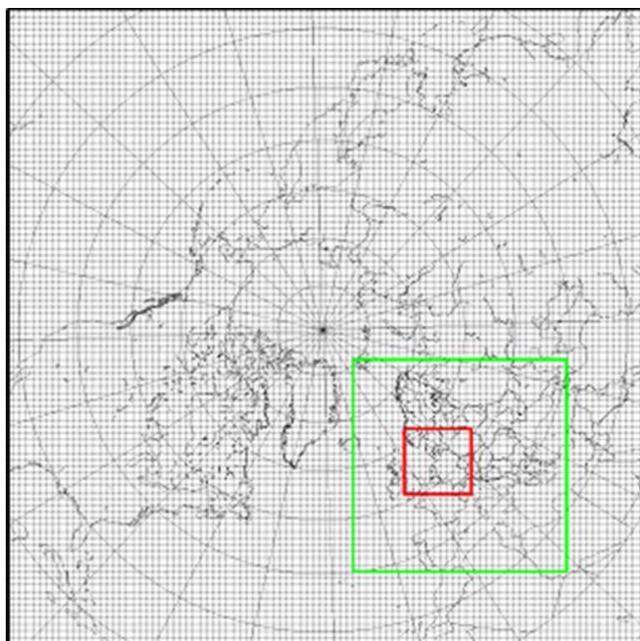


Figure 7: The three domains of the DEHM-POP model³.

3 Case-studies

As already mentioned, four case studies were selected in this project (i) cVMSs in the Inner Oslofjord, (ii) cVMSs in the Norwegian Arctic, (iii) SCCPs in the Nordic environment and (iv) risk-based model screening of chemicals in commerce in the Nordic countries.. This chapter provides a brief background to and description of these studies, and highlights their key results with a stronger focus on the model results than the monitoring results. The interested reader can consult the published scientific literature for details (Arnot et al., 2012, Krogseth et al., 2013a, Krogseth et al., 2013b, Krogseth et al., 2013c, Whelan and Breivik, 2013, Breivik et al., 2012,

³ <http://envs.au.dk/en/knowledge/air/models/dehm/>

Krogseth, 2013). The chemical structures of cVMSs and SCCPs and their positions in the chemical space plot are illustrated in Figure 8 and 9, respectively.

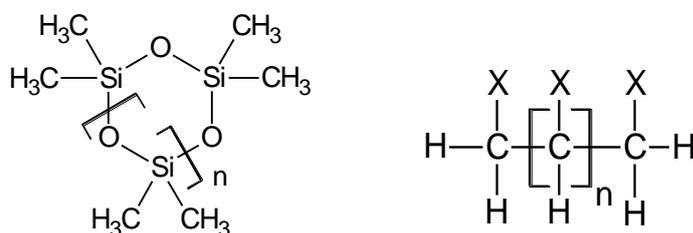


Figure 8: Molecular structures of cVMSs (left) and SCCPs (right). For cVMSs, $n = 1 - 4$ for D3 (hexamethylcyclotrisiloxane), D4 (octamethylcyclotetrasiloxane), D5 (decamethylcyclopentasiloxane), and D6 (dodecamethylcyclohexasiloxane), respectively. For SCCPs with 30-70 % Cl by mass, $n = 8 - 11$ with X representing either H or Cl ($1 < Cl < n + 2$).

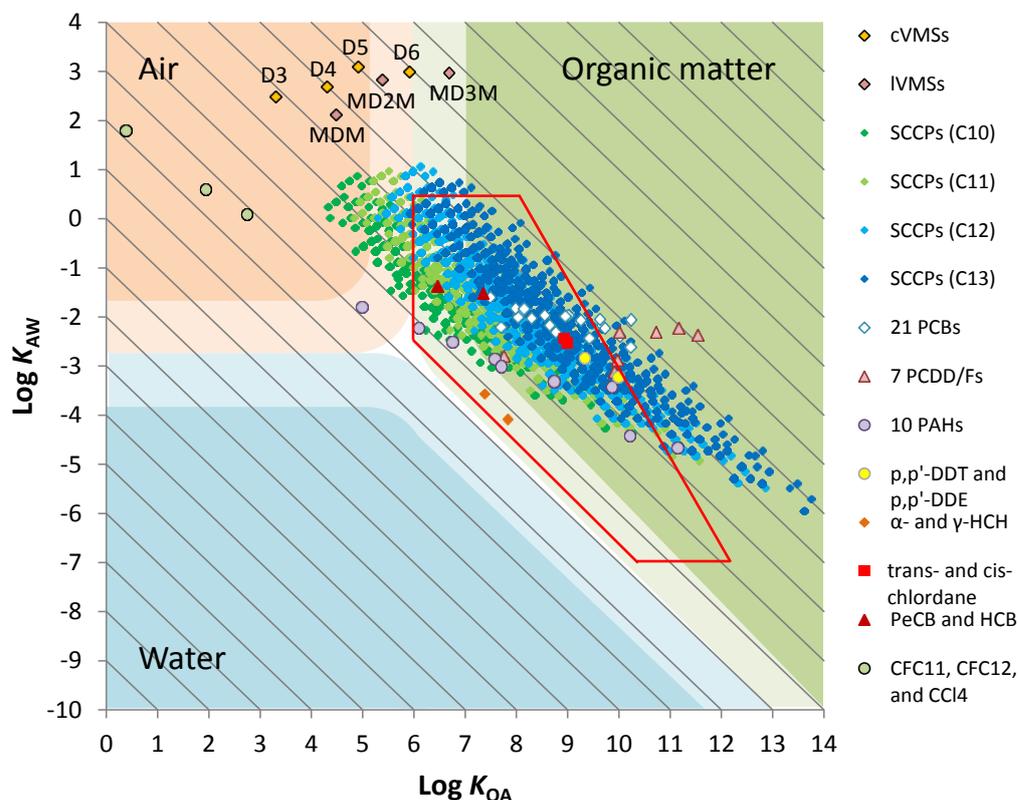


Figure 9: Chemical space plot where the dark and lighter coloured fields show predicted phase distribution in the environment with $> 90\%$ and $> 50\%$ of the total mass, respectively, residing in air, water, or organic matter, based on a hypothetical environment and the assumption that the chemicals are perfectly persistent (Gawor and Wania, 2013, Gouin et al., 2000). The red outline shows typical partitioning properties of chemicals with a high accumulation potential in the Arctic environment and food-chains (Brown and Wania, 2008). Partitioning properties are displayed for cVMSs, linear VMSs, SCCPs with 30-70 % Cl by mass, and selected organic contaminants (Krogseth, 2013).

3.1 Cyclic volatile methyl siloxanes (cVMSs)

Volatile methyl siloxanes (VMSs) are organosilicone compounds that consist of a backbone of alternating oxygen and silicone atoms with methyl side groups. The structures are either cyclic or linear, and the cyclic VMSs (cVMSs) have been the main focus in this project. The main uses of cVMSs are in the production of silicone polymers and in personal care products, as well as in a range of technical applications. There are currently no restrictions on the use and production of cVMSs. The highest emissions of cVMSs are from the use of personal care products, either through wastewater effluents or directly through volatilization to the atmosphere (Wang et al., 2012). The last years have seen increasing scientific and regulatory focus in particular on the three cVMSs octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6), due to their suspected potential for persistence, bioaccumulation, and long-range atmospheric transport. While D4 has been classified as a reproductive toxicant, there is still very limited information on possible adverse effects of D5 and D6 (Brooke et al., 2009a, Brooke et al., 2009c, Brooke et al., 2009b).

The cVMSs combine a high hydrophobicity with a very high volatility (Figure 9). cVMSs emitted to the atmosphere are believed to mainly stay in the atmosphere and not partition to particles or to deposit to surface media. On the other hand, cVMSs emitted through wastewater effluents are expected to be found in compartments rich in lipids and organic carbon such as in fish and sediments as they have a very low water solubility (Figure 9). As a result, the atmosphere, sediments, and aquatic water-respiring organisms are considered to be key compartments for cVMSs.

Trace levels of cVMSs in the environment are very challenging to measure, as samples are easily contaminated from the presence of cVMSs in indoor air, laboratory equipment, and in personal care products (Varaprath et al., 2006). Consequently, only a few laboratories are currently analyzing for cVMSs in environmental samples, of which NILU is one of the most experienced ones (Warner et al., 2012, Warner et al., 2010). This means that existing environmental measurements of cVMSs are scarce; another good reason for using models to understand the environmental behavior of cVMSs. This project focused on cVMSs in both an aquatic environment receiving direct emissions of cVMSs (the Inner Oslofjord) (Whelan and Breivik, 2013) as well as a remote atmospheric site (the Zeppelin observatory) (Krogseth et al., 2013b), with the aim to increase the understanding of cVMSs in these disparate environments.

3.1.1 cVMSs in the Inner Oslofjord

In 2005 and 2007, two reports were published that showed elevated concentrations of cVMSs in liver from cod sampled in the Inner Oslofjord, compared to cod from other sites in the Nordic countries (Kaj et al., 2005, Schlabach et al., 2007). Partly because of this, the Oslofjord POP Model was used in combination with the aquatic component of ACC-HUMAN to attempt to mechanistically explain the observed concentrations. At the same time, it provided a good possibility to explore aquatic exposure and pelagic food chain transfer of cVMSs in an urban, marine food chain using a dynamic multimedia model (Whelan and Breivik, 2013). In particular, this

study is relevant for the ongoing scientific debate on whether or not cVMSs bioaccumulate in aquatic food chains (Borgå et al., 2013, McGoldrick et al., 2014).

The Oslofjord POP model was used to model the fate of D4, D5, and D6 in the physical environment of the Inner Oslofjord based on the chemical properties of cVMSs and estimated emissions of cVMSs from the wastewater treatment plants (WWTPs) in Oslo. The predicted concentrations of cVMSs in the dissolved water phase were then used as input to the ACC-HUMAN model to predict concentrations at three trophic levels, represented by zooplankton, herring, and cod.

The predicted concentrations of cVMSs in the influent to the WWTPs were up to 8 times higher than previously measured in the influent to Bekkelaget and VEAS WWTPs. This could be because the per capita usage of personal care products is lower in Norway than in the UK where the numbers had been derived from, or because the assumed 10% wash off for cosmetic products was too high. The consistency between predicted and measured cVMS concentrations in WWTP effluent was better, suggesting that the removal of cVMSs in the treatment process may have been overestimated (Whelan and Breivik, 2013).

The estimated concentrations from the Oslofjord POP Model of cVMSs in water and sediments were highest for D5, followed by D6 and then D4. The concentrations in water were predicted to be below current analytical detection limits, and to rapidly decrease if emissions were to cease. In earlier monitoring studies, cVMSs in the water of Oslofjorden were not measured above the detection limits of 20-30 ng/L. The predicted concentrations in sediment compared well with the measured concentrations of 93-920 ng/g dw for D5, <17-100 ng/g dw for D6, and <38 ng/g dw for D4 (Schlabach et al., 2007). This good consistency supports the validity of the model predictions. The most important processes for removal of cVMSs from the water phase were predicted to be degradation through hydrolysis for D4, and volatilization for D5 and D6. In sediments, degradation of cVMSs is very slow, except for D4, and the major process for removal of cVMSs was predicted to be sediment burial.

Compared to measurements, the predicted concentrations in biota from ACC-HUMAN were underestimated for D4, while they were overestimated for D5 and D6. The model predicted trophic dilution of all cVMSs, i.e. higher concentrations in zooplankton than in herring than in cod, which is in agreement with measurements from Oslofjorden (Powell et al., 2010). Experimental studies in lake systems have shown both trophic dilution (McGoldrick et al., 2014, Powell et al., 2009) and trophic magnification (Borgå et al., 2012, Borgå et al., 2013) of cVMSs, and this issue is still not fully understood. In the model, the prediction of trophic dilution could be explained by the reduced gut uptake efficiency of cVMSs due to their high hydrophobicity as well as biotransformation of cVMSs in fish. The comparison between the model and the measured data suggested that the biotransformation rate may have been underestimated for D4 and overestimated for D6.

Overall, the model predictions for the environmental and food chain behavior of cVMSs in the Inner Oslofjord seemed to be reasonable, despite some mismatches which highlight remaining uncertainties. Of these, the uncertainties in

biotransformation rate constants and emission rates of cVMSs are among key issues that need to be addressed. The application of dynamic models to explore the fate, transport, and food-web transfer of cVMSs in this study generated several useful insights. This includes insights about the probable dominance of different loss processes of cVMSs in the environment and the importance of biotransformation in influencing trophic transfer. Future use of this approach is encouraged to increase the understanding of possible bioaccumulation of cVMSs in both marine and fresh water environments. It would also be interesting to incorporate a benthic link in the model to investigate possible bioconcentration of cVMSs from the sediments to benthic-dwelling organisms, followed by propagation through the benthic and benthic-pelagic food webs. The influence of environmental characteristics is also a key issue, as the behavior of cVMSs have been shown to vary considerably between different aquatic systems. Some of these questions will be looked into in a new project that combines modeling and measurements - "Nordic lake exposure to cyclic siloxanes: assessment of transport, distribution, and fate" - which is led by NILU and that was recently funded by the Research Council of Norway under the Miljø 2015 program (259).

3.1.2 cVMSs in the Arctic atmosphere

The high volatility of cVMSs means that the majority of the environmental burden of cVMSs resides in the atmosphere. The last years, several multimedia modeling studies have been done for the behavior of cVMSs, in particular of D5, in the atmosphere (MacLeod et al., 2011, McLachlan et al., 2010, Navea et al., 2011, Xu and Wania, 2012). The major atmospheric removal mechanism of cVMSs is believed to be degradation by hydroxyl radicals that are produced by sunlight (Whelan et al., 2004). As a result, a pronounced seasonality in D5 concentrations is expected in Northern environments that have a strong seasonality in the amount of sunlight (McLachlan et al., 2010). cVMSs have also been predicted to be able to undergo long-range atmospheric transport to the Arctic, although they are not believed to be deposited to surface media in the Arctic to the same extent as semivolatile POPs (Xu and Wania, 2012). Measurements of cVMSs in background air have previously been restricted by the high method detection limits, but this has now been made feasible by development of methods with lower detection limits (Genualdi et al., 2011, Kierkegaard and McLachlan, 2013, Kierkegaard and McLachlan, 2010, Krogseth et al., 2013b, Krogseth et al., 2013c).

The aim of this study was to evaluate some of the earlier model predictions by investigating the occurrence and seasonality of cVMSs in Arctic air. More specifically, air samples were collected at the Zeppelin observatory (79 °N, 12 °E), Svalbard, from August to December of 2011, by the use of an active air sampling method (Kierkegaard and McLachlan, 2010, Krogseth et al., 2013b). The DEHM-POP model was used to predict the concentrations of D5 at Zeppelin during the sampling period, based on specific meteorological data as well as emission estimates and physical-chemical properties for D5 (Krogseth et al., 2013b, McLachlan et al., 2010). In addition to D5, the air samples were also analyzed for D3 (hexamethylcyclotrisiloxane), D4, and D6.

Both D5 and D6 were measured in the air at Zeppelin above detection limits. The average concentrations of D5 and D6 were 0.73 ± 0.31 and 0.23 ± 0.17 ng/m³ in

late summer (August – October) and 2.94 ± 0.46 and 0.45 ± 0.18 ng/m³ in early winter (November – December), respectively (Figure 10). This is 100-1000 times higher than typical concentrations of PCBs at Zeppelin (Hung et al., 2010). The D5 concentrations at Zeppelin were also comparable to, but somewhat lower than, D5 concentrations measured with the same method in rural Sweden in 2009 (0.3 – 9 ng/m³) and 2011 (5.6 – 28 ng/m³) (Kierkegaard and McLachlan, 2013). The samples in 2011 were collected in the same period as the samples at Zeppelin, and the relatively small gradient between the two sites reflects the long atmospheric half-life of cVMSs during winter at high latitudes (Kierkegaard and McLachlan, 2013). The Zeppelin observatory is located close to the research settlement of Ny Ålesund, but above the local inversion layer. Thus, any impact from local sources is expected to be at a minimum. The fact that D5 and D6 were measured here, confirms that these cVMSs are able to undergo long-range atmospheric transport to the Arctic from source regions much further away. Remote measurements of the presence of chemicals in the Arctic, backed up by model simulations that can mechanistically explain their occurrence and concentrations, is one of the strongest evidences of long-range transport. However, it is not yet known whether, and to which extent, D5 and D6 would be able to deposit from the atmosphere to surface media in the Arctic. The two other cVMSs, D3 and D4, were also measured in the

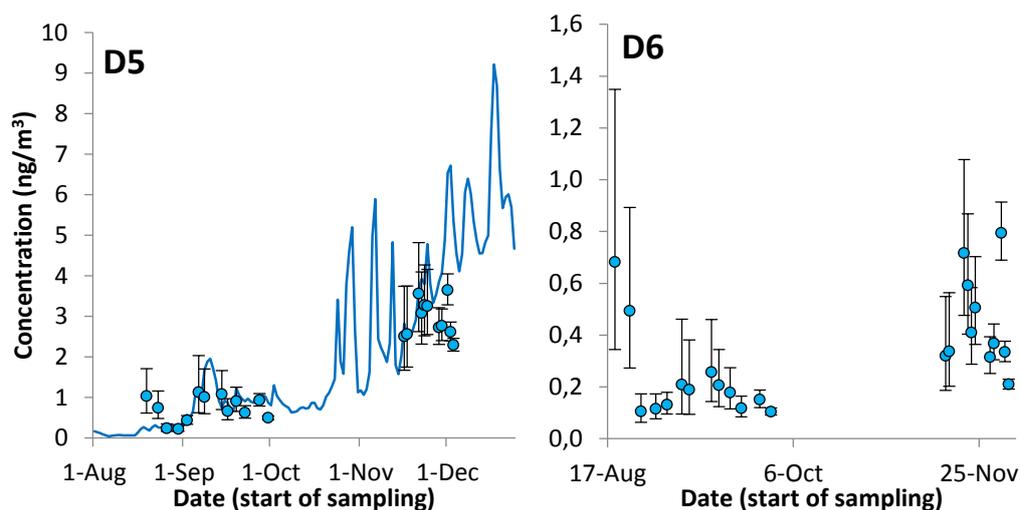


Figure 10: Measured concentrations of D5 and D6 in air at Zeppelin in 2011. The concentrations are storage-corrected with the uncertainties as error bars (Krogseth et al., 2013b). The predicted concentrations from DEHM-POP of D5 in Arctic air from August to December 2011 is displayed as a line. Note the different scales on the y-axes.

samples from Zeppelin, but unfortunately no conclusion could be made about their presence in Arctic air due to some problems with the method for these congeners.

The concentrations of D5 and D6 in the air at Zeppelin were higher in winter than in summer, which is in accordance to the earlier model predictions and the existing theory (MacLeod et al., 2011, McLachlan et al., 2010, Whelan et al., 2004, Xu and Wania, 2012). There was also a good consistency between the measurements and the model predictions from DEHM-POP for D5 at Zeppelin, with an average ratio of the modeled to the measured concentrations of 1.3 ± 0.5 (Figure 10). This means that we appear to have a relatively good understanding of both the emissions as well as the atmospheric behavior of D5. It also increases the confidence in DEHM-POP

to predict atmospheric concentrations of D5, not only in temperate regions but also at high latitudes. The other cVMSs are less well understood, and a less pronounced seasonality for D6 than for D5 at Zeppelin could not be adequately explained by seasonality in atmospheric degradation. The consistency between the DEHM-POP predictions and the measured concentrations for D5 was better in summer than in winter in both this and a previous study (Kierkegaard and McLachlan, 2010). It has been suggested that reaction of cVMSs on aerosols could make an important contribution to removal of cVMSs from the atmosphere when gas-phase degradation by hydroxyl radicals is slow (Navea et al., 2011). This could possibly explain some of the larger discrepancies between the model and the measurements for D5 in winter.

Overall, the air measurements carried out in this project contributed to important insights about the occurrence and seasonality of cVMSs in Arctic air. However, the DEHM-POP model and the insights from it contributed significantly both prior to, and after the study. The previous DEHM-POP simulations (McLachlan et al., 2010) for D5 contributed to postulate the hypothesis of the project, and in advising the ideal time and place for carrying out the sampling. Prior to the field campaigns, the model simulations were invaluable in predicting which concentrations that could be expected, and hence the detection limits that were required to be able to measure cVMSs at Zeppelin. Increased use of model simulations to guide field campaigns is encouraged to maximize the utility of limited resources for sampling and analysis. At the same time, combination of measurements and site- and time- specific model simulations can be very fruitful to gain mechanistic insight into the observations and to identify key uncertainties and knowledge gaps (Halse et al., 2013).

3.2 Short chain chlorinated paraffins (SCCPs)

Short chain chlorinated paraffins (SCCPs) are polychlorinated *n*-alkanes with 10 to 13 carbon atoms and normally 30 to 70 % degree of chlorination on a weight-basis (Fiedler, 2010). The SCCPs are used for various industrial applications such as in metal cutting fluids, as flame retardants, and as plasticizers. SCCPs have been included in the Aarhus protocol, are currently undergoing review for inclusion in the Stockholm Convention, and production and use of SCCPs is increasingly phased out in Europe. However, production is still high in other parts of the world, such as in China which is currently the largest producer of SCCPs (Fiedler, 2010). The technical mixtures are very complex, and the SCCPs can theoretically consist of more than 7000 individual compounds (Shojania, 1999, Tomy et al., 1997). This is challenging for both measurements and modeling of these chemicals. Measured concentrations of SCCPs is often reported as total SCCPs (Σ SCCPs), although the formula group ($C_xCl_yH_{2x+2-y}$) composition is increasingly reported. There is also a considerable uncertainty in the measured concentrations due to various aspects that influence the quantification process of these complex mixtures (Sverko et al., 2012). As for cVMSs, only a few laboratories have good analytical methods for measuring SCCPs, of which NILU is one of them. In models and risk assessments, the SCCPs are often represented with only a single set of properties, which cannot cover the range in physical-chemical properties and reactivity within the group (Gawor and Wania, 2013). This complexity is easy to grasp when the SCCPs are displayed in the chemical space (Figure 9).

3.2.1 SCCPs in the Nordic environment

There were several good reasons for including SCCPs in the Nordic environment as a case study in this project. The CoZMoMAN model has been parameterized for the environmental characteristics of the western part of the Baltic Sea drainage basin. In this region there is also available measurement data for SCCPs, which facilitates a model-measurement comparison. As CoZMoMAN has previously only been thoroughly evaluated for PCBs, this provided a good opportunity for evaluating the model for a more complex and less well-known group of compounds. At the same time the mechanistic understanding of the behavior of SCCPs in the Nordic environment could be evaluated. In addition, it provided an opportunity to model the individual formula groups of SCCPs rather than just one “average” SCCP, and thus to evaluate the variability within the group.

Emissions of SCCPs to the model domain (the western part of the Baltic Sea drainage basin) were estimated based on reported use of SCCPs in the database for substances in preparations in the Nordic countries (SPIN) in Norway, Sweden, Denmark, and Finland in the years 2000-2007. Model simulations were performed for individual formula groups of SCCPs, and information on the composition of technical mixtures of SCCPs were used to estimate concentrations of Σ SCCPs. The predictions were compared to environmental measurements of SCCPs, preferably from the Nordic countries in the years 2000 to 2007 (Krogseth et al., 2013a).

The total predicted emissions of Σ SCCPs to the model domain were 2.08 kilotonnes per year (t/y), with a range from 0.71 to 15.35 t/y. This is in good accordance with other emission estimates for SCCPs scaled to this region, including the recently released report on the Baltic Sea Action Plan Hazardous Substances (Andersson et al., 2012). The emissions were predicted to be mainly released to water, with minor emissions to air (9 %) and soil (4 %). The final predicted composition of the emissions consisted of 22 formula groups and had an average chlorination degree of 61 %.

The predicted concentrations of Σ SCCPs from CoZMoMAN corresponded best with measured concentrations in the Nordic environment when the highest emission estimate was used (15 t/y). When using this emission estimate, the ratio between the median value of the measured concentrations and predicted concentrations was typically within a factor of 6, including concentrations in air, the three soil compartments, freshwater sediments, cod, and human breast milk (Figure 11). This is small when put in a larger context, in particular considering that the measured concentrations in different media span ten orders of magnitude. The good consistency across a range of compartments means that the model succeeded in reproducing the concentration ratios in the different environmental media, and that we have a relatively good mechanistic understanding of the environmental behavior of SCCPs. When CoZMoMAN was evaluated for PCBs, the ratio between

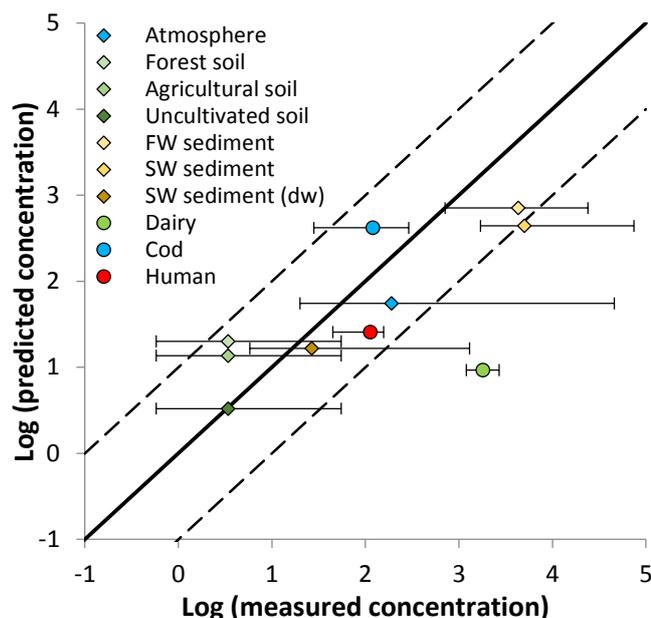


Figure 11: The logarithm of the predicted Σ SCCPs concentrations based on the maximum emission scenario (15 t/y) versus the logarithm of measured Σ SCCPs concentrations. The error bars display the ranges in measured concentrations. The solid line is the one-to-one line between predictions and measurements, while the dashed lines mark deviations of \pm one order of magnitude. FW = freshwater, SW = seawater, dw = dry weight (Krogseth et al., 2013a).

predictions and measurements were typically within a factor of 2 to 4 (Breivik et al., 2010). The fact that the model performed nearly equally well for a less well-known group of compounds as for the PCBs strengthens the confidence in the model. This implies that CoZMoMAN is likely to also work well for other compound groups that are similar in nature to PCBs and SCCPs.

The model performed less well in reproducing the observed composition of SCCPs in the environment, i.e. the formula group profiles. In particular, the predicted degree of chlorination was overestimated in sediments, fish, and humans compared to what have been measured in the Baltic Sea environment (Figure 12). However, this discrepancy is not surprising considering the limited information about individual formula groups. It could be explained by overestimation of the chlorination degree of the emissions, underestimation of the environmental and metabolic reactivity of the highly chlorinated formula groups, or a combination of both. Considerable variation in environmental behavior and distribution was predicted between the individual formula groups. It was illustrated in the study that reasonable predicted concentrations of Σ SCCPs could be achieved by using only a single set of properties for the SCCPs, for example based on the properties that were used in the European Union Risk Assessment Reports for SCCPs (European Chemicals Bureau, 2000, European Chemicals Bureau, 2008). However, this should only be done with great caution. The representativeness of a single set of properties cannot be assumed because it will depend on the composition of the SCCP emissions as well as on the environmental conditions.

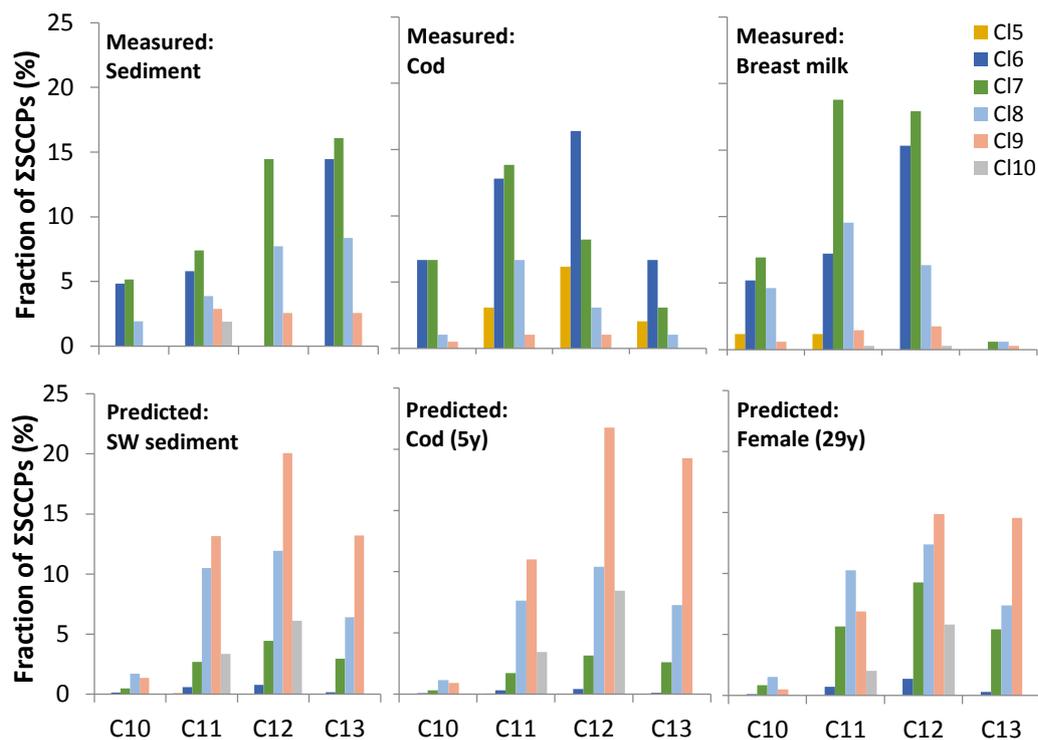


Figure 12: Measured SCCPs composition in sediment (Hüttig and Oehme, 2006) and cod (Reth et al., 2005) from the Baltic Sea and in human breast milk from the United Kingdom (Thomas et al., 2006), as well as predicted SCCPs composition in seawater sediments, 5 year old cod, and 29 year old human female (Krogseth et al., 2013a).

Overall, this study was helpful in several ways. It provided an evaluation of our current mechanistic understanding of the environmental behavior of SCCPs, which appears to be relatively good for Σ SCCPs, but less so for the individual formula groups. The study helped to identify and confirm several knowledge gaps and remaining uncertainties for SCCPs. In particular, more information is needed on the emissions of SCCPs, especially on the composition of the emissions, as well as on the environmental degradation and biotransformation half-lives of the formula groups. Moreover, improved and more consistent analytical and quantification methods for SCCPs is needed, in particular to improve comparability across methods and laboratories. The study also increased the confidence in the CoZMoMAN model, and it illustrated the substantial value of combining models and monitoring data in evaluating the understanding of the environmental behavior of organic contaminants.

3.3 Risk-based model screening of chemicals in commerce

The case studies that were carried out in this project for cVMSs and SCCPs are so-called targeted studies, where an individual compound or group of compounds is investigated in detail. However, in the context of the thousands of chemicals that are used and produced today, screening studies that “screen” a large number of chemicals for those that give reason for concern are increasingly popular. These are not contradictory, but complementary, approaches. Non-target analytical methods that can be applied to look for “new” contaminants in environmental samples have been discussed in a NILU-report published last year (Schlabach et al., 2013).

However, screening studies can also be carried out by the use of models. Typically, physical-chemical properties are estimated for chemicals that are included in lists of chemical inventories, and fugacity-based multimedia models can then be used to predict selected relevant endpoints (Brown and Wania, 2008, Muir and Howard, 2006). These endpoints have often been hazard-based, such as the potential for persistence, bioaccumulation, or long-range transport. That they are hazard-based means that they depend on the intrinsic properties of the chemicals, and not on the amounts of the chemicals that are emitted to the environment. However, the question of whether or not the chemicals are potentially harmful to the environment and humans is ultimately a question of quantities – whether the amounts emitted to the environment are high enough to cause adverse effects in humans and wildlife. In contrast to hazard-based approaches, risk-based approaches take emission quantities and/or predicted concentrations in the environment and biota into account. In a cooperation between this project and other projects, three studies that address risk-based model screenings were, and are still, carried out (Arnot et al., 2012, Breivik et al., 2012). Here, they are only briefly presented, as the results from the most relevant project, screening of chemicals in commerce in the Nordic countries, are not yet finalized.

Knowledge about emissions may represent the least understood feature of overall contaminant fate, exposure, and risk (Breivik et al., 2012). Here, a simple and consistent high-throughput emission estimation method was developed that facilitate emission estimation for a large number of chemicals. The method was based upon the European Union Technical Guidance Document for Risk Assessment (European Chemicals Bureau, 2003). As such, it uses information on quantities in commerce, usage patterns, and physical-chemical properties to estimate emissions to air, water, and soil (Breivik et al., 2012). This method was subsequently applied in a screening study where the RAIDAR model was used to prioritize more than 12 000 organic chemicals. The chemicals were ranked based on both predicted exposure to humans through food, air, and water (external exposure) as well as predicted concentrations in humans (internal exposure) (Arnot et al., 2012). Both studies stressed the large uncertainties in predicted emissions that are partly caused by the strict confidentiality with regard to production quantities and use patterns of commercial chemicals. The emission quantities was clearly the greatest contribution to uncertainty in the estimates of external and internal human exposure from the RAIDAR model, and hence also to the uncertainty in the ranking of the chemicals. To address this, a follow-up study that specifically focuses on the Nordic region is underway. In the Nordic countries, the SPIN-database contains information on chemical use patterns and quantities for more than 2000 commercial chemicals for the years 2000 to 2007. This information could potentially be used to reduce the uncertainty in the emission estimates, and hence to increase the confidence in the predicted concentrations and the ranking of chemicals of concern.

4 Summary and conclusions

A key goal of environmental authorities is to minimize the exposure and effects on the environment and humans from harmful organic contaminants. Sound chemical control strategies therefore require the determination of the quantitative relationship between emissions, environmental levels, and human exposure to chemicals of concern (or so-called source-receptor relationships). To achieve this, substantial information is required on which chemicals that are present in the environment and on their concentrations and behaviour in the environment and the food-chains. Large resources are already invested into monitoring trace levels of POPs and screening for chemicals of emerging concern in air, sediments, fish, birds, or other environmental compartments through various monitoring and screening programmes. This report has explored the potential added value of combining empirical results from monitoring and screening studies with the use of multimedia environmental models.

Environmental measurements and modelling approaches each have their strengths and limitations that can complement each other. Model simulations can help to optimize sampling design for measurement campaigns by for example predicting the key physical matrices or biota where the compounds of interest are expected to be found at elevated levels, the anticipated concentrations and hence necessary detection limits, the optimal sampling region or even time of sampling for the specific objectives of the study. Hence, use of limited resources in future monitoring and screening studies can be optimized and invested where they are predicted to maximize the value of the results. This was illustrated by the study of cVMSs in the Arctic atmosphere, where predictions of the atmospheric behavior of D5 was a key to design both the hypotheses, the method development, and the location and timing of the field campaigns.

Models can also serve as tools to rationalize existing observed measurements and hence provide mechanistic explanations for the observations that can be hard to derive from the measurements alone. This was clearly exemplified by the study of cVMSs in the Inner Oslofjord, which was spurred by the detection of elevated levels of cVMSs in fish from this fjord. The models served to rationalize these measurements and to provide important insights into key processes of the environmental and food-chain behavior of cVMSs in this environmental system. Also, the detection of D5 and D6 in air at the Zeppelin observatory is a much stronger evidence for long-range atmospheric transport of these compounds when they in addition can be backed up by mechanistic models that explain the observations.

Models gather the existing understanding about relevant systems and processes in one place. This means that comparisons of model predictions and observations can contribute to evaluate our current understanding, and to identify key knowledge gaps where models and measurements do not agree. This was seen in both the study of cVMSs in the Arctic atmosphere and the Inner Oslofjord, as well as in the study of SCCPs in the Nordic environment where this was one of the key objectives. The latter study also confirmed that our overall understanding of the link between environmental emissions and human body burdens of SCCPs in the Nordic

environment is fair, but also highlighted aspects which require further research for this complex group of chemicals. Moreover, to facilitate these model-measurement comparisons, strategic sampling is encouraged to provide observations that are comparable to results from the model simulations.

Only by combining measurements and models can uncertainties be identified and reduced and confidence in source-receptor relationships increased. The case-studies in this project illustrate the immense value of integrating multimedia models and observations in concert as a tool for improved understanding and management of organic contaminants in the Nordic environment. We hope that these modelling tools could be of relevance to future Norwegian and Nordic screening and monitoring efforts, as well as to relevant policy activities in the Nordic region related to organic contaminants.

5 References

- Andersson, H., Cousins, A.P., Westerdahl, J., Braun, H., Bergfors, L., Brorström-Lundén, E., Pettersson, M., Wickman, T., Jamtrot, A., Parkman, H., Krupanek, J., Fridmanis, J., Toropovs, V., Verta, M., Nielsen, U. (2012) Major sources and flows of the Baltic Sea action plan hazardous substances, WP4 final report. Stockholm, Sweden, IVL Swedish Environmental Research Institute.
- Arnot, J.A., Brown, T.N., Wania, F., Breivik, K., McLachlan, M.S. (2012) Prioritizing chemicals and data requirements for screening-level exposure and risk assessment. *Environ. Health Perspect.*, 120, 1565-1570.
- Arnot, J.A., Mackay, D. (2008) Policies for chemical hazard and risk priority setting: Can persistence, bioaccumulation, toxicity, and quantity information be combined? *Environ. Sci. Technol.*, 42, 4648-4654.
- Arnot, J.A., Mackay, D., Parkerton, T.F., Zaleski, R.T., Warren, C.S. (2010) Multimedia modeling of human exposure to chemical substances: the roles of food web biomagnification and biotransformation. *Environ. Toxicol. Chem.*, 29, 45-55.
- Arnot, J.A., Mackay, D., Webster, E., Southwood, J.M. (2006) Screening level risk assessment model for chemical fate and effects in the environment. *Environ. Sci. Technol.*, 40, 2316-2323.
- Binnington, M.J., Quinn, C.L., McLachlan, M.S., Wania, F. (2014) Evaluating the effectiveness of fish consumption advisories: modeling prenatal, postnatal, and childhood exposures to persistent organic pollutants. *Environ. Health Perspect.*, 122, 178-186.
- Borgå, K., Fjeld, E., Kierkegaard, A., McLachlan, M.S. (2012) Food web accumulation of cyclic siloxanes in Lake Mjøsa, Norway. *Environ. Sci. Technol.*, 46, 6347-6354.
- Borgå, K., Fjeld, E., Kierkegaard, A., McLachlan, M.S. (2013) Consistency in trophic magnification factors of cyclic methyl siloxanes in pelagic freshwater food webs leading to brown trout. *Environ. Sci. Technol.*, 47, 14394-14402.
- Breivik, K., Arnot, J.A., Brown, T.N., McLachlan, M.S., Wania, F. (2012) Screening organic chemicals in commerce for emissions in the context of environmental and human exposure. *J. Environ. Monit.*, 14, 2028-2037.
- Breivik, K., Bjerkgeng, B., Wania, F., Helland, A., Magnusson, J. (2004) Modeling the fate of polychlorinated biphenyls in the inner Oslofjord, Norway. *Environ. Toxicol. Chem.*, 23, 2386-2395.
- Breivik, K., Bjerkgeng, B., Wania, F., Magnusson, J., Helland, A., Pacyna, J.M. (2003) The Oslofjord POP Model v 1.0. A fugacity-based non-steady state non-equilibrium multimedia fate and transport model. Kjeller, Norway, NILU – Norwegian Institute for Air Research (NILU OR 24/2003).
- Breivik, K., Czub, G., McLachlan, M.S., Wania, F. (2010) Towards an understanding of the link between environmental emissions and human body burdens of PCBs using CoZMoMAN. *Environ. Int.*, 36, 85-91.
- Breivik, K., Wania, F. (2003) Expanding the applicability of multimedia fate models to polar organic chemicals. *Environ. Sci. Technol.*, 37, 4934-4943.
- Brooke, D., Crookes, M., Gray, D., Robertson, S. (2009a) Environmental risk assessment report: Decamethylcyclopentasiloxane. Bristol, Wales, Environment Agency of England and Wales.

- Brooke, D., Crookes, M., Gray, D., Robertson, S. (2009b) Environmental risk assessment report: Dodecamethylcyclohexasiloxane. Bristol, Wales, Environment Agency of England and Wales.
- Brooke, D., Crookes, M., Gray, D., Robertson, S. (2009c) Environmental risk assessment report: Octamethylcyclotetrasiloxane. Bristol, Wales, Environment Agency of England and Wales.
- Brown, T.N., Wania, F. (2008) Screening chemicals for the potential to be persistent organic pollutants: A case study of Arctic contaminants. *Environ. Sci. Technol.*, *42*, 5202-5209.
- European Chemicals Bureau (2000) European Union Risk Assessment Report: Alkanes, C10-13, chloro-. Luxembourg (EUR 19010 EN).
- European Chemicals Bureau (2003) Technical Guidance Document on Risk Assessment. Luxembourg (EUR 20418 EN/2).
- European Chemicals Bureau (2008) Updated Risk Assessment of Alkanes, C10-13, chloro-. Luxembourg (EUR 23396 EN).
- Czub, G., McLachlan, M.S. (2004) A food chain model to predict the levels of lipophilic organic contaminants in humans. *Environ. Toxicol. Chem.*, *23*, 2356-2366.
- Czub, G., Wania, F., McLachlan, M.S. (2008) Combining long-range transport and bioaccumulation considerations to identify potential Arctic contaminants. *Environ. Sci. Technol.*, *42*, 3704-3709.
- Fiedler, H. (2010) Short-chain chlorinated paraffins: Production, use and international regulations. In: *The handbook of environmental chemistry: Chlorinated Paraffins*. 1st ed. De Boer, J. Heidelberg, Springer (The handbook of environmental chemistry). pp. 1-40.
- Gama, S., Mackay, D., Arnot, J.A. (2012) Selecting and designing chemicals: application of a mass balance model of chemical fate, exposure and effects in the environment. *Green Chem.*, *14*, 1094-1102.
- Gawor, A., Wania, F. (2013) Using quantitative structural property relationships, chemical fate models, and the chemical partitioning space to investigate the potential for long range transport and bioaccumulation of complex halogenated chemical mixtures. *Environ. Sci. Process. Impacts*, *15*, 1671-1684.
- Genualdi, S.G.S., Harner, T., Cheng, Y., MacLeod, M., Hansen, K.M., van Egmond, R., Shoeib, M., Lee, S.C. (2011) Global distribution of linear and cyclic volatile methyl siloxanes in air. *Environ. Sci. Technol.*, *45*, 3349-3354.
- Gouin, T., Mackay, D., Webster, E., Wania, F. (2000) Screening chemicals for persistence in the environment. *Environ. Sci. Technol.*, *34*, 881-884.
- Gouin, T., van Egmond, R., Price, O.R., Hodges, J.E.N. (2012) Prioritising chemicals used in personal care products in China for environmental risk assessment: Application of the RAIDAR model. *Environ. Pollut.*, *165*, 208-214.
- Halse, A.K., Eckhardt, S., Schlabach, M., Stohl, A., Breivik, K. (2013) Forecasting long-range atmospheric transport episodes of polychlorinated biphenyls using FLEXPART. *Atmos. Environ.*, *71*, 335-339.
- Hansen, K.M., Christensen, J.H., Brandt, J., Frohn, L.M., Geels, C. (2004) Modelling atmospheric transport of alpha-hexachlorocyclohexane in the Northern Hemisphere with a 3-D dynamical model: DEHM-POP. *Atmos. Chem. Phys.*, *4*, 1125-1137.
- Hansen, K.M., Christensen, J.H., Brandt, J., Frohn, L.M., Geels, C., Skjoth, C.A., Li, Y.F. (2008) Modeling short-term variability of alpha-

- hexachlorocyclohexane in Northern Hemispheric air. *J. Geophys. Res. - Atmos.*, *113*, D02310.
- Hung, H., Kallenborn, R., Breivik, K., Su, Y., Brorström-Lundén, E., Olafsdottir, K., Thorlacius, J.M., Leppänen, S., Bossi, R., Skov, H., Manø, S., Patton, G.W., Stern, G., Sverko, E., Fellin, P. (2010) Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006. *Sci. Total Environ.*, *408*, 2854-2873.
- Hüttig, J., Oehme, M. (2006) Congener group patterns of chloroparaffins in marine sediments obtained by chloride attachment chemical ionization and electron capture negative ionization. *Chemosphere*, *64*, 1573-1581.
- Jager, T., Gingnagel, P., Bodar, C.W.M., Hollander, H.A.d., Poel, P.v.d., Rikken, M.G.J., Struijs, J., Veen, M.P.v., Vermeire, T.G. (1998) Evaluation of EUSES: inventory of experiences and validation activities. Bilthoven (RIVM Report 679102048).
- Johansson, N., Wiberg, R., Bertino, L., Kallenborn, R. (2013) Evaluation of "Tilførselsprogrammet". Programme for monitoring and modelling of contaminant loads and levels in Norwegian marine areas. Oslo, Norway, Miljødirektoratet (M 70-2013).
- Kaj, L., Schlabach, M., Andersson, J., Cousins, A.P., Schmidbauer, N., Brorström-Lundén, E. (2005) Siloxanes in the Nordic environment. Copenhagen, Denmark, Nordic Council of Ministers (TemaNord 2005:593).
- Kierkegaard, A., McLachlan, M.S. (2010) Determination of decamethylcyclopentasiloxane in air using commercial solid phase extraction cartridges. *J. Chromatogr. A*, *1217*, 3557-3560.
- Kierkegaard, A., McLachlan, M.S. (2013) Determination of linear and cyclic volatile methylsiloxanes in air at a regional background site in Sweden. *Atmos. Environ.*, *80*, 322-329.
- Krogseth, I.S. (2013) From emissions to exposure - Environmental behavior of volatile methyl siloxanes and short-chain chlorinated paraffins. PhD-thesis, Department of chemistry, biotechnology and food science, Norwegian University of Life Sciences.
- Krogseth, I.S., Breivik, K., Arnot, J.A., Wania, F., Borgen, A.R., Schlabach, M. (2013a) Evaluating the environmental fate of short-chain chlorinated paraffins (SCCPs) in the Nordic environment using a dynamic multimedia model. *Environ. Sci. Process. Impacts*, *15*, 2240-2251.
- Krogseth, I.S., Kierkegaard, A., McLachlan, M.S., Breivik, K., Hansen, K.M., Schlabach, M. (2013b) Occurrence and seasonality of cyclic volatile methyl siloxanes in Arctic air. *Environ. Sci. Technol.*, *47*, 502-509.
- Krogseth, I.S., Zhang, X., Lei, Y.D., Wania, F., Breivik, K. (2013c) Calibration and application of a passive air sampler (XAD-PAS) for volatile methyl siloxanes. *Environ. Sci. Technol.*, *47*, 4463-4470.
- Li, Y.F. (1999) Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997. *Sci. Total Environ.*, *232*, 121-158.
- Mackay, D. (1979) Finding fugacity feasible. *Environ. Sci. Technol.*, *13*, 1218-1223
- Mackay, D. (2001) Multimedia environmental models: The fugacity approach. Boca Raton, FL, CRC Press.
- MacLeod, M., Scheringer, M., McKone, T.E., Hungerbühler, K. (2010) The state of multimedia mass-balance modeling in environmental science and decision-making. *Environ. Sci. Technol.*, *44*, 8360-8364.

- MacLeod, M., von Waldow, H., Tay, P., Armitage, J.M., Wöhrnschimmel, H., Riley, W.J., McKone, T.E., Hungerbühler, K. (2011) BETR global - A geographically-explicit global-scale multimedia contaminant fate model. *Environ. Pollut.*, *159*, 1442-1445.
- McGoldrick, D.J., Chan, C., Drouillard, K.G., Keir, M.J., Clark, M.G., Backus, S.M. (2014) Concentrations and trophic magnification of cyclic siloxanes in aquatic biota from the Western Basin of Lake Erie, Canada. *Environ. Pollut.*, *186*, 141-148.
- McLachlan, M.S., Kierkegaard, A., Hansen, K.M., van Egmond, R., Christensen, J.H., Skjøth, C.A. (2010) Concentrations and fate of decamethylcyclopentasiloxane (D5) in the atmosphere. *Environ. Sci. Technol.*, *44*, 5365-5370.
- Meyer, T., Wania, F., Breivik, K. (2005) Illustrating sensitivity and uncertainty in environmental fate models using partitioning maps. *Environ. Sci. Technol.*, *39*, 3186-3196.
- Muir, D.C.G., Howard, P.H. (2006) Are there other persistent organic pollutants? A challenge for environmental chemists. *Environ. Sci. Technol.*, *40*, 7157-7166.
- Navea, J.G., Young, M.A., Xu, S.H., Grassian, V.H., Stanier, C.O. (2011) The atmospheric lifetimes and concentrations of cyclic methylsiloxanes octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) and the influence of heterogeneous uptake. *Atmos. Environ.*, *45*, 3181-3191.
- Nøst, T.H., Breivik, K., Fuskevåg, O.M., Nieboer, E., Odland, J.O., Sandanger, T.M. (2013) Persistent organic pollutants in Norwegian men from 1979 to 2007: Intraindividual changes, age-period-cohort effects, and model predictions. *Environ. Health Perspect.*, *121*, 1292-1298.
- Powell, D.E., Durham, J., Huff, D.W., Böhmer, T., Gerhards, R., Koerner, M. (2010) Bioaccumulation and trophic transfer of cyclic volatile methylsiloxane (cVMS) materials in the aquatic marine food webs of the inner and outer Oslofjord, Norway. Auburn, MI, USA, Dow Corning Corporation, Health and Environmental Sciences. (HES study no: 11060-108).
- Powell, D.E., Woodburn, K.B., Drotar, K.D., Durham, J., Huff, D.W. (2009) Trophic dilution of cyclic volatile methylsiloxane (cVMS) materials in a temperate freshwater lake. Internal report conducted for Centre Européen des Silicones (Report number 2009-10000-60988).
- Quinn, C.L., Wania, F. (2012) Understanding differences in the body burden-age relationships of bioaccumulating contaminants based on population cross sections versus individuals. *Environ. Health Perspect.*, *120*, 554-559.
- Quinn, C.L., Wania, F., Czub, G., Breivik, K. (2011) Investigating intergenerational differences in human PCB exposure due to variable emissions and reproductive behaviors. *Environ. Health Perspect.*, *119*, 641-646.
- Reth, M., Zencak, Z., Oehme, M. (2005) First study of congener group patterns and concentrations of short- and medium-chain chlorinated paraffins in fish from the North and Baltic Sea. *Chemosphere*, *58*, 847-854.
- Schlabach, M., Andersen, M.S., Green, N., Schøyen, M., Kaj, L. (2007) Siloxanes in the environment of the Inner Oslofjord. Kjeller, NILU (Norwegian Pollution Control Authority. Report no 986/2007. TA-2269/2007) (NILU OR 27/2007).
- Schlabach, M., Haglund, P., Rostkowski, P., Dye, C. (2013) Non-target screening - A powerful tool for selecting environmental pollutants. Kjeller, NILU (Miljødirektoratet M-27/2013) (NILU OR 9/2013).

- Shojania, S. (1999) The enumeration of isomeric structures for polychlorinated n-alkanes. *Chemosphere*, 38, 2125-2141.
- SPIN (2014) Substances in Preparations in Nordic Countries [online]. Nordic Product Registers. Available from www.spin2000.net [Accessed September 2012].
- Sverko, E., Tomy, G.T., Marvin, C.H., Muir, D.C.G. (2012) Improving the quality of environmental measurements on short chain chlorinated paraffins to support global regulatory efforts. *Environ. Sci. Technol.*, 46, 4697-4698.
- Thomas, G.O., Farrar, D., Braekevelt, E., Stern, G., Kalantzi, O.I., Martin, F.L., Jones, K.C. (2006) Short and medium chain length chlorinated paraffins in UK human milk fat. *Environ. Int.*, 32, 34-40.
- Tomy, G.T., Stern, G.A., Muir, D.C.G., Fisk, A.T., Cymbalisky, C.D., Westmore, J.B. (1997) Quantifying C-10-C-13 polychloroalkanes in environmental samples by high-resolution gas chromatography electron capture negative ion high resolution mass spectrometry. *Anal. Chem.*, 69, 2762-2771.
- Toose, L., Woodfine, D.G., MacLeod, M., Mackay, D., Gouin, J. (2004) BETR-World: a geographically explicit model of chemical fate: application to transport of alpha-HCH to the Arctic. *Environ. Pollut.*, 128, 223-240.
- Undeman, E., McLachlan, M.S. (2011) Assessing model uncertainty of bioaccumulation models by combining chemical space visualization with a process-based diagnostic approach. *Environ. Sci. Technol.*, 45, 8429-8436.
- Varaprath, S., Stutts, D., Kozerski, G. (2006) A primer on the analytical aspects of silicones at trace levels - challenges and artifacts – a review. *Silicon Chemistry*, 3, 79-102.
- Vermeire, T., Rikken, M., Attias, L., Boccardi, P., Boeije, G., Brooke, D., de Bruijn, J., Comber, M., Dolan, B., Fischer, S., Heinemeyer, G., Koch, V., Lijzen, J., Muller, B., Murray-Smith, R., Tadeo, J. (2005) European Union System for the Evaluation of Substances: the second version. *Chemosphere*, 59, 473-485.
- Vermeire, T.G., Jager, D.T., Bussian, B., Devillers, J., denHaan, K., Hansen, B., Lundberg, I., Niessen, H., Robertson, S., Tyle, H., vanderZandt, P.T.J. (1997) European Union System for the Evaluation of Substances (EUSES). Principles and structure. *Chemosphere*, 34, 1823-1836.
- Wang, D.-G., Norwood, W., Alaei, M., Byer, J.D., Brimble, S. (2012) Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment. *Chemosphere*, 93, 711-725.
- Wania, F. (1999a) Differences, similarities, and complementarity of various approaches to modelling persistent organic pollutant distribution in the environment. In: *WMO/EMEP/UNEP Workshop on Modelling of Atmospheric Transport and Deposition of Persistent Organic Pollutants and Heavy Metals. Geneva, Switzerland, 16-19 November 1999*. WMO. pp. 115-140.
- Wania, F. (1999b) On the origin of elevated levels of persistent chemicals in the environment. *Environ. Sci. Pollut. R.*, 6, 11-19.
- Wania, F. (2003) Assessing the potential of persistent organic chemicals for long-range transport and accumulation in polar regions. *Environ. Sci. Technol.*, 37, 1344-1351.
- Wania, F. (2006) Potential of degradable organic chemicals for absolute and relative enrichment in the Arctic. *Environ. Sci. Technol.*, 40, 569-577.

- Wania, F., Breivik, K., Persson, N.J., McLachlan, M.S. (2006) CoZMo-POP 2 - A fugacity-based dynamic multi-compartmental mass balance model of the fate of persistent organic pollutants. *Environ. Modell. Softw.*, 21, 868-884.
- Wania, F., Mackay, D. (1996) Tracking the distribution of persistent organic pollutants. *Environ. Sci. Technol.*, 30, A390-A396.
- Wania, F., Mackay, D. (1999) The evolution of mass balance models of persistent organic pollutant fate in the environment. *Environ. Pollut.*, 100, 223-240.
- Wania, F., Persson, J., Di Guardo, A., McLachlan, M.S. (2000) The POPCYCLING-Baltic model. A non-steady state multicompartment mass balance model of the fate of persistent organic pollutants in the Baltic Sea environment. Kjeller, NILU (NILU OR 10/2000).
- Warner, N.A., Evenset, A., Christensen, G., Gabrielsen, G.W., Borgå, K., Leknes, H. (2010) Volatile siloxanes in the European Arctic: assessment of sources and spatial distribution. *Environ. Sci. Technol.*, 44, 7705-7710.
- Warner, N.A., Kozerski, G., Durham, J., Koerner, M., Gerhards, R., Campbell, R., McNett, D.A. (2012) Positive vs. false detection: A comparison of analytical methods and performance for analysis of cyclic volatile methylsiloxanes (cVMS) in environmental samples from remote regions. *Chemosphere*, 93, 749-756.
- Whelan, M.J., Breivik, K. (2013) Dynamic modelling of aquatic exposure and pelagic food chain transfer of cyclic volatile methyl siloxanes in the Inner Oslofjord. *Chemosphere*, 93, 794-804.
- Whelan, M.J., Estrada, E., van Egmond, R. (2004) A modelling assessment of the atmospheric fate of volatile methyl siloxanes and their reaction products. *Chemosphere*, 57, 1427-1437.
- Wong, F., Wania, F. (2011) Visualising the equilibrium distribution and mobility of organic contaminants in soil using the chemical partitioning space. *J. Environ. Monit.*, 13, 1569-1578.
- Xu, S., Wania, F. (2012) Chemical fate, latitudinal distribution and long-range transport of cyclic volatile methylsiloxanes in the global environment: A modeling assessment. *Chemosphere*, 93, 835-843.



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ABSTRACT: This report summarizes results from a project funded by the Research Council of Norway (196191/S30). The overall goal was to better understand and predict relationships between emissions of organic chemicals of emerging concern and their levels in the environment and food-chains of the Nordic region through integrated monitoring and modeling studies. Four case studies were selected (i) cyclic volatile methyl siloxanes (cVMSs) in the Inner Oslofjord, (ii) cVMSs in the Norwegian Arctic (iii) short-chain chlorinated paraffins (SCCPs) in the Nordic environment and (iv) risk-based model screening of chemicals in commerce in the Nordic countries. We also provide a brief introduction to the key multimedia modelling tools which were used. It is our hope that these tools, targeting the behaviour of contaminants under relevant environmental and climatic conditions, may assist Nordic environmental authorities interested in understanding and managing organic contaminants.			
NORWEGIAN TITLE Multimediamodeller og observasjoner i fellesskap – Et kraftfullt verktøy for å forstå og forvalte organiske miljøgifter.			
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Multimedia models	Organic contaminants		Nordic environment
ABSTRACT (in Norwegian) Denne rapporten oppsummerer resultater fra et forskningsprosjekt finansiert av Norges Forskningsråd (196191/S30). Det overordnede målet var å forbedre forståelsen av sammenhenger mellom utslipp og eksponering av nye organiske miljøgifter i Norden gjennom studier som kombinerer målinger av nivåer i miljøet med modellering. Det ble fokusert på fire enkelttilfeller (i) sykliske flyktige metylsiloksaner i Oslofjorden, (ii) sykliske flyktige metylsiloksaner på Svalbard (iii) kortkjedede klorparaffiner i nordisk miljø og (iv) risikobasert screening av kommersielle kjemikalier i Norden. Vi introduserer også de viktigste multimedia modelleringsverktøyene som ble brukt i prosjektet. Vi håper at disse verktøyene, som er rettet mot miljøskjebnen til organiske kjemikalier under relevante miljø- og klimabetingelser, kan være til hjelp for miljømyndigheter i Norden som ønsker å forstå og forvalte organiske miljøgifter.			

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