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# Advancements of Concepts for Identification of Substances of Very High Concern (SVHC) In Terms of the REACH Regulation

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. Besonders besorgniserregende Stoffe müssen aufgrund ihrer intrinsischen Eigenschaften einer Zulassung unterzogen werden. Die Kriterien für die PBT- und vPvB-Bewertung sind im Annex XIII der REACH-Verordnung festgelegt. Das Ferntransportpotenial einer Substanz und damit die Gefährdung für weit entlegene Gebiete werden jedoch nicht explizit in der REACH-Verordnung berücksichtigt. Das Vorhaben hatte deshalb zum Ziel, neue wissenschaftliche Ergebnisse zum Ferntransport zu erarbeitenund spezifische Optionen für die Einbeziehung des Ferntransportpotentials als eine kritische Substanzeigenschaft zur Identifikation von besonders besorgniserregenden Stoffen zu entwickeln. Die Relevanz verschiedener Transportwege (Luft, Wasser, an Plastikpartikel gebunden) wurde untersucht. Während für wasserlösliche Substanzen das Ferntransportpotential im Ozean durch die Halbwertszeit im Wasser erfasst wird, ist dies im Flusswasser nicht erfüllt.Mit dem Lagrange-Partikeldispersionmodell FLEXPART und dem Multimedia-Massenbilanzmodell BETR-Global konnten für PCBs wichtige Aspekte von Monitoringmessungen an den arktischen Stationen Zeppelin und Alert nachvollzogen werden.Die Canadian Domestic Substances List (CDSL) und die Liste der unter REACH registrierten Substanzen wurden systematisch auf Stoffe mit Ferntransportpotential untersucht. Durch die Anwendung verschiedener Filter konnten elf Substanzen aus der CDSL und zwölf Substanzen aus der REACH-Liste ermittelt werden, die ein Ferntransportpotential besitzen, aber nicht PBT-Substanzen sind. Alle identifizierzten Substanzen beider Listen sind persistent, aber nicht bioakkumulativ oder toxisch und bedürfen der weiteren Untersuchung.

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16. Abstract
For chemicals identified as substances of very high concern (SVHC) due to their intrinsic properties, an authorization might be required for production and use. The criteria for the PBT and vPvB assessment are defined in Annex XIII of the REACH-regulation. However, a substance's long range transport potential (LRTP) and the subsequent hazard to remote regions are not explicitly included in the REACH legislation. Therefore, the objective of the project was to evaluate new scientific findings on long-range transport in the environment and to develop specific options for including LRTP as critical substance property in the SVHC identification according to REACH. The relevance of different transport pathways (air, water, plastic particles present in water, migratory species) for different types of chemicals has been investigated. A main finding is that for sufficiently water-soluble chemicals riverine transport may be highly effective, but would not be captured by the current half-life criteria (chemicals that are clearly below the half-life criteria in water may still long-lived enough to undergo long-range transport in rivers). Monitoring data for polychlorinated biphenyls measured at the Arctic stations, Zeppelin and Alert, are used as a reference point for model results for the LRT of PCBs. With two models, a Lagrangian Particle Dispersion Model (FLEXPART) and a multimedia mass-balance model (BETR-Global), various aspects are identified where one or the other model showed better agreement with the field data. Chemicals with high LRTP are systematically searched in the Canadian Domestic Substances List (CDSL) and the list of chemicals currently registered under REACH. Application of a series of filters for LRTP evidence led to a list of eleven substances of the CDSL with high LRTP that are not PBT Using the same approach for filtering the list of 3,908 registered substances under REACH, twelve substances could be identified with high LRTP that are not PBT substances. All identified non-PBTs with LRTP of both lists are persistent, but not bioaccumulative and need further elaboration on their P, B and T properties.

17. Keywords
Long-range transport
PBT assessment
LRTP evidence

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# 1. INTRODUCTION

The European chemicals legislation REACH[1] (Registration, Evaluation, Authorisation and Restriction of Chemicals) focuses on the “registration, evaluation, authorization and restriction of chemicals”. Its preferential aims are to ensure on the one hand “free circulation of substances on the international market” and on the other hand a “high level of protection of human health and the environment” in accordance with the precautionary principle. For substances with properties of very high concern (SVHC) an authorization is required for production and use. These SVHC include chemicals which are

(i) carcinogenic, mutagenic, or toxic to reproduction (CMR),

(ii) persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB) or

(iii) substances of “equivalent concern” as identified from scientific evidence, such as endocrine disruptors.

However, a substance’s long range transport potential (LRTP) and the subsequent hazard to remote regions are not explicetely included in the REACH legislation. LRTP in air, with ocean currents and in migrating animals is though considered a critical substance property according to the Stockholm Convention[2] in addition to persistence, bioaccumulation and adverse effects. Besides measurements in remote regions, e.g. the Arctic, substance properties describing environmental fate and modelling results are considered as indicators for LRTP under the Stockholm Convention. LRTP in air is explicitly mentioned in terms of a half-life in air of more than 2 days. Substances with LRTP cross international boundaries and may be transported to particularly sensitive ecosystems like the Arctic. Based on the precautionary principle as embedded in the REACH legislation and based on the responsibility of each Member State to ensure that activities within their control do not impact the environment of other States, inclusion of substances with LRTP in the SVHC list is desirable. Therefore, the objective of this research project is to develop a strategy, based on the example of chosen substances, to evaluate whether long-range transport potential (LRTP) as critical substance property

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[1] Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). Official Journal of the European Union L396 (http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L: 2006 :396:0001:0849:EN:PDF)

[2] Stockholm Convention on Persistent Organic Pollutants. United Nations Environment Programme, Geneva, Switzerland (http://chm.pops.int/)

should be integrated into identification of substances of very high concern according to REACH.

This final report summarizes the results of the working packages of the research project as outlined in the project proposal.

# 2. STATE OF THE ART

## 2.1. *LONG-RANGE TRANSPORT IN THE ATMOSPHERE*

Atmospheric air flow presents a fast transport mode for compounds mainly partitioning into air. Therefore, the Stockholm Convention has defined the long-range transport potential based on the substance's atmospheric half-life, which means that substances characterized by a half-life in air of more than 2 days may become subject to long-range transport. Assuming an average global wind speed of 6.64 m $s^{-1}$ 10 m above the ground (Archer and Jacobson 2005), this corresponds to a transport distance of roughly 1000 km. Thus, according to the Stockholm Convention a substance shows long-range transport potential in air if at least 50% of the compound is transported more than 1000 km. This screening criterion does, of course, not reflect the actual variability in possible transport mechanisms and influencing parameters. Lipophilic, persistent compounds like γ-HCH, HCB, some PCBs and DDT primarily adsorb to aerosol particles and are thus transported into remote regions, including the Arctic. More volatile substances, on the other hand, like short-chained alkanes, slightly chlorinated PCBs and chlorinated benzenes directly partition into the gas phase and can be transported over long distances (Beyer et al. 2000). In northern regions these compounds will deposit with precipitation, especially snow.

The "global distillation or cold condensation hypothesis" was put forward in the 1990s to describe the possible transport mechanism of airborne substances to cold regions such as the arctic. According to this hypothesis, semi-volatile compounds are washed out of the atmosphere in cold regions and are stored within the water or soil compartment. During warmer times, semi-volatile compounds may by remobilized again by evaporation processes and continue to be transported to the Arctic by atmospheric currents (Wania and Mackay 1999). However, recent investigations have shown that the global temperature gradient plays no significant role for atmospheric LRT (von Waldow et al, 2010). Instead, fractionation patterns can best be explained by competition between removal processes and transport in the atmosphere ("differential removal hypothesis").

Monitoring of persistent organic pollutants (POPs) in air like in the GAPS study (Pozo et al. 2009) or for PBDEs in British Columbia (Noël et al. 2009) shall help to differentiate between local sources of contaminants and long-range transport derived concentrations. In this way, Pozo et al. (2009) could show that on a global basis no seasonal patterns of the distribution of POPs occurred and that highest concentrations can be found in the latitudes of the northern hemisphere, especially in developed and industrialized regions. Also active samplers have been used extensively to monitor the occurrence of semivolatile chemicals in remote regions (EMEP 2010). However, monitoring is limited to a set of relatively few substances (normally less than 50) that can be detected in measurable quantities, but cannot be used to identify new SVHCs in a large set of chemicals on the market.

In addition, different models have been developed estimating the long-range transport potential of organic chemicals in order to understand the global distribution of these compounds. These models are either based on a multimedia approach or represent atmospheric transport models. Due to different calculation methods for LRTP and in dependence of spatial resolution, the models show a different ranking for investigated reference chemicals assuming emission into air (Hollander et al. 2008). One of the models, for example, defines LRTP as the chemical fraction which not only reaches the Arctic but also remains there. The characteristic travel distance (CTD) is another measure to define LRTP. It describes the distance a substance may travel to be reduced to 37% of its initial concentration. This depends on the partitioning behaviour, on degradation half-lives and on the assumed wind-speed. Based on reference chemicals, an LRTP boundary in air has already been defined to classify further substances (e.g. Beyer et al. 2000, Klasmeier et al. 2006). This model-based approach to identifying substances with high LRTP has been adopted by the OECD (Wegmann et al. 2009) and is also used in the evaluation of potential Persistent Organic Pollutants by the POP Review Committee of the Stockholm Convention.

However, many (emerging) compounds are transported over longer distances in water than in air (Matthies et al. 2009), which will be discussed in the following section.

## 2.2. *LONG-RANGE TRANSPORT WITH OCEAN CURRENTS*

The main difference between long-range transport with atmospheric currents and with ocean currents is the transport velocity. By accident, the water flux could be traced within the Northern hemisphere from 1975 to 1985 when radioactive isotopes, e.g. Cs-137 and Iod-129, were emitted into the environment by a leakage of the reprocessing plant in Sellafield, UK. In this way, isotope measurements could be compared with simulations of ocean models (Karcher et al. 2004, Orre et al. 2010). In addition, monitoring of $^{134}$Cs could show that water transport from South Norway to the North Cape (i.e. approximately 1500 km) takes about two years (Aarkrog et al. 1987). Mean flow velocities of many ocean currents, however, are about one order of magnitude higher. The North Equatorial Current, for instance, is characterized by a mean flow velocity of 20 cm $s^{-1}$ (Jingzhi et al. 2006), the water flux along the Bering Strait averages 33 cm $s^{-1}$ (Spall 2007) and the velocity of the Westspitsbergen Current carrying water out of the Atlantic Ocean along the Fram Strait into the Arctic may even reach 40 cm $s^{-1}$ (Cisewski 2001).

Some multimedia models thus differentiate between fresh water and ocean compartment to describe the environmental fate of organic compounds on a continental or even global scale (e.g. Globo-POP: Wania & Mackay 1995, SimpleBox: Brandes et al. 1996, Evn-BETR: MacLeod et al. 2001). Nevertheless, global and European assessment of organic chemicals has mainly focused on transport in air. But long-range transport with ocean currents as well as with rivers is especially important for polar and water soluble compounds, like for many pesticides. Perfluorinated acids have also turned out to serve as a chemical tracer of global circulation of sea water (Yamashita et al. 2005, Yamashita et al. 2008). These compounds might be transported by ocean currents into the Arctic as well as by transport of precursor compounds through the air and subsequent degradation and deposition (Ahrens et al. 2009a). Wania (2007) and Schenker et al. (2008) compared these two transport pathways of perfluorcarboxylic acids (PFCAs) into the Arctic by applying the global multimedia models Globo-POP and CliMoChem. On the one hand, advection of volatile fluorotelomer alcohols (FTOH) with atmospheric currents and their subsequent wet deposition and degradation may lead to PFCAs in the Arctic. On the other hand, PFCAs may directly be emitted into the marine ecosystem by several industrial processes and transport with ocean currents. Resulting estimates of the Arctic contamination potential underline the efficiency of the substance transport with ocean currents in comparison to the atmospheric transport of FTOH and its subsequent degradation to PFCA. However, the most significant pathway of long-chain PFCAs depends on their direct emission amount in relation to the emission amount of FTOH, i.e. a general conclusion on the dominant transport route is not possible. Armitage et al. (2009) applied CliMoChem, a contaminant fate model dividing the global environment into several latitudinal bands, to PFOS and its precursor compounds to investigate the consequences of the production phase-out in 2000-2002. In response to the phase-out, simulated PFOS concentrations in surface waters of remote regions continue to increase until 2030 whereas simulated concentrations of the precursor compounds in both compartments, atmosphere and ocean, decline directly. This may also explain observations on increasing body burdens of PFOS in marine mammals mainly exposed to PFOS in sea water instead to air borne precursors which degrade to PFOS in vivo.

But regardless of the transport mechanism, perfluorinated compounds can be found in biota all over the world (Giesy et al. 2001). Brown and Wania (2008) combined the global chemical fate model Globo-POP with the human accumulation model ACC-HUMAN (Czub et al. 2008) and identified 120 substances with potential to accumulate in the Arctic environment and the Arctic human food chain. Biota may also serve as a transport vector for organic pollutants when they accumulate in migrating animals.

### 2.3. *LONG-RANGE TRANSPORT WITH MIGRATING ANIMALS (BIOMAGNIFICATION)*

Several articles have already been published describing long-range transport of pollutants, accumulation of chemicals in organisms along food chains, and transport of organic substances by migrating fish and birds. Bioaccumulation in Arctic food webs has also been the focus of many investigations. Hickie et al. (2005) developed a bioaccumulation model to estimate the chemical burden of Arctic ring seals by POPs. This model is based on populations and individuals to simulate bioaccumulation during the seals’ lifetime. It considers the effects of age, growth, sex, condition and reproduction.

Ikonomou et al. (2008) investigated the transfer of polybrominated diphenyl ethers (PBDEs) from female seals to their pups by lactation. PBDE concentrations were measured in several mother-pup pairs from two different seal colonies in Canada, i.e. one from Sable Island (Nova Scotia) and one from British Columbia. Concentrations in the female grey seals were twice as high as in the pups. Higher brominated PBDEs showed a significant decrease in their transfer efficiency. Hepta-BDEs were not transferred by lactation. The main reason for the chemical burden of the animals is foraging behaviour influenced by emissions in the specific region. Since measurements were taken in remote regions long-range transport with ocean and atmospheric currents play an important role as well.

Tomy et al. (2004) investigated perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorooctanesulfonamide (PFOSA) and N-ethyl-perfluorooctanesulfonamide (N-EtPFOSA) in an Eastern Arctic food web to gain more insight into bioaccumulation on different trophic levels (TL). The food web included zooplankton, mussels, shrimps, Arctic cod, perch, walrus, narwhale, beluga, kittiwake, and glaucus gull. PFOS was found in all species whereas PFOA was restricted to only a few of them. N-EtPFOSA and other precursors were only detected in the liver of beluga and narwhale and might be transformed to PFOSA within the organisms. PFOS concentrations and the trophic levels were positively correlated. Concentrations of the other compounds did not show a significant dependence on the TL. Nevertheless, biomagnification factors (BMF), which represent an indicator for accumulation along the food chain, were in most cases higher than one, i.e. these substances are characterized by a distinct bioaccumulation potential. This was confirmed by measurements of perfluorinated compounds in the feathers and livers of birds from different trophic levels (Meyer et al. 2009) as well as in Arctic mammals foraging on different trophic positions (Martin et al. 2004). Tomy et al. (2009) published analogous results for a Western Canadian Arctic food web and two classes of chemicals of emerging concern (CEC), namely per- and polyfluorinated surfactants and brominated flame retardants. Herzke et al. (2009) could also show that foraging behaviour and trophic level are the most important factors influencing accumulation of lipophilic POPs.

Transport of pollutants by migrating mammals, fishes and birds has already been investigated with different species. Ewald et al. (1997) observed the transport of organic pollutants out of the ocean into inland Alaska lakes by salmon. Salmons are born in lakes, stay there during the first one to two years and subsequently migrate into the ocean. Here, they feed and accumulate pollutants for another two to three years until they return to the lake to spawn and finally to die. In the lakes they serve as prey for local, territorial fish species like the greyling. Ewald et al. (1997) measured concentrations of DDT and PCBs in greylings of a lake visited by salmons and of another lake in the vicinity which does not serve as spawning ground for salmons. The greylings of the lake with the salmons showed significantly higher pollutant concentrations. Concurrently, atmospheric deposition into both lakes was documented to exclude an additional emission pathway of the investigated compounds. The transport mechanism from marine to freshwater ecosystems could also be observed for mercury in sockeye salmons in Bristol Bay, Alaska, which differentiates between fluxes into freshwater (via adults) and out of the freshwater (via juveniles). Although mercury concentrations were higher in juveniles, the mercury export was significantly exceeded by total mercury import (Baker et al. 2009).

Evenset et al. (2007) investigated the influence of seabirds on the ecosystem of Arctic lakes. Migration of seabirds is considered to be the main reason for contamination of remote Arctic lakes. Therefore, two lakes in close vicinity were investigated on an island in the Barents Sea. One of these lakes is a resting place for three sea bird species: the little auk, the kittiwake and the glaucus gull. The little auk is a small bird feeding on zooplankton whereas the kittiwake is larger and feeds on zooplankton and, in addition, on small fish. The glaucus gull is the largest of the three species and feeds opportunistically on species of a higher trophic level than the two other birds. Consequently, the gull is highly contaminated by bioaccumulation. The accumulated pollutants are emitted into the lake by the excrements of the birds, i.e. higher substance concentrations could be observed in water and sediment of the lake serving as resting place in comparison to the “unvisited” lake. Similar observations are published by Blais et al. (2005, 2007) for PCBs transported by northern fulmar to high Arctic ponds in Canada.

Gewurtz et al. (2008) developed a food chain model to investigate PCB concentrations in fishes of two Arctic lakes. The main reason for the different chemical burden is the influence of seabirds on one of these lakes. The excrements change the relation of the fugacities between sediment and water. The model was developed for the higher contaminated lake applying the parameter values of the less contaminated lake. The results point out that the seabirds are the main influencing factor but that small differences within the food webs of the two lakes also lead to a different contamination level.

Blais et al. (2007) define the expression of biovector transport. This definition represents the pollutant transport by organisms. Transport may occur by migration in air as well as in water in that way that the pollutants are transferred from one region to another. The transporting animals may serve as food and, thus, transfer the pollutant into the food chain or they influence the receiving system by excrements or by their own cadaver after death. Blais et al. (2007) give salmons, Arctic and Antarctic seabirds, and whales as example. In contrast to mass transport in the atmosphere or in water biovector transport is restricted to one direction and does not lead to steady state. Blais et al. (2007) developed a fugacity model considering four abiotic compartments and equations for two fish species, birds and bears for migrating salmon to Karluk Lake, Alaska. The results underline the significant impact of biovector transport by salmons.

## 2.4. LONG-RANGE TRANSPORT WITH PLASTIC PARTICLES AS ABSORBED POLLUTANTS

Since plastics have been commonly developed in the 1950s worldwide production has expanded within the last few decades from 1.5 million tonnes in 1950 to 245 million tonnes in 2008 (PlasticsEurope 2009) and will probably exceed 300 million tonnes in 2010 (Thompson et al. 2009a). 100 kg plastics per year and capita are currently used in Western Europe and expected to exceed 130 kg in 2015. In total, Europe produces approximately 60 million tonnes of plastics with Germany being the major producer (7.5% of global production) followed by Benelux (4.5%), France (3%), Italy (2%), the UK and Spain (1.5% each). 48.5 million tonnes of virgin resin is demanded by European plastic converters, the net export of primary plastics is amounted to 8.7 billion € and the net export of converted plastics to 4.4 billion € with non-EU countries (PlasticsEurope 2009).

But what does the term “plastics” imply? Beginning from the use of natural plastic material like natural rubber or waxes the development of completely synthetic plastics increased within the first half of the 20th century (Andrady and Neal 2009). Today, there are several distinct groups of plastics available to serve as the best choice for each specific application. Nevertheless, all plastics have in common to be synthesized by polymerization of monomers derived from gas or oil (8% of world oil production) and by addition of various chemical additives (Thompson et al. 2009b). The five main high-production-volume plastics which account for approximately 90% of the total demand are polyethylene (low density (LDPE) and high density (HDPE)), polypropylene (PP), polyvinylchlorid (PVC), polystyrene (PS), and polyethylene terephthalate (PET) (Andrady and Neal 2009). PE and PP are mainly applied for packaging which is one of the main end-use segments for plastics (38% in Europe 2008), PP is also used for textiles, PVC for flooring or window profiles, PS is the basic material for styrofoam, and beverage bottles, plastic films and fibre are made of PET. The unique properties (versatile, lightweight but strong, chemical- and light-resistant, hygienic, cost-efficient) support many technological advances, energy savings, improved consumer health, e.g.

by a facilitated clean water drinking supply and by several medical devices (surgical equipment, aseptic packaging, drips, implants like cardiac valves and sockets of a joint), and reduced transportation costs (PlasticsEurope 2009, Andrady and Neal 2009).

However, the same properties turn plastics into one of the most drastic and observable impact factors on the environment which is still of growing concern. It is estimated that plastic litter accounts for 10% of municipal waste mass worldwide, but even comprises 50 to 80% of the waste stranded on beaches, floating on the ocean surface and incorporated into the seabed (Barnes et al. 2009). A complete ban of dumping all forms of plastics from ships into the sea came into force in 1989 by the MARPOL regulation Annex V[3]. However, plastic production is still increasing, the sources of plastic waste are both, marine- and land-based, and, in addition, the longevity of plastic materials which is expected to be hundreds to thousands of years, led to several reports on plastic accumulation and spread of plastic waste all over the world (Barnes et al. 2009). Even plastic pellets, the industrial raw material, which are emitted into the environment during manufacturing or transport, have been detected on beaches all over the world (e.g. Ogata et al. 2009). Browne et al. (2010) could show that downwind acting habitats represent a potential sink for the accumulation of plastic debris as far as spatial patterns are concerned.

The aesthetic effect of littered beaches and polluted recreation areas gave soon way to findings of seabirds, marine mammals and fish entangled in lost network, ropes and monofilament lines. Entanglement and ingestion of plastic pieces or bags, misleadingly considered as prey, lead to death from suffocation or starvation. Dead fulmars (*Fulmarus glacialis*) found at the coastline of the North Sea and fulmars in the Canadian Arctic served as indicator for the waste pollution of the oceans (Guse et al 2005, Provencher et al 2009). This study also showed that almost every seabird (95%) had swallowed plastic pieces of different size. Further investigations even focus on ingestion patterns of seabirds favouring specific plastic types or colours (Ryan 1987). Also the significant role of plastics as transport matrix of non-indigenous species to remote areas has been described (Barnes 2002). In addition, so-called microplastics have attracted attention of environmental researchers. These particles which are smaller than 1 mm (Browne et al. 2010) result from fragmentation of larger plastics through photo-oxidation and a combined effect of wave action and abrasion, from the use of small plastic particles, especially polyethylene and polystyrene, as abrasive scrubbers in cleaning

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[3] International Maritime Organization, 1982. International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto (MARPOL). http://www.imo.org/

products which are directly emitted into surface waters (Fendall and Sewell 2009), and from resin pellets as raw material (0.1 to 0.5 mm). Microplastics account for over 80% of stranded plastics in the Tamar Estuary of the UK (Browne et al. 2007) whereas in the Los Angeles watershed they contribute 90% by count and 13% by weight to the total plastic debris (Moore 2008). Also, a significant increase of microplastics has been observed in seawater archived in plankton samples since the 1960s (Thompson et al. 2004). Since, e.g. for filter feeders, the optimum size for ingestion appears to be less than 1 mm (Moore 2008) these microparticles are bioavailable and ingested by lugworms (deposit feeder), barnacles (filter feeder) and amphipods (detrivores) (Thompson et al. 2004). Plastic particles also accumulate in the gut cavity of birds (van Franeker 1985, Colabuono et al. 2009), fish (Derraik 2002) and polychaete worms (Carpenter et al. 1972) and thus directly affect organisms of various sizes and on different levels of the food chain. In addition, plastics may even be ingested indirectly via the food chain, e.g. as demonstrated in fur seals accumulating plastic particles by feeding on fish (Eriksson and Burton 2003). Recent investigations identify a translocation of microplastics from the gut to the circulatory system of mussels (Browne et al. 2008). Even on the cellular level a pronounced immune response during the exposure to microplastics could be observed for mussels (*Mytilus edulis*) (Höher et al. 2010).

Besides these mechanic impacts of plastics on organisms a relationship between chemical burden and plastic ingestion has been indicated by Ryan et al. (1988): In Great Shearwaters, a large migrating seabird, the amount of polychlorinated biphenyls (PCBs) was positively correlated with the mass of ingested plastic. Further studies underline that PCBs are absorbed by plastics from surrounding seawater (Carpenter et al. 1972, Mato et al. 2001). Respective sorption coefficients on PP pellets turned out to be two orders of magnitude higher than for suspended particles (Mato et al. 2001). Besides absorption from surrounding seawater several additives are contained within the plastic matrix. Among colorants, UV-stabilizers and matting agents, brominated flame retardants, phthalate plasticizers, bisphenol A and anti-microbial agents are additives of particular concern (Thompson et al. 2009b). Experimental results indicate that phthalates and other endocrine disrupting chemicals like antimony may leach from PET bottles into the contents of the bottle (Wagner and Oehlmann 2009, Hansen et al. 2010, Sax 2010).

Sorption of pollutants into plastics has already been investigated in regard to monitoring methods since plastic, e. g. PE, serves as passive sampler accumulating high amounts of organic chemicals in aquatic environments (Lohmann and Muir 2010). Equilibrium partition coefficients with PE are thus available for several compounds including PCBs, polycyclic aromatic hydrocarbons (PAHs), and organochlorine pesticides (OCPs). These partition coefficients range from $10^2$ to $10^8$ L $kg^{-1}$ and are positively correlated with the respective octanol-water partition coefficient $K_{OW}$ (Adams et al. 2007, Smedes et al. 2009, Hale et al. 2010). In addition, partitioning of PCBs to microplastics does not seem to be influenced by weathering (Beckingham and Ghosh 2010).

Incorporated into the plastic matrix, chemical compounds escape a fast degradation and may thus become more persistent than in a freely dissolved state and subject to long-range transport. Upon ingestion by organisms, plastic particles could be a “biomagnification” route of organic chemicals absorbed to or contained in the plastics what was indicated by investigations on polybrominated diphenyl ethers (PBDE), polycyclic aromatic hydrocarbons (PAH), triclosan and nonylphenol (NP) (Teuten et al. 2009). Colabuono et al. (2010) showed the occurrence of PCBs and organochlorine pesticides in plastics ingested by seabirds proving that plastic particles represent an additional exposure pathway for organic pollutants to marine organisms.

## 2.5. *IDENTIFICATION OF MECHANISMS AND RELEVANT PARAMETER VALUES*

The potential of an organic pollutant to be transported over long distances depends on several substance properties and environmental conditions. First of all, partition coefficients determine to what extent the respective compound is distributed into the transporting compartments air, water, biota and plastics. Degradation half-lives influence the residence time within the transport medium. Therefore, a combination of both, partition coefficients and half-lives, is necessary to give a first estimate on a substance’s LRTP, e.g. compounds characterized by a half-life in air larger than two days and, thus, fulfilling the LRTP criterion according to the Stockholm Convention, are only subject to long-range transport in air if they are also distributed into this compartment. Substances mainly transported with rivers or ocean currents need to show long degradation half-lives in water and may consequently fall in the category of a persistent compound according to the REACH legislation (half-lives larger than 40 days (fresh water) and 60 days (seawater), respectively).

Additional mechanisms, which have already been indicated above, influence the different transport routes specifically. Advection with atmospheric air flow is affected by wind speed, wet and dry deposition as well as by deposition with aerosol particles. In air, degradation mainly occurs due to direct photolysis as a function of light intensity and substance-specific absorption spectra and to reactions with free radicals, e.g. OH or $NO_3$ radicals. Transport in water is, in analogy to deposition from air, influenced by sedimentation of the investigated compounds. This process strongly depends on the flow velocity of the transporting medium, i.e. freshwater in rivers and seawater in ocean currents, and on the substances' sorption to suspended particles, thus on the above mentioned partition coefficients (Scheringer et al. 2004). In addition, substances partitioning into water and with high $K_{OW}$ may also absorb into plastics since sorption into plastics has been shown to be one to two orders of magnitude stronger than to natural sediments (e.g. Teuten et al. 2007). Knowledge on amounts of plastics flowing in the world oceans is necessary to estimate the relative importance of plastics as transport vectors for organic pollutants.

Migrating animals define the most complex aspect adding to a substance's LRTP. Besides knowledge on migration pathways, which should end up in remote regions in order to be of concern for LRTP, insight into respective food chains and population size is required to estimate the contribution of migrating animals to the LRTP of investigated substances. In addition, bioaccumulation behaviour and metabolization rates influence substance concentrations in migrating animals and, finally, in top predators and humans. First results on the relevance of the different transport mechanisms in dependence of different parameters are given in the following section.

## 2.6. *References*

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# 3. INVESTIGATION OF RESEARCH QUESTIONS

## 3.1. *COMPARISON OF DIFFERENT TRANSPORT PATHWAYS*

Pollutant transport with air is one to two orders of magnitude faster than with water and is thus the most dominant pathway for many compounds. However, Matthies et al. (2009) have shown that several current-use pesticides are transported over longer distances in water than in air. Thus, based on the environmental fate model ETAPOS we identified the substances' parameter range for which transport is dominated by the water pathway. To this end, hypothetic compounds with different parameter values for partition coefficients and half-lives in the compartments air, water, soil and sediment were simulated. In the ETAPOS model, the characteristic travel distance (CTD) in water exceeds the one in air for substances with log $K_{OW} < 5$, log $K_{AW} < -4$ and half-life in water larger than 75 days (= persistent in water according to REACH) (in other models, these limits are somewhat different, but the general point is that LRT in water is relevant for chemicals with sufficiently long half-life in water and sufficiently low $K_{AW}$; this can be supported by selected pesticides like bromuconazole and dichlofluanid (Matthies et al. 2009)).

As far as transport with plastics is concerned, a rough mass calculation for transport of PCBs, PBDEs and PFOA into the Arctic showed that the mass flux of the compounds with atmospheric currents and ocean currents dominates the pollutant transport with plastics by up to five orders of magnitude. Thus, the contribution of plastic vectors to the mere mass transport of organic compounds to the Arctic seems to be negligible. However, plastic-mediated transport may contribute to LRTP of additives already contained in the plastic matrix at high concentrations, of non-volatile compounds with high absorption potential into plastics, and of substances not preferably transported by air or water. This requires a substance screening on preferred modes of long-range transport. In addition, amounts of plastics and especially microplastics in the oceans are increasing and pose a direct exposure pathway into marine organisms and the aquatic food chain. For details of the investigation we refer to the attached publication (Zarfl and Matthies 2010).

In order to account for LRTP with migrating animals we investigated the global distribution of concentrations of PBDEs and PFOS in seals, one of the most important top predators in the marine environment. Measurements of PBDEs in seals cover North

America and Europe with focus on the North Sea region (Fig. 1). BDE 47 shows highest concentrations at each of the monitoring sites. Total chemical concentrations of PBDEs are higher in North America than in Europe presumably because of continued PBDE production in the USA (although production of most PBDE mixtures has been voluntarily ceased[4]) whereas in (some) European countries industry agreed to abandon the use of PBDEs already in the late 1980s. Investigations also show a decreasing concentration gradient from the Wadden Sea into the northern North Sea (Fig. 2). Relative distribution of the congeners is similar at all monitoring sites resulting in following decreasing concentration pattern: BDE 47 > BDE 99 > BDE 153 > BDE 100 > BDE 154 > BDE 28 > BDE 183.

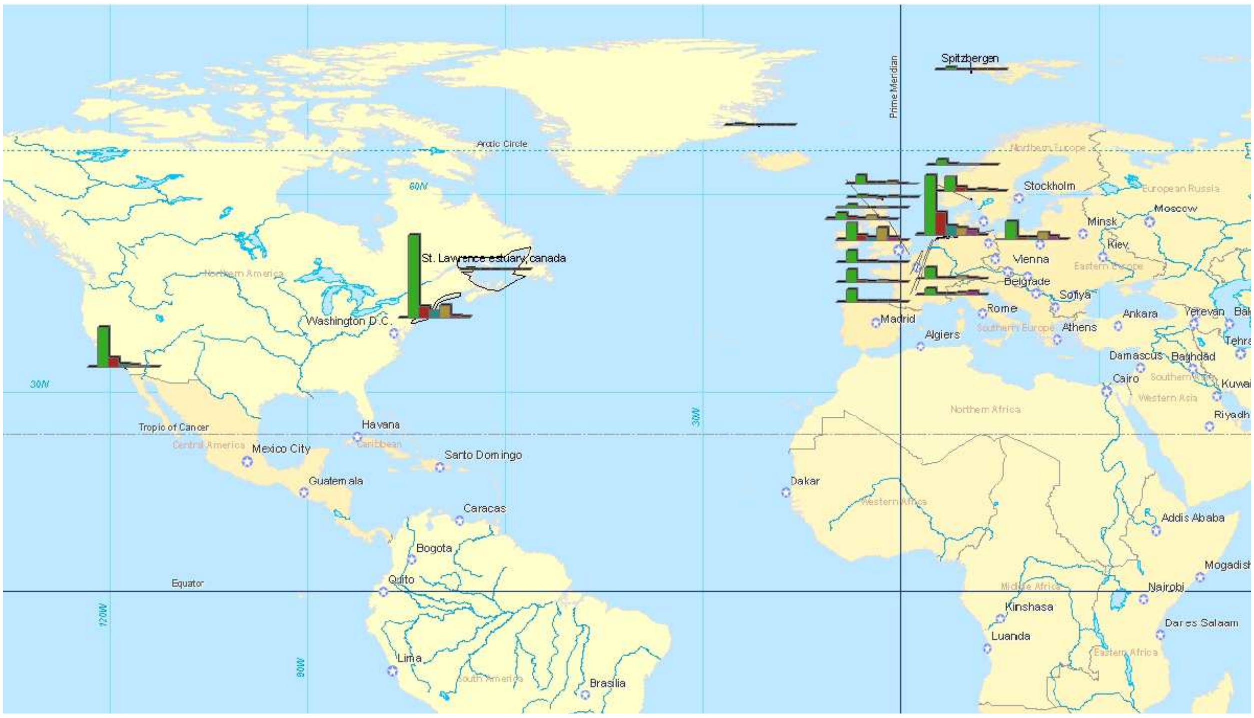

**Figure 1: Global distribution of PBDE concentrations of congeners BDE 28 (blue), 47 (green), 99 (red), 100 (turquoise), 153 (khaki), 154 (pink) and 183 (brown) in seal blubber.**

The distribution of PFOS concentrations in liver and blood of seals represents the same decreasing gradient from the Wadden Sea to the northern North Sea which is

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[4] NOAA Report Calls Flame Retardants Concern to U.S. Coastal Ecosystems (online 2009: http://www.noaanews.noaa.gov/stories2009/20090401_ecosystems.html)

in

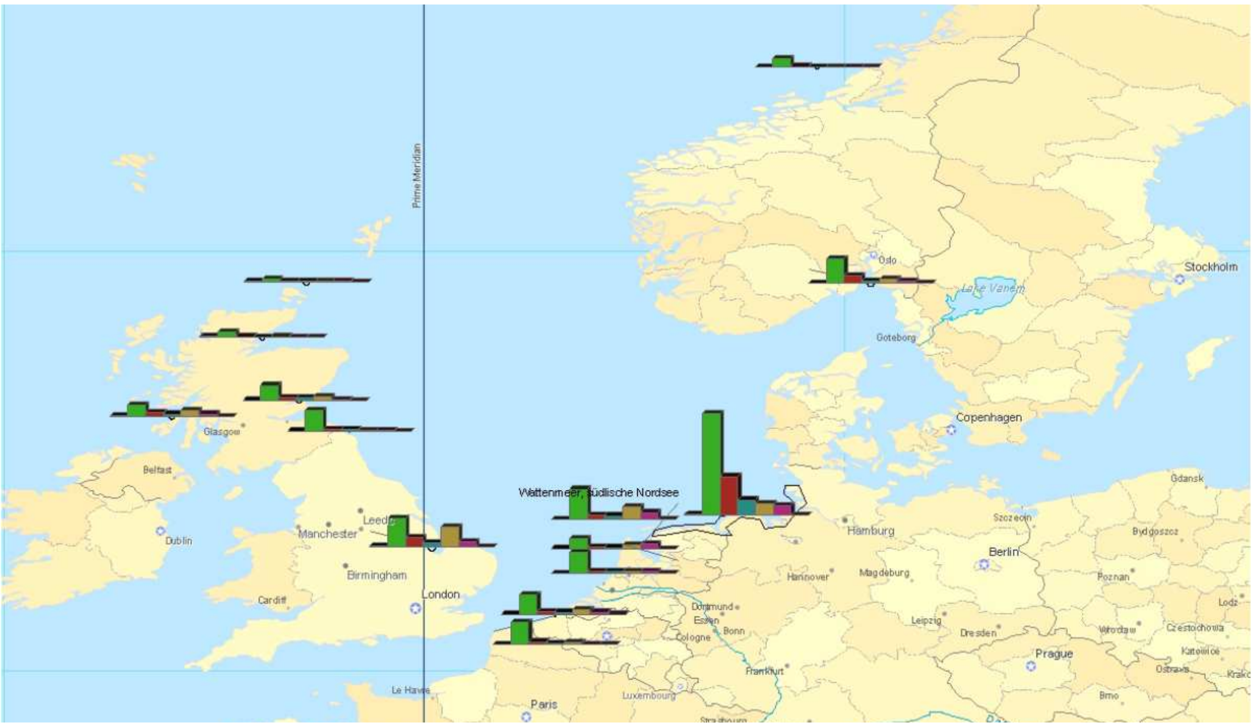

**Figure 2: Enlarged detail of the distribution of PBDE concentrations in seal blubber in the North Sea. Congeners are given in analogy to Fig. 1: BDE 28 (blue), 47 (green), 99 (red), 100 (turquoise), 153 (khaki), 154 (pink) and 183 (brown).**

analogy to a concentration gradient in seawater (Ahrens et al. 2009b). In addition, it is known that PFOS is mainly emitted via the large rivers like Rhine and Elbe flowing into the North Sea (Möller et al. 2009, Pistocchi and Loos 2009). Consequently, a significant long-range transport of these compounds with marine organisms along the food chain of the seal seems to be negligible. This is in accordance with the investigated literature on biovector transport of organic compounds mentioned above which proves pollutant transport with migratory animals into locally defined regions, especially remote lakes, and investigations of Wania (1998). Thus, biovector transport does not seem to play a crucial role on a global scale but becomes important as soon as local hotspots of organism accumulation (e.g. resting places at lakes or in the Wadden Sea) are concerned.

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## 3.2. *IDENTIFICATION OF INTRINSIC SUBSTANCE PROPERTIES (LRTP WATER)*

We employed different approaches to identify intrinsic substance properties which may lead to long-range transport (LRT) of organic chemicals. First of all, the Stockholm Convention[5] on Persistent Organic Pollutants (POPs) defines that an organic chemical is prone to LRT in air if its atmospheric half-life exceeds 2 days. In analogy to this, we deduced half-life criteria for substances primarily transported in water. We differentiated between transport on a regional scale in freshwater with mean flow velocities of European rivers (0.7-1 m/s) and transport on a global scale applying flow velocities of ocean currents running into the Arctic Ocean (0.28-0.9 m/s). The results indicate that substances with a half-life of more than 10 days in freshwater may undergo long-range transport. This value is significantly below the current persistence criterion in freshwater of 40 days as defined within the REACH regulation[6]. Consequently, substances which are not persistent according to REACH may still show long-range transport in freshwater. In contrast, substances are only prone to LRT in oceans if their half-life exceeds 90 days, which is significantly higher than the persistence criterion of 60 days in oceans (Zarfl et al. 2011).

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[5] Stockholm Convention on Persistent Organic Pollutants. United Nations Environment Programme, Geneva, Switzerland (http://chm.pops.int/)

[6] Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). Official Journal of the European Union L396 (http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L: 2006 :396:0001:0849:EN:PDF)

The half-life criteria, however, do not consider the partitioning behaviour of the investigated organic compound. Thus, we applied the multimedia model ETAPOS to identify the parameter range for which transport in air is dominated by transport in water. Simulations for the environmental fate also result in the characteristic travel distance (CTD), which is a spatial metric similar to the temporal metric of the half-life criterion. It is based on a steady-state assumption and describes the distance which a substance can travel until its concentration drops to 1/e (approximately 37%) of its initial value (Bennett et al. 1998). Our investigations reveal that the CTD in water dominates the CTD in air only for those compounds which are characterized by a long half-life in water and a low partition coefficient between air and water. This group of compounds includes about 38% of the non-ionic organic substances selected from the Canadian Domestic Substance List (CDSL) (Zarfl et al. 2011). Further investigations on substances of the CDSL are described below and will give additional insight on intrinsic substance properties inducing a potential for LRT.

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## 3.3. *EVALUATION OF MONITORING DATA FROM REMOTE LOCATIONS, COMPARISON OF MONITORING DATA AND MODEL RESULTS*

In this work package, we used concentrations of polychlorinated biphenyls (PCBs) that were measured in the field (Arctic: Zeppelin; southern Norway: Birkenes) and two models (FLEXPART and BETR Global) to investigate the mechanisms and significance of long-range transport of PCBs to the Arctic; we focused on PCB-28 and PCB-153.

### 3.3.3. *Methods: Measurement Data, Emission Data and Models*

**Measurement Data.** The measurement data were collected at Birkenes and Zeppelin. Birkenes (58º N, 8 Eº) is situated in Southern Norway; it is an intensive EMEP (European Monitoring and Evaluation Programme) monitoring site (e.g. Amundsen et al, 1992 and Yttri, et al 2007) mainly surrounded by forest. A lake and a few low-intensity agricultural fields are nearby and two small cities (Lillesand and Krisitansand) are in the vicinity. The measurements are taken once a week and for each measurement a sample volume of about 500 m³ air is taken over a 24-hour period.

Zeppelin (79º N, 12º E) is situated on a ridge of Zeppelin mountain on the west coast of Spitsbergen. For Zeppelin, 48-hour samplings collected ~1000 m³ of air every week were taken.

The air sampling was conducted by high-volume air samplers with glass fiber filters (GFF) and polyurethane foam plugs (PUFs) as sampling media. Detailed descriptions of the sampling processes, analytical methods and QA/QC procedures can be found in Hung et al. (2005), Bossi et al. (2008), Eckhard et al, (2009) and on the UNECE-EMEP website:http://www.emep.int, from where we downloaded the concentration data sets.

The lighter PCBs (e.g. PCB 28) are mostly present in the gas phase. The Long Range Transport Potential (LRTP) of lighter PCBs is limited by OH-radical reactions. The concentration of OH radicals in the Arctic atmosphere is rather low (Lelieveld et al, 2004), which reduces the efficiency of OH-radical removal of the lighter PCBs.
On the contrary, heavier PCBs (e.g. PCB 153) are more strongly associated with airborne particles; the size of the particle-bound fraction depends on the concentration of particles in the atmosphere and on the ambient temperature. The dry and wet deposition of these particle-bound PCBs are stronger than those of gas-phase PCBs. Consequently, heavier PCBs are deposited to the ground in regions relatively close to the source regions (Wania et al 2002), and the fraction that undergoes long-range transport is largely associated with particulate matter. For this reason the amount of heavier PCBs can be expected to be increased during events of rapid transport in comparison to average conditions, when travel times are longer.

**Emission Inventory.** We used annual emission rates for PCB 28 and PCB 153 for the years 1998 to 2009. The emission inventory was created by Breivik et al. (2007). We applied the maximum emission scenario, which seems the most realistic one (Breivik et al, 2007). However, there are still large uncertainties of the actual emission estimates (Breivik et al. 2002b, 2007). The main emission regions for PCB 28 are found over eastern North America, Europe, western Russia and Japan, see Fig.1.

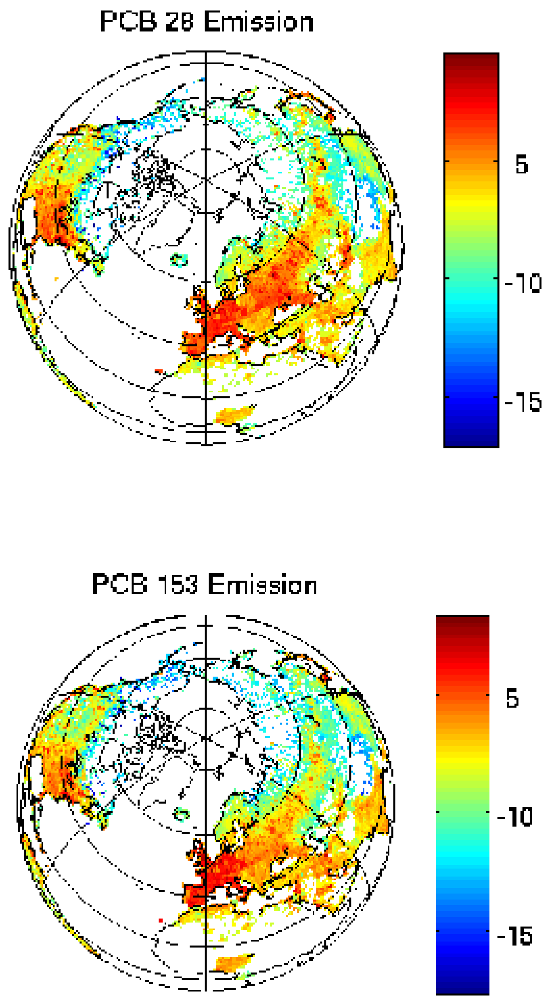

**Figure 1: Yearly emission of PCB 28 (top) and PCB 153 (bottom) in t/year on a 1° x 1° grid taken from Breivik et al. (2007)**

**BETR-Global.** We used the Berkeley-Trent global multimedia mass balance model (BETR Global) to model the fate and transport of PCBs in the environment (MacLeod et al. 2005, Lamon et al. 2009). The BETR-GLOBAL model is discretized on a 15° x 15° grid, with 288 grid cells. Each of these grid cells consists of 7 bulk compartments (ocean water, fresh water, planetary boundary layer, free atmosphere, soil, freshwater sediments, and vegetation). The model represents advective transport between the regions in air and water and intercompartment transport processes such as dry and wet deposition and reversible partitioning. To model degradation of PCB in the gas phase, spatially and temporally resolved concentrations of OH radicals in the global atmosphere are used. Meteorological and oceanic data were used with a monthly time resolution, but monthly mean values were applied and thus interannual variability is neglected. With BETR, monthly concentrations for PCB 28 and PCB 153 were calculated by Lamon et al (2009), and were used in the present work.

**Lagrangian Particle Dispersion Model.** To identify the source regions of PCBs measured at Birkenes and Zeppelin, we used the Lagrangian Particle Dispersion Model (LPDM) FLEXPART (Stohl et al. 1998, 2005). FLEXPART calculates trajectories of so-called tracer particles. The particles move according to the mean wind field and turbulent fluctuations and can be traced forward or backward in time. Here we took backward runs which were calculated by the Nilu-Atmos research group and are available from http://transport.nilu.no/flexpart-projects. To calculate the backward runs, FLEXPART was driven with operational analysis from the European Center for Medium Range Weather forecast (ECMWF) with 1º x 1º resolution for the years 1998 to 2009. The meteorological fields were updated every three hours and 40000 particles were released during each three hourly interval and followed backward in time for 20 days. In backward mode, FLEXPART calculates an emission sensitivity function *S*, called source-receptor relationship (Stohl et al. 2003, Seibert et al. 2004). The *S* value, in units of $s/m^3$, of a particular grid cell is proportional to the particle residence time in that cell. The spatial distribution of *S* close to the surface is of particular interest, as most emissions occur near the ground. Thus, *S* values are calculated near the ground, for the so-called footprint layer 0–100 m above the ground. The footprint indicates where the air has resided near the ground, and thus had the potential to take up pollutants, before arriving at the measurement site. Footprints were calculated for each measurement interval (24 hours at Birkenes and 48 hours for Zeppelin). To look at the general atmospheric transport to the two measurement sites, we calculated seasonal average footprints for summer and winter (see Fig. 4 and Fig. 5). The average footprints were calculated by summing up the footprints for the respective season and dividing by the total number of footprints available.

To identify potential source regions for extraordinarily high and low PCB concentrations, we summed up the footprints for times when the 20% highest and lowest PCB concentrations were measured and again divided by the number of footprints. The resulting fields are divided by the average seasonal footprints; values above 0.2 suggest that high measured concentrations are preferentially associated with transport originating from the respective grid cell (e.g. Fig. 6).

### 3.3.4. *Results*

**Measured Time Series.** Time series for PCB 28 and PCB 153 measured at Birkenes are shown in Fig. 2. PCB 28 concentrations have a slightly negative trend without a clear seasonal cycle. The concentrations of PCB-153 have a stronger negative trend and a seasonal cycle with increased concentrations in winter.

At Zeppelin (Fig. 3), PCB 28 concentrations decrease from 1998 to 2009 and have a seasonal cycle with higher concentrations in summer. The negative trend is also found for PCB 153. The seasonal cycle is especially pronounced for the years 2004 and 2005, but different from PCB 28, PCB 153 shows concentrations that are enhanced during winter.

At Birkenes, mean PCB 153 concentrations are 200% of the corresponding values at Zeppelin. The opposite is found for PCB 28 concentrations, where concentrations at Birkenes are 60% of the values of Zeppelin.

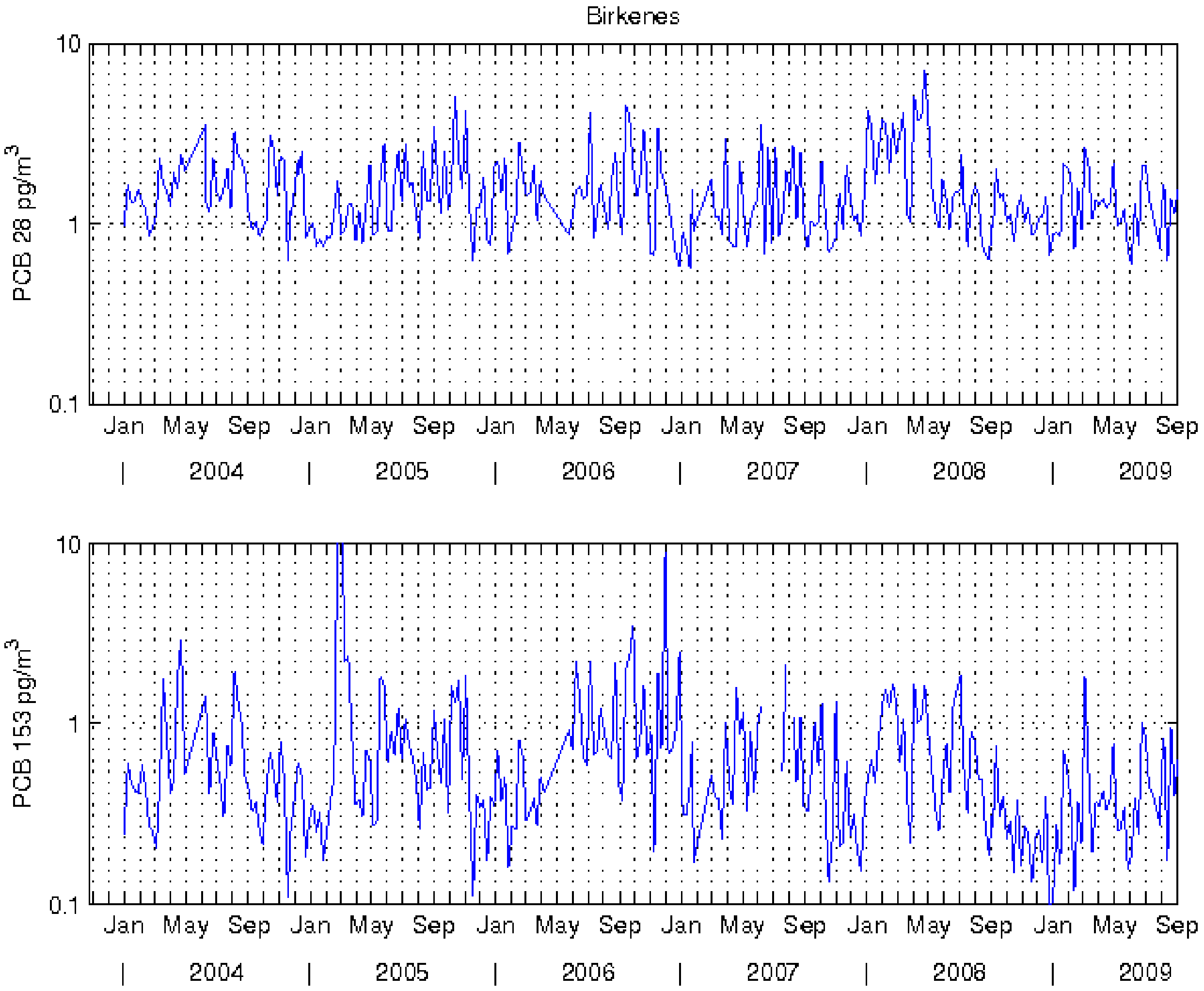

**Figure 2: Measured PCB 28 (top) and PCB 153 (bottom) concentrations in pg/m$^3$ at Birkenes**

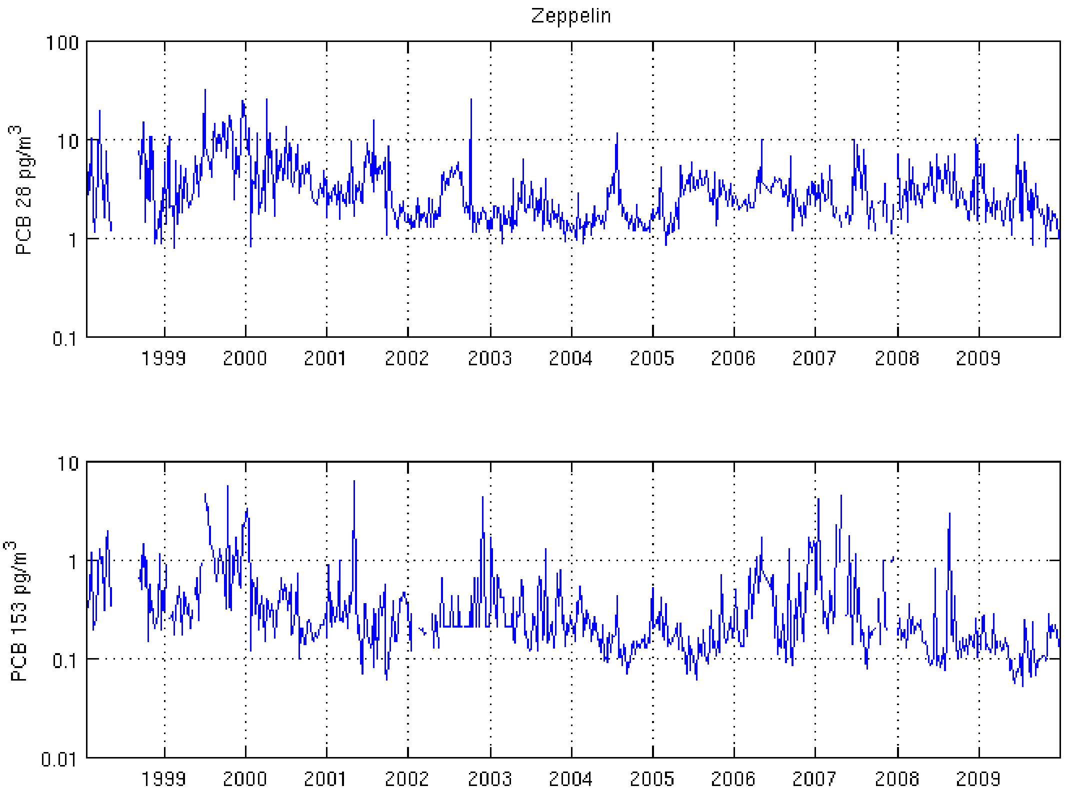

**Figure 3: Measured PCB 28 (top) and PCb 153 (bottom) in pg/m$^3$ measured at Zeppelin**

**Footprints and Potential Source Regions.** Since the meteorological conditions differ mainly for the summer (July to August, JJA) and the winter (December to February, DJF) (Klonecki et al. 2003) we look at the average footprints for these two seasons.

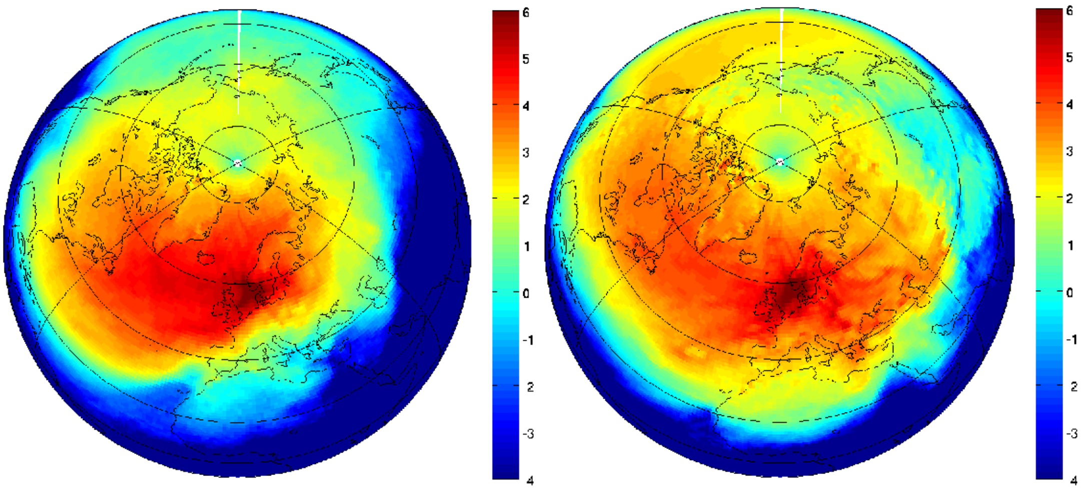

**Figure 4: Average footprint for Birkenes for summer (left) and winter (right). Red and orange regions indicate long residence times and thus high potential of pollution uptake.**

Highest *S* values are, of course, found in the vicinity of the measurement site, and *S* decreases with distance from the station.

At Birkenes, in summer (Fig. 4, left) the decrease with distance is much stronger in the east of the site than in the west. In winter (Fig. 4, right), in contrast, the decrease is similar for both directions, indicating a stronger influence of the European continent in winter. Sources in northwestern Europe have a similar influence for Birkenes in summer and winter, but sources in southern and eastern Europe are important only in winter. Also transport from North America to Birkenes is more important in winter than in summer. Overall, Eckhard et al. (2009) reported that more than 50% of PCB 28 can be attributed to emissions from Europe.

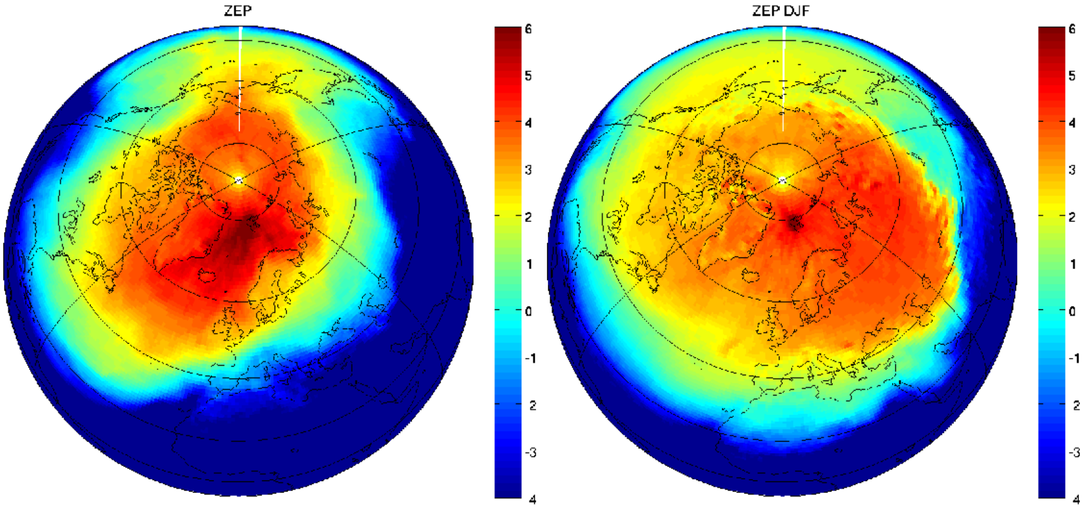

**Figure 5: Average footprint for Zeppelin for summer (left) and winter (right). Red and orange regions indicate long residence times and thus high potential of pollution uptake.**

In summer, at Zeppelin (Fig. 5, left) high *S* values are found over the Arctic Ocean. The *S* values decrease sharply near the continental coasts, indicating that air arriving from the land masses is not likely to reach the Zeppelin station within the 20 days of transport. However, there is still influence from the northern parts of Europe and Asia and Canada. In winter (Fig. 5, right), in contrast, high *S* values are found even in western and southern Europe and over Russia. This is consistent with the general understanding of atmospheric transport patterns to the Arctic in winter (Barrie et al. 1986, Klonecki et al. 2003, and Stohl et al. 2006).

In summer, residence times over the main primary emission regions are rather low, whereas in winter air arrives at Zeppelin that has passed over the main PCB emission regions in Europe and Russia (Compare Fig. 1 and Fig. 5).

We now look at the average footprints for the 20% highest and lowest PCB concentrations to identify potential source regions for these particularly high/low concentrations. At Birkenes, in summer, high PCB concentrations are associated with transport from Europe and the western part of the US and Canada (Fig. 6, top left; only PCB 28 is shown).

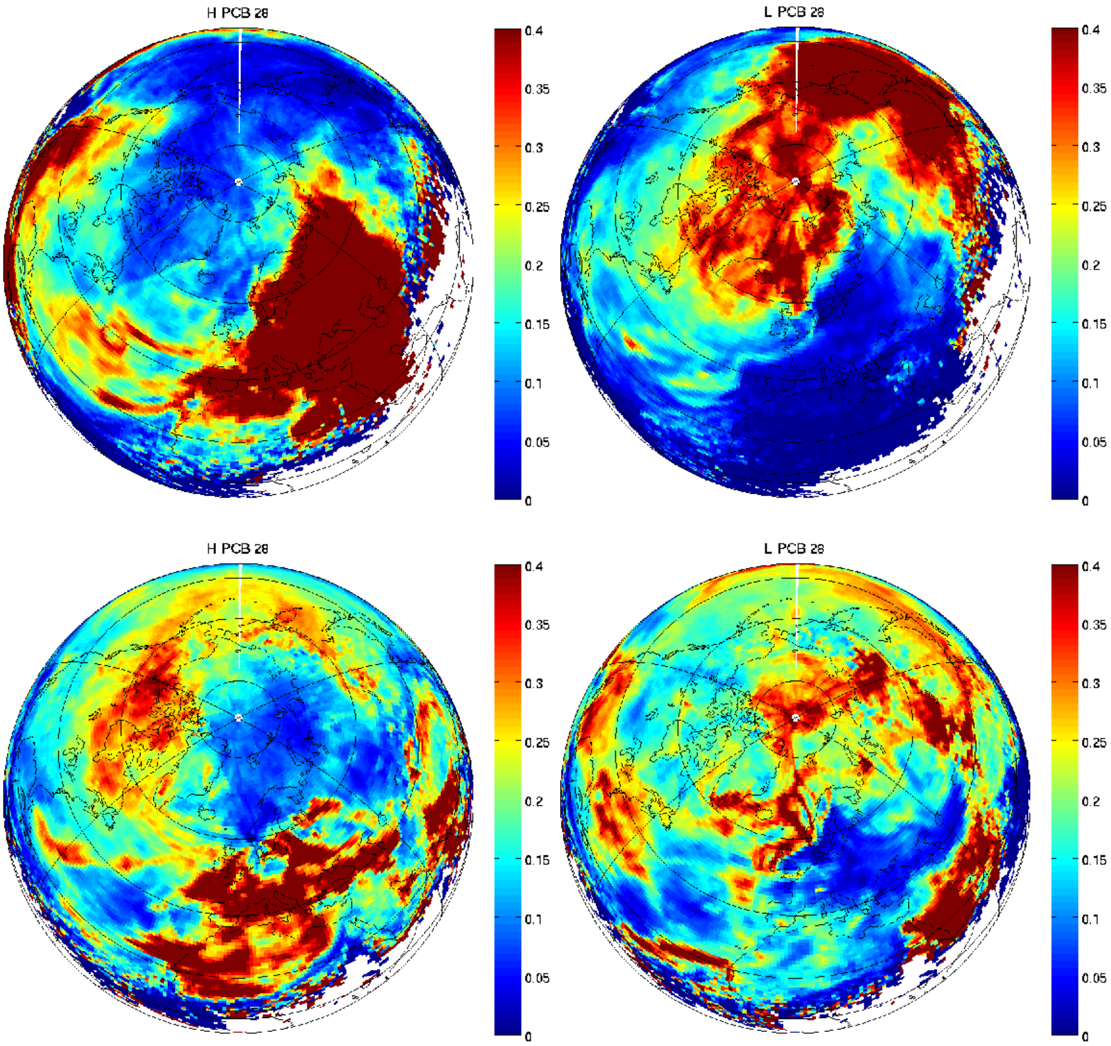

**Figure 6: Fields resulting for the 20% highest (left) and lowest (right) PCB 28 concentrations for Birkenes in summer (top) and in winter (bottom). Regions with values exceeding 0.2 (yellow to dark red colors) indicate that high measured concentrations are preferentially associated with transport from these regions.**

Thus the 20 % highest values are due to transport events which are rather untypical for this season, because the general summer footprint proposes transport from the North Atlantic and the Arctic Ocean. For the lowest 20% of the concentrations, on the other hand, the potential source regions are found over the Arctic and Pacific Ocean (Fig. 6, top right). In winter (Fig. 6, bottom left), the pattern is more patchy, but Europe is still the major source region for high PCB 28 concentrations at Birkenes. The patchy pattern can be explained by the generally high *S* values over Europe in winter (see Fig. 4, right). Finally, Fig. 6, bottom right, indicates that low concentrations of PCB 28 measured at Birkenes in the winter correspond to values below 0.2 in large parts of Europe, western and central Russia, and Canada (blue to yellow colors). In other words, these areas, which include large fractions of the PCB emission sources, are no likely source regions of air arriving at Birkenes when low concentrations of PCB 28 are measured.

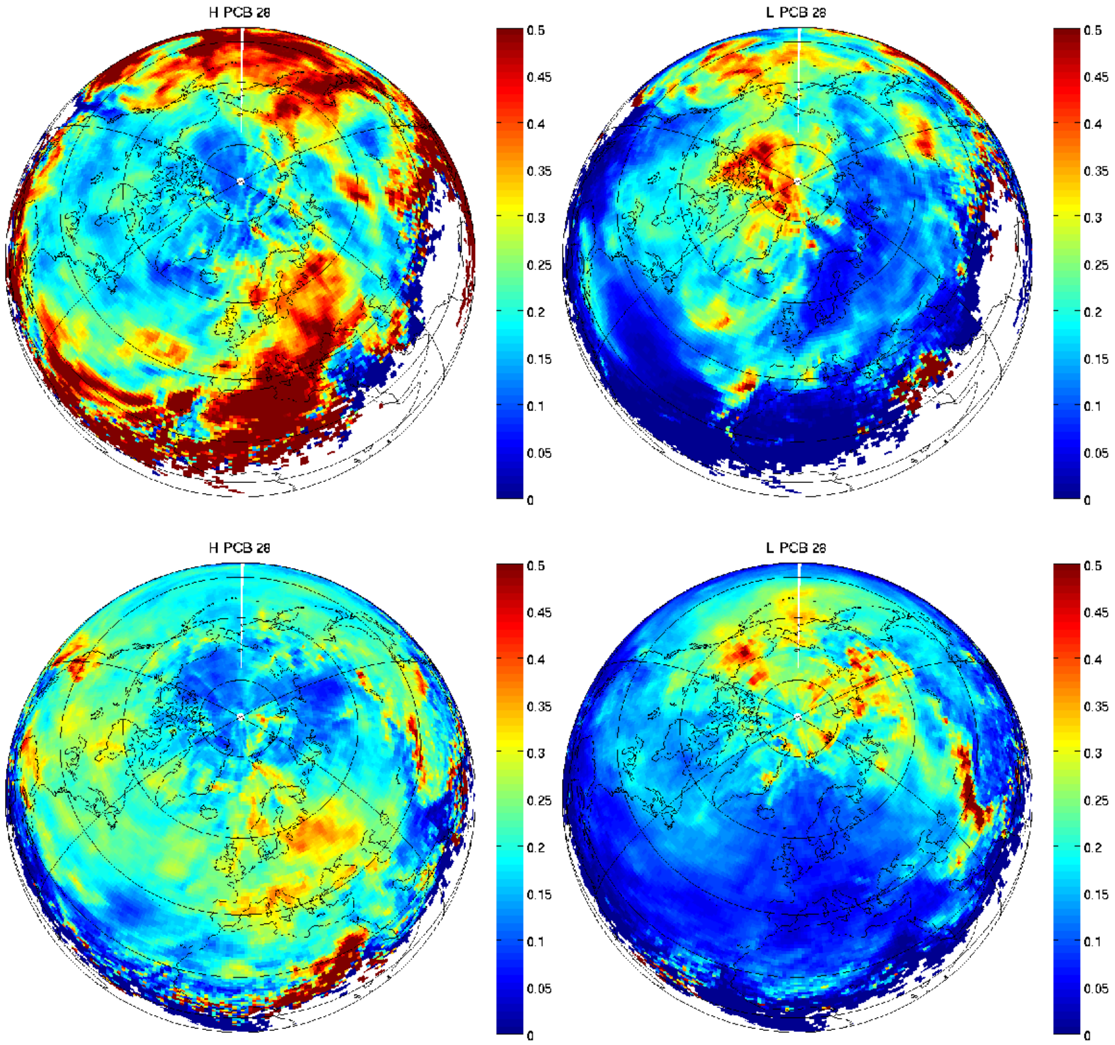

**Figure 7: Fields resulting for the 20% highest (left) and lowest (right) PCB 28 concentrations for Zeppelin in summer (top) and in winter (bottom). Regions with values exceeding 0.2 (yellow to dark red colors) indicate that high measured concentrations are preferentially associated with transport from these regions.**

Also at Zeppelin, high PCB concentrations – in summer (Fig 7, top left, only PCB 28 is shown) and winter (Fig. 7, bottom left) – are associated with transport from Europe, but the pattern is less pronounced than at Birkenes. Low concentrations, on the other hand, correspond to values below 0.2 (blue to yellow colors) in the main regions of PCB emissions in summer and winter (Fig. 6, top and bottom right).

Finally, we also found that the 20% highest concentration values measured at Birkenes and Zeppelin account for 50% of the total concentration for the respective season.

**Comparison of Measured and Modeled PCB Concentrations.** Because the model set up that was used for FLEXPART in the current work neglects dry and wet deposition, as well as the reaction of PCBs with OH radicals, FLEXPART generally overestimates PCB concentrations. We therefore used the results of the BETR model to compare measured and modeled PCB concentrations. From the measured data, we calculated average concentrations for each month over the ten-year period from 1998 to 2009. For BETR, the monthly concentrations are also averaged over the ten-year period (1998 to 2009), yielding an average concentration for each month.

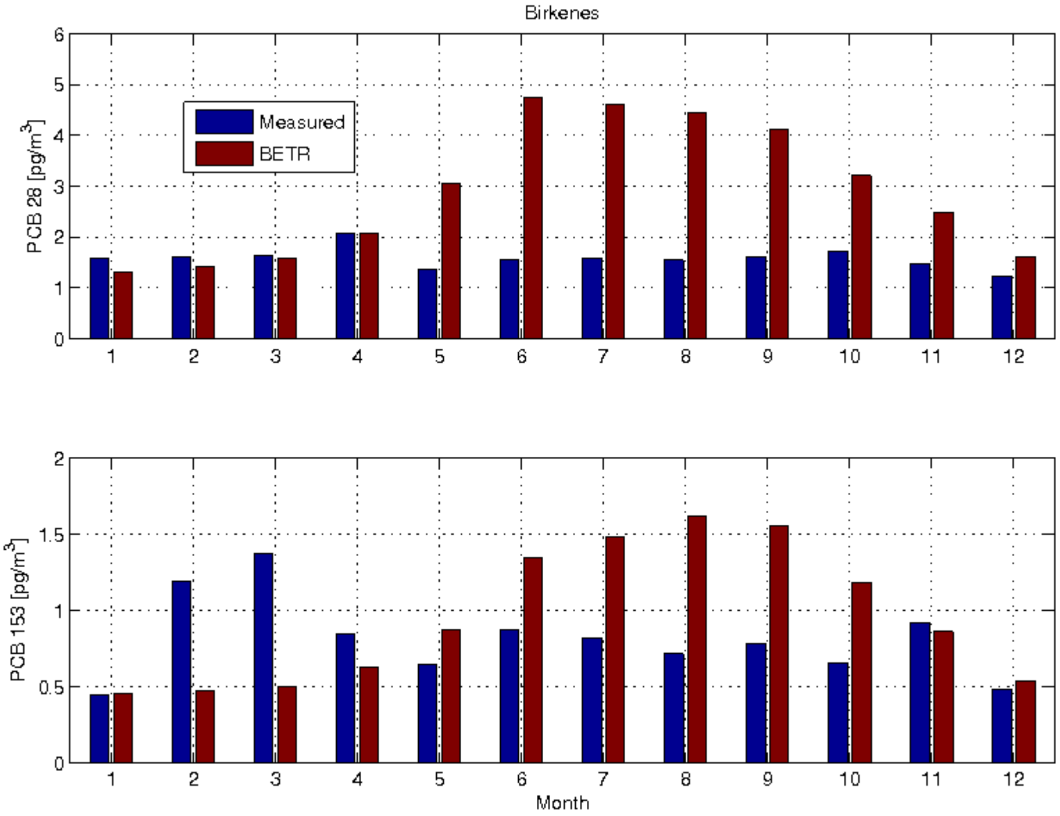

**Figure 8: Monthly averaged PCB 28 (top) and PCB 153 (bottom) concentrations for Birkenes. Measured concentrations are shown in blue and the modeled (BETR) ones in red.**

Fig. 8 shows the averaged concentrations of PCB 28 and PCB 153 for the measurements in blue and the BETR model in red for Birkenes. Absolute values of PCB 28 are quite well reproduced by BETR from January to April and are overestimated for the rest of the year. The modeled PCB 28 concentrations have a strong seasonal cycle with highest values in summer. Modeled and measured PCB 153 concentrations agree very well in winter, but not for the other seasons: whereas model values peak in summer, measured PCB 153 values are highest during spring.

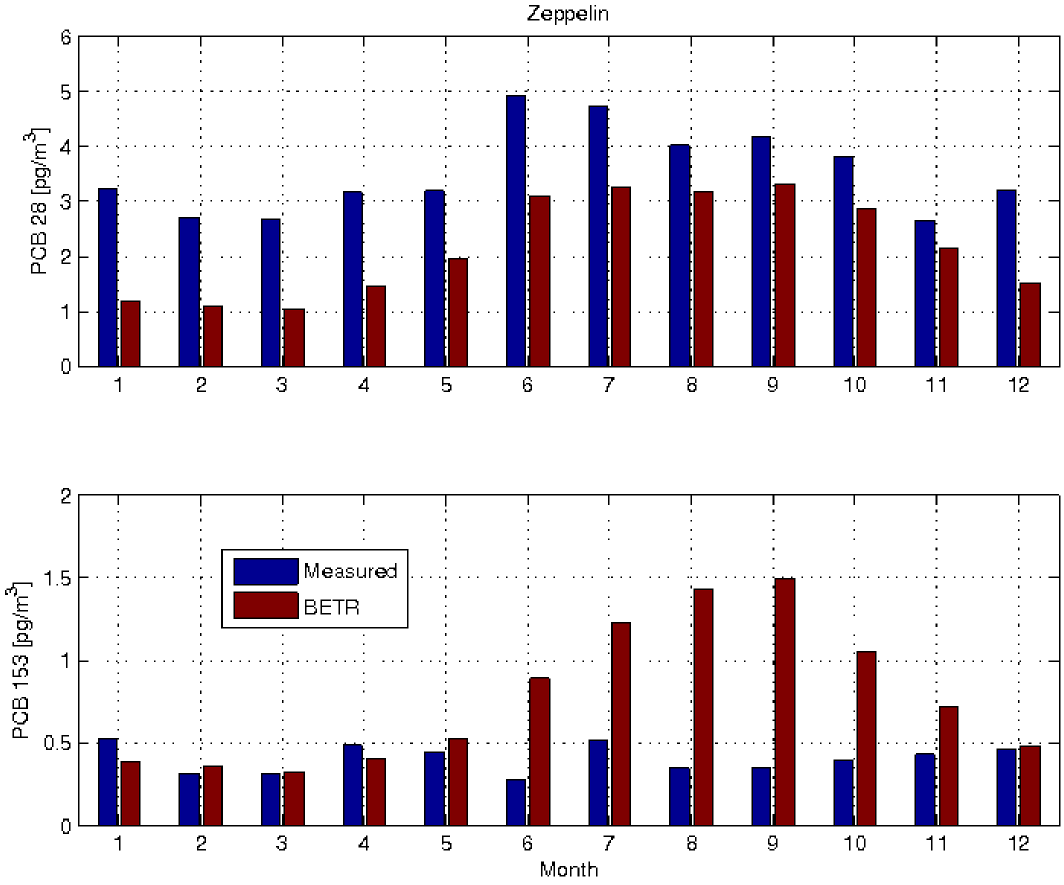

**Figure 9: Monthly averaged PCB 28 (top) and PCB 153 (bottom) concentrations for Zeppelin. Measured concentrations are shown in blue and the modeled (BETR) ones in red.**

The results for Zeppelin are shown in Fig. 9. Again, the model calculates a significant seasonal cycle for PCB 28 and PCB 153 that is reflected by the measurements for PCB 28 but not for PCB 153. PCB 28 concentrations are underestimated by the model, especially in spring and winter. PCB 153 concentrations are quite well reproduced in spring and winter but not in summer.

### 3.3.5. *Discussion and Conclusions*

The field data shown in Figures 2 and 3 are the empirical indication of environmental long-range transport of PCB (and similarly for other chemicals that are also detected at Birkenes and Zeppelin, but are not discussed in the present work). As empirical results, field data are essential, but at the same time they do not provide any indication of source regions, travel times and pathways of the chemicals towards the Arctic.

With the FLEXPART model, it has been possible to identify the different potential source regions that prevail during summer and winter (Figs. 4 and 5). In the winter, these potential source regions coincide with known regions of ongoing PCB emissions, namely Europe and Northern/Eastern Russia.

In addition, for the particular times when highest/lowest PCB concentrations were measured at the two sites, the analysis with the FLEXPART model has shown a dominance of potential source regions with high/low PCB emissions (Figs. 6 and 7).

In other words, for the concentration maxima observed at Birkenes and Zeppelin, our analysis indicates relatively direct transport of PCBs primarily from sources located in Europe and Russia. This analysis is based on the highly resolved model FLEXPART and cannot be performed with multimedia box models, because the temporal and spatial resolution of these models is too low. Note that only meteorological information was used in FLEXPART in this exercise; the FLEXPART calculations were combined with chemical-specific information present in the field data and in the emission inventory (points in time when high/low PCB concentrations were measured; regions with high/low PCB emissions).

The multimedia box model BETR-Global (and other multimedia box models), on the other hand, contains chemical-specific processes in air and surface media (wet and dry deposition, volatilization, degradation). In general, PCB concentrations calculated with BETR-Global and concentrations measured at Birkenes and Zeppelin agree within a factor of 3 or less. Given the uncertainties in emission data and chemical properties, this is a good agreement (Scheringer 2009). However, there are seasonal patterns that are clearly different in the BETR results and in the field data. The increase in concentrations during the summer that is visible in the BETR results is caused by the chemical-specific temperature dependence of the vapor pressure and the air-water and octanol-air partition coefficients. This temperature dependence causes stronger volatilization of PCBs from primary and secondary sources when the temperature is higher. In three of the four sets of field data, this seasonality is not visible (both PCBs at Birkenes; PCB-153 at Zeppelin), but the measured concentrations remain relatively stable throughout the year and are lower than the BETR results during summer and fall.

One possible reason for this finding is that in reality the primary emission sources of PCBs are less influenced by variable ambient temperatures than it is assumed in the BETR model. A second aspect is that the BETR grid cells including Birkenes and Zeppelin may receive PCBs from other/more PCB source regions than is the case in reality (and indicated by the potential source regions identified by FLEXPART: summer footprints are in regions with low emissions). This point could be clarified by a detailed analysis of the PCB mass fluxes in BETR.

Finally, from the current analysis it can be concluded that BETR does not systematically underestimate the PCB concentrations measured at Birkenes and Zeppelin. It has been hypothesized that multimedia box models such as BETR might systematically underestimate transport of airborne chemicals to the Arctic because these models do not explicitly describe highly effective short-term transport events (but employ long-term average meteorological data). The current results of our analysis do not support this hypothesis.

As a recommendation concerning the use of monitoring data in assessments of environmental long-range transport of chemicals, we conclude that monitoring data provide an important empirical indication of LRT but their interpretation should always be supported by model results. Highly resolved Langrangian Particle Dispersion Models such as FLEXPART and multimedia box models such as BETR-Globoal complement each other in a useful way.

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# 4. ASSESSMENT TOOL CONSIDERING LONG-RANGE TRANSPORT POTENTIAL

The screening tool ETAPOS (Environmental Transport, Accumulation and Persistence of Organic Substances) (Ehling et al. 2010) combines a level III multimedia fate model with a dynamic bioaccumulation model that considers accumulation along the aquatic as well as the terrestrial food chain leading to man. The multimedia part of ETAPOS is based on ELPOS (Environmental Long-Range Transport Potential of Organic Substances) (Beyer and Matthies 2001, Matthies et al. 2009). Screening criteria are overall persistence ($P_{ov}$) and characteristic travel distance (CTD) as a metric for LRTP. ETAPOS calculates all indicators within the same generic multimedia environment. The model enables a multi-criteria evaluation of organic chemicals with respect to their POP and PBT properties.

Initially, it was planned to integrate substance transport by migrating animals as well as by plastic particles. Both transport pathways turned out to be of minor importance on a global scale as described in previous project reports. Pollutant transport by migrating animals plays a significant role only if local hotspots such as rest areas of migrating birds are concerned (e.g. Blais et al. 2007, Evenset et al. 2007). Plastics as a transport vector for organic pollutants to the Arctic were also identified as a minor transport pathway in comparison to air and water as far as the amounts of organic chemicals sorbed to the plastic particles are concerned (Zarfl et al. 2010, Gouin et al. 2011). Nevertheless, many questions concerning plastics and pollutants absorbed to or contained in plastics remain still unsolved and need further research (Zarfl et al. 2011). Consequently, since the assessment tool is designed to investigate the environmental fate and the transport of organic pollutants on a global scale, migrating animals and plastic particles are not included in the software.

## 4.1. Model Structure

The level III environmental model provides the integral core of ETAPOS. The essential structure of the generic model environment is represented by homogeneous compartments that are interconnected via various exchange processes (Figure 1). The compartments air, freshwater, sediment and three different types of soil (natural, agricultural, industrial) were supplemented by an ocean compartment. Calculation of the CTD, a well-acknowledged concept for LRTP assessment, is independent of the ocean compartment. Steady-state is assumed in order to simulate the long-term distribution behaviour of organic compounds in the environment, i.e. substance input equals substance output for each compartment. For in-depth information concerning steady-state multimedia models we refer to the literature (Trapp and Matthies 1997; Mackay et al. 2001; Scheringer et al. 2009). In this study, level III simulation results were corrected to represent a more realistic intermittent rainfall situation (Matthies et al. 2009). For this reason, the time-weighted average of steady-state concentrations under conditions with and without rainfall was calculated by the intermittent rain approximation for steady-state models proposed by Jolliet and Hauschild (2005). The sea water environment including the respective sediment and air compartment (Figure 1) represents an extension of ELPOS to consider bioaccumulation in a simple marine food chain. However, the sea water compartment is only necessary as far as the aquatic food chain is concerned.

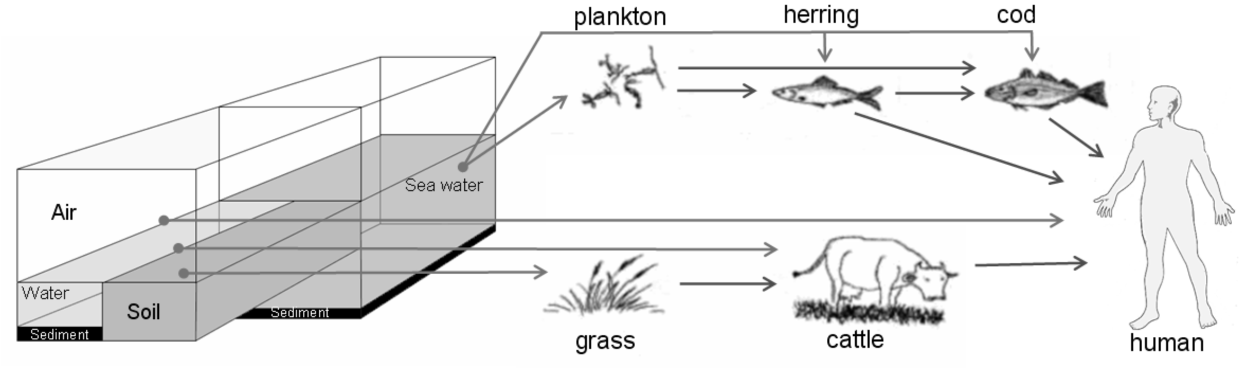

**Figure 1: Schematic representation of the terrestrial and aquatic food chain and their interconnections with the multimedia model.**

Parameterisation of food chain organisms is chosen according to the bioaccumulation model ACC-Human (Czub & McLachlan 2004a). Humans represent the top of both food chains consisting of plankton, herring and cod, and of grass, beef cattle and dairy cow, respectively. Organisms take up the chemicals via food as well as directly from the environment, e.g. modelled humans nourish on herring, cod, beef and dairy products on the one hand, but drink water and breathe air from the environment on the other hand. An overview on the interconnections between the food chains and the environmental model as well within the food chains is given in Figure 1. Organisms as elements of the food chains are modelled as homogeneously mixed compartments. Each compartment is regarded as mixture of different phases (air, water, and lipid) which are in equilibrium. These "organism compartments" are linked to different abiotic environmental compartments and interconnected with organisms on neighboured trophic levels. For each organism, a mass balance is defined including all uptake (input) and excretion (output) fluxes. In contrast to the environmental model, organisms are not necessarily assumed to be in steady-state. Since the time-scale to reach steady state may surpass the lifetime of the organisms, organism growth and temporally variable uptake and excretion processes during the different phases of life are explicitly considered.

Based on the fugacity concept (Mackay 2001) substance mass fluxes can be calculated from the different volume flows of air, water and food. Mathematically, this is described by a set of linear differential equations with variable coefficients. To determine the substance mass in an organism at a given point in time the differential equations have to be solved. Only in a few exceptional cases analytical solutions can be established for this kind of problem. Thus, a numerical method e.g. using time-consuming iterative procedures would be necessary which converge to the exact solutions for different time points. Here, we use an alternative approximation method instead that delivers good estimates of the desired values. An upper and a lower boundary for the substance mass in an organism at time $t$ (related to a certain age of the organism) can be calculated analytically using stepwise linearized growth functions. The mean of the two boundaries constitutes a good approximation of the substance mass in a given organism for a specified age. A detailed derivation of the required numerical method including error estimate can be found in the supporting information.

## 4.2. Description of assessment indicators

Predicted environmental concentrations from multimedia fate models suffer from the fact that accurate emission estimate are not available for many chemicals. In this study, we focused on the potential of a substance to persist in the environment, to be transported over long distances and to accumulate in food chains. Evaluation of these properties can be done on a relative basis using emission independent indicators. Therefore, ETAPOS does not require numbers on the magnitude of the chemical’s emission. However, environmental steady-state distribution is quite sensitive to the emission compartment, e.g. 100% emission into air delivers different results than 100% emission into water or soil. For this reason, we calculate three different numbers for each indicator assuming 100% emission into air, water or soil, respectively.

**Persistence.** Overall persistence ($P_{ov}$) is already accepted as screening criterion for persistence in the environment (Scheringer et al. 2009). The $P_{ov,i}$ for 100% emission into the compartment *i* (i= air, water, soil) considers both, half-lives in the different compartments as well as the chemical's distribution behaviour:

$$P_{ov,i} = \left(\varphi_{A,i} \cdot k_A + \varphi_{W,i} \cdot k_W + \varphi_{S,i} \cdot k_S + \varphi_{Sed,i} \cdot k_{Sed}\right)^{-1}$$

$\varphi_j$ is the substance mass fraction in compartment *j* (*A*: air, *W*: water, *S*: soil, *Sed*: sediment) of the total mass in the system at steady state, and $k_j$ is the cumulated loss rate following first order kinetics in compartment *j*. Calculation of $P_{ov}$ is restricted to actual loss processes. Advective transport processes across system boundaries are not considered except for deep sea burial, leaching into groundwater and escape to higher atmospheric layer. $P_{ov}$ corresponds to the substance's overall residence time within the respective environmental section. Loss processes are less weighted in compartments where only a small mass fraction of the compound resides.

**LRTP.** For evaluation of the long-range transport potential (LRTP) the characteristic travel distance (CTD) has been introduced (Bennett et al. 1998, Beyer et al. 2002). It is defined for advective transport by air and water as follows:

$$CTD_i = u_i \cdot \varphi_i \cdot P_{ov,i}$$

$u_i$ is the flow velocity in compartment *i* (*i* = air or water), $\varphi_i$ is the substance mass fraction in compartment *i* referred to the total mass in the system, and $P_{ov,i}$ is the residence time in the environment (100% emission into compartment *i)*. Maximum *CTD* is reached when the substance almost completely distributes into the compartment where the advective transport takes place. The CTD corresponds to the fictitious distance a substance would need to be transported until its concentration in the transport medium decreased to 37% of its initial value (Beyer et al. 2000).

**Bioaccumulation.** To evaluate the bioaccumulation potential of chemicals in humans, we use the intake fraction (IF) according to Bennett et al. (2002). It is defined as the total intake of an average man from birth ($t_0$ = 0) to the age of 30 years via food, drinking water and breathing (air) normalized by the total emission into the environment.

$$IF_i = \frac{\int_{t_0}^{t} \vec{I}(\tau) \times \vec{C} \; d\tau}{E(t - t_0)}$$

$\vec{I}(\tau)$ is the age-depending intake vector ($m^3$ per day) and $\vec{C}$ the concentration vector of the chemical in the abiotic and biotic compartments (mole per $m^3$) resulting from 100% emission into compartment *i* (*i* = air, water, soil) with constant emission rate *E*. A detailed description of the calculation of the intake fraction in ETAPOS can be found in the supporting information. In terms of bioaccumulation potential the intake fraction is superior to the commonly used BCF because it explicitly considers accumulation in man along the aquatic and the terrestrial food chain. However, for comparison the program also shows user-defined BCF values (e.g. from measured data or estimated from the partitioning coefficient between 1-octanol and water at equilibrium).

## 4.3. Output features

ETAPOS offers three output features: *table view*, *scatterplot* and *spiderplot*. They are illustrated using simulation results for three hypothetic substances for which strong impact of distribution behaviour on persistence and/or LRTP evaluation has been shown (Klasmeier et al. 2006). Important physico-chemical properties needed for the simulation of the compounds are summarized in Table 1.

**Table 2: Properties of the hypothetic compounds for ETAPOS application**

| substance label | log $K_{ow}$ | log $K_{aw}$ | half-life (days) | | | |
|---|---|---|---|---|---|---|
| | | | air | water | soil | sediment |
| **Hypo-A** | 5.0 | -4.0 | 7 | 41.7 | 83.3 | 417 |
| **Hypo-B** | 5.0 | 2.0 | 365 | 7 | 14 | 70 |
| **Hypo-C** | 0.0 | -5.0 | 0.17 | 3650 | 7300 | 36500 |

A comprehensive representation of model results for a single substance is given in tabular form (*table view*). It displays values for the three indicators ($P_{ov}$, *CTD, IF*) for all three emission scenarios (air, water, and soil). Pie charts representing the steady-state mass distribution of the compound between the different environmental compartments supplement the *table view*. In addition, BCF is included in the results table for comparison. Figure 2 shows a screenshot of the *table view* for the hypothetic substance Hypo-C.

Name: Hypo-C

CAS: Hypo-C

List: Hypos-A-B-C

| | Overall Persistence | Characteristic Traveling Distance | human Intake Fraction | aquatic food chain |
|---|---|---|---|---|
| 100% Emission to Air | 7.21 days | 84.43 km | **1.18E-08** | BCF<br>0.1 |
| 100% Emission to Water | **1708.47** days | **7612.17** km | 7.56E-10 | TMF > 1<br>**True** |
| 100% Emission to Soil | 850.49 days | | 3.65E-09 | |

**Figure 2: Screenshot of the table view of the hypothetic substance Hypo-C**

Results can be displayed by two kinds of graphical plots which enable the comparison with reference chemicals. We use the maximum approach to account for the mode of entry into the environment (Stroebe et al., 2004), i.e. for each substance and each indicator only the maximum value of the three emission scenarios (100% into air, 100% into water, 100% into soil) is displayed. The temporal ($P_{ov}$) and spatial (*CTD*) substance range within the simulated environment is illustrated by *CTD/*$P_{ov}$*- scatterplots* adopted from ELPOS. Figure 3 shows the *scatterplot* for the three hypothetic compounds. They are compared against two classes of reference compounds which are classified as persistent organic pollutants (POP) according to the Stockholm Convention or as non-POP (“POP-reference” and “non-POP-reference”, respectively). These reference chemicals define boundary lines for LRTP and persistence. “LRTP boundary” and “$P_{ov}$ boundary” subdivide the *CTD/*$P_{ov}$*-scatterplot* into four sections. Actual POPs surpass both lines, while non-POPs are located in the region below the two boundaries (Klasmeier et al. 2006). This allows for simple first evaluation of persistence and LRTP potential.

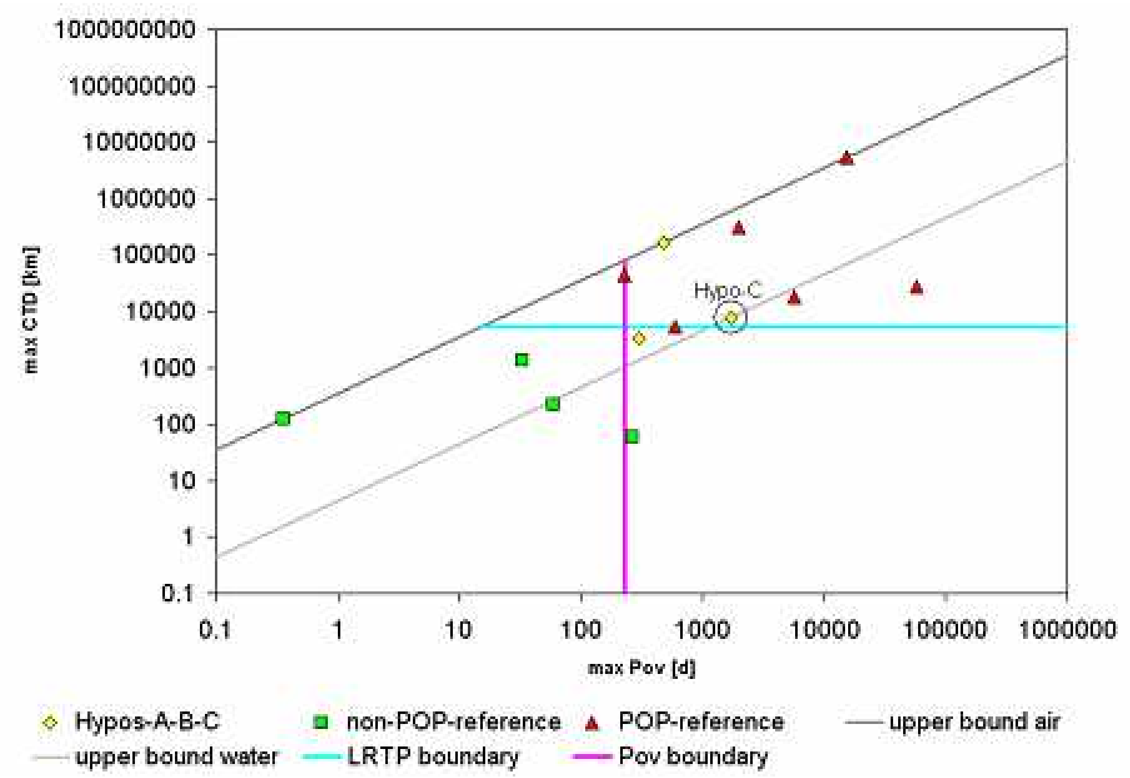

**Figure 3: Screenshot of the scatterplot for the three hypothetic compounds**

Alternatively, ETAPOS offers a *spiderplot* option in form of a radar plot. Results of the three indicators *CTD*, $P_{ov}$ and *IF* are presented along with the BCF on four logarithmic axes. Up to three substances can be shown simultaneously allowing for relative evaluation of a compound of interest against suitable references. The objective of this multi-criteria *spiderplot* is to identify similarities between different compounds that are not necessarily obvious from input data. Figure 4 shows the *spiderplot* with the three hypothetic substances. This plot impressively illustrates how different evaluation of the bioaccumulation potential can be when based on *IF* as compared to BCF. Inclusion of the terrestrial food chain leads to different accumulation potentials expressed as *IF*, while evaluation by BCF alone suggests that the compounds are equal bioaccumulative. The exact weighting between the both food chains due the human nutritional habits is described in the supporting information.

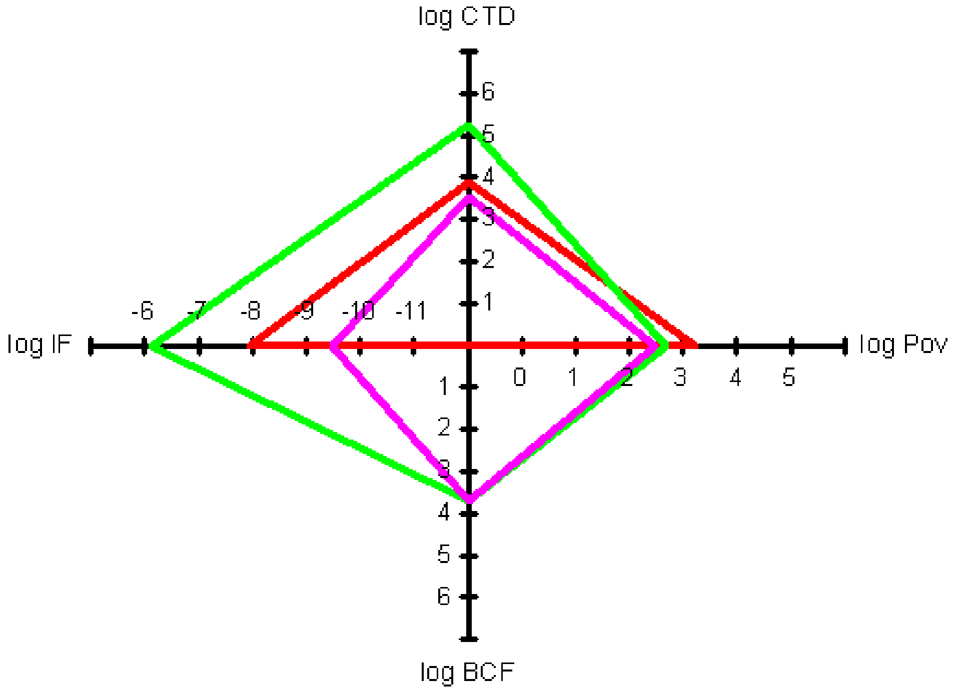

**Figure 4: Screenshot of the spiderplot for the three hypothetic compounds**

## 4.4. Conclusions

The multimedia model ETAPOS is an easy-to-use spreadsheet for evaluation and identification of substances with POP, PBT or vPvB properties. Graphic menu navigation and simple management of input data and output results via substance lists improve the operability in comparison to ELPOS or the OECD-Tool (Wegmann et al. 2009). Consideration of non-steady state bioaccumulation was achieved without loss of performance in terms of computing time. The approximate solution of the linear differential equation system with variable coefficients proved appropriate to assess the dynamic substance accumulation in the organisms during the different phases of life.

ETAPOS provides multifunctional possibilities to represent simulation results by *table view*, *scatterplot* and *spiderplot*. The *spiderplot* provides an additional output feature not available in ELPOS to evaluate compounds in comparison to reference chemicals. Simultaneous representation of three indicators (plus BCF) for up to three chemicals allows intensive evaluation of single chemicals by simple comparison of its potential for persistence, long-range transport and bioaccumulation against references with well-known environmental fate and behaviour. With the newly included features ETAPOS allows a fast multi-criteria evaluation of organic compounds in regard of their POP, PBT and vPvB properties.

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# 5. SELECTION OF CRITICAL COMPOUNDS

## 5.1. Selection of Non-PBT Compounds with Long-Range Transport Potential

Based on the precautionary principle as embedded in the REACH legislation and on the responsibility of each State to ensure that activities within their control do not impact the environment of other States, inclusion of substances with LRTP in the SVHC list is desirable. Brown and Wania (2008) published a list of 120 high production volume chemicals (HPVCs) which match the structure of known Arctic contaminants or which they had identified by a modelling approach as potential Arctic contaminants. Similar results were recently gained by Howard and Muir (2010) screening a combination of substance lists on persistence, bioaccumulation potential and LRTP. Moreover, Muir & Howard (2006) summarized the main 28 compounds identified to be persistent, bioaccumulative and showing LRTP according to the assessment criteria defined in the Stockholm Convention.

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Consequently, our overall aim was to screen chemicals which do not fulfil the PBT criteria and are thus not considered as SVHC with respect to their potential to be transported via air across significantly long distances by applying different approaches. Transport with ocean currents and transfer into food chains and subsequent transport with migrating animals might be further important transport routes but were not considered here. Different screening methods should be applied to a list of more than 20,000 substances with regard to persistence, bioaccumulation potential, toxicity and long-range transport potential. Finally, our results should be compared with the list of potential Arctic contaminants identified by Brown and Wania (2008) to elucidate the most relevant substance candidates which might be SVHCs due to their LRTP but are not yet identified as those as far as current REACH criteria are concerned.

### 5.1.1. *Methods*

**Outline.** The procedure described as follows was applied to the Canadian Domestic Substance List (CDSL)[7], which contains 22,438 compounds in use on the Canadian market. Identification of substances with long-range transport potential follows a

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[7] See Chapter 7. Summary of the Workshop “Long Range Transport – New Findings & Integration into REACH” for the application of the same procedure to the list of registered susbtances under REACH.

screening methodology which is, in a first step, based on substance properties estimated by quantitative structure-activity relationships (QSAR). Since these property estimation methods implemented in the EPISuite software package assume that all molecules are available in their non-ionized state, the screening procedure is reduced to compounds which mainly appear in their neutral form within the environmentally relevant pH range. Our screening criteria used for LRTP are based on two different concepts: The Stockholm Convention defines a substance to be prone to long-range transport if its atmospheric oxidation half-life exceeds two days. This criterion, however, does not consider the environmental distribution and degradation behaviour in various compartments. Therefore, the well-acknowledged concept of the characteristic travel distance (CTD) in combination with the multimedia model ELPOS was applied as a screening tool for identification of compounds with LRTP. This approach is based on the assumption that compounds which show a similar CTD to the CTD of acknowledged reference chemicals for POP-like behaviour should also be considered as substances that might have LRTP.

Finally, each substance of the reduced list of compounds with LRTP is crosschecked with an available list of 120 organic high production volume chemicals (HPVCs) identified by Brown and Wania (2008) and indicating transport to remote regions.

**Screening for non-ionized compounds.** The CDSL was stepwise analyzed and searched for organic compounds which are non-ionized to at least 95% in the environmentally relevant pH range of 4 to 10. Therefore, all substances flagged as organic compounds in the CDSL were chosen for further analyses. To identify the dissociation constants $pK_a$ the list of organic substances was investigated with the SPARC On-line Calculator v4.5 estimating $pK_a$ values from the molecular structure based on QSAR. SPARC has already been evaluated in earlier literature for more than 4300 dissociating species (Hilal & Karickhoff, 1995). SPARC also delivers the fraction of each of the possible dissociated and non-ionized species for several pH values. This means that only substances for further screening were chosen if the non-ionized fractions at pH 4 and 10 amount to 95% or more. This condition is sufficient to ensure that the non-ionized fraction does not drop below 95% within the whole range from pH 4 to 10 since the graph of the species fraction in dependence of the pH value is convex in the nearest neighbourhood of the global maximal value.

**Estimation of substance properties.** The list of organic non-ionized compounds was run through the software package EPISuite v4.0 such that physical-chemical substance properties were quantified by the implemented estimation methods based on quantitative structure-activity relationships (QSAR). To this end, the SMILES code of the substances as given in the CDSL was used as input parameter. EPISuite delivers parameters needed for the screening methods. These are CAS number and substance name for identification, molecular mass (g $mol^{-1}$), the logarithmic octanol-water partition coefficient log $K_{OW}$ estimated with KOWWIN v1.67, air-water partition coefficient $K_{AW}$, degradation half-lives ($t_{1/2}$) in air, water, sediment and soil (in days), atmospheric oxidation half-life (in days) and the bioconcentration factor (BCF) according to Arnot and Gobas. If the $K_{AW}$ value was not directly available it was calculated based on Henry's law coefficient which was given by simulation results of EPISuite.

**Screening for LRTP**. The estimated parameter values were used to identify compounds that would not be classified as PBT substances but are prone to LRTP (non-PBT-L substances). In a first step, the list was edited in two ways to identify compounds with LRTP. On the one hand, the half-life criterion for long-range transport in air as defined in the Stockholm Convention was applied (half-life in air ($t_{1/2(air)}$) exceeding two days). On the other hand, all organic and mainly (> 95%) non-ionized compounds were simulated with the multimedia model ELPOS which calculates relative indicators for persistence (overall persistence Pov) and LRTP (characteristic travel distance CTD). More details concerning these indicators are given by Beyer et al. (2000). Resulting values of the indicators were compared with the implemented and well-established set of reference chemicals. According to the boundaries derived from these reference chemicals and defined for LRTP and persistence by Klasmeier et al. (2006) four substance categories can be differentiated:

A: high persistence, high LRTP
B: low persistence, high LRTP
C: high persistence, low LRTP
D: low persistence, low LRTP

Category A represents the group of compounds which are characterized by POP-like behaviour. Category B is of interest as far as our initial aim is concerned, namely to identify non-PBT substances characterized by LRTP. Thus, categories C and, especially, D are of minor importance since included compounds will not be of very high concern in terms of LRTP and in relation to PBT.

In a second step, all investigated compounds were classified into 8 sub-categories of PBT combinations which are:

1. PBT (persistent, bioaccumulative, toxic),
2. PB¬T (persistent, bioaccumulative, not toxic),
3. P¬BT (persistent, not bioaccumulative, toxic),
4. P¬B¬T (persistent, not bioaccumulative, not toxic),
5. ¬PBT (not persistent, bioaccumulative, toxic),
6. ¬PB¬T (not persistent, bioaccumulative, not toxic),
7. ¬P¬BT (not persistent, not bioaccumulative, toxic),
8. ¬P¬B¬T (not persistent, not bioaccumulative, not toxic).

Threshold values for P and B were chosen according to the European regulation for identification of PBT substances:

P: half-life of degradation in fresh water > 40 d or in sediment > 120 d or in soil > 120 d

B: BCF > 2000 L kg$^{-1}$

Toxicity information was given in the CDSL. This classification was applied to all screening steps to identify property combinations of special concern with regard to figuring out compounds which are not PBT (category 2 to 8) but show LRTP.

**Chemical Space Plots**. Since many substances are screened for a characteristic property at the same time, screening results were illustrated in chemical space plots (CSP) which show a selected target value in dependence of the substances' partition coefficients log $K_{OW}$ and log $K_{AW}$. In this case, the distribution of substance numbers within the CSP was the main target value. This means that the maximal available number of substances characterized by a specific log $K_{AW}$ – log $K_{OW}$ combination in the CSP was set to 100% (red regions in the plot) whereas the subsequent numbers were scaled to that value. This allows the identification of substance "hot spots" in dependence of their environmental partitioning. The CSPs were calculated for the underlying set of organic, non-ionized compounds as a reference figure and for all subsequent substance lists resulting from the different screening steps.

**Comparison with potential Arctic contaminants**. Muir and Howard (2006) hypothesised that 28 substances of the investigated CDSL can be regarded as the top compounds which show LRTP according to the Stockholm Convention, i.e. the half-life criterion t1/2 > 2, and according to the distribution coefficient between air and water ($K_{AW}$) restricting LRTP to compounds characterized by a log $K_{AW} \leq 1$ or $\geq 5$. Brown and Wania (2008) published a list of 120 HPVCs which match the structure of known Arctic contaminants or which they had identified by a modelling approach as potential Arctic contaminants. We thus compared this substance list with the results of our multimedia model based methodology to identify limits of our screening approach, but also to suggest a first prioritization for further research as far as a possible environmental exposure of remote regions is concerned. Potential Arctic contaminants which were, at the same time, identified not to be PBT but to show high LRTP according to all investigated screening methods were investigated by an additional literature research with regard to parameter values, environmental behaviour and monitoring data in remote regions.

### 5.1.2. *Results and Discussion*

**Screening for non-ionized compounds**. Within the Canadian Domestic Substance List (CDSL) 11,317 (50.4%) compounds of the total 22,438 substances are flagged as organic compounds with 556 (5%) of these classified as high production volume chemicals (HPVCs) according to the CDSL. Simulations with the on-line calculator SPARC identified 5485 compounds which are available in their non-ionized form to at least 95% within the environmentally relevant pH range of 4 to 10. For 17 substances (0.15%) of the organic compounds SPARC could not calculate $pK_a$ values and respective fractions of their species. These compounds were neglected during the subsequent screening steps. In addition, toxicity data needed for PBT classification are flagged as unknown within the CDSL for 394 compounds of the 5485 organic non-ionized substances. Thus, 5091 chemicals remain to be screened for long-range transport potential.

Based on the SMILES code of the compounds, EPISuite provided estimated chemical property information on the environmental partitioning for the list of 5091 substances. The numbers of chemicals characterized by a specific combination of the partition coefficients, log $K_{OW}$ and log $K_{AW}$, is shown in the chemical space plot (CSP) (Figure 1). Colours represent the number of substances within a specific combination of partition coefficients scaled to the maximal available number of compounds (red region in the plot=100%). The CSP illustrates that most of the 5091 investigated substances are characterized by log $K_{OW}$ values ranging from 3 to 5 and by log $K_{AW}$ values ranging from –2 to –1. Figure 1 is thus the reference distribution for comparison with the subsequent CSPs which resulted from the different selection steps.

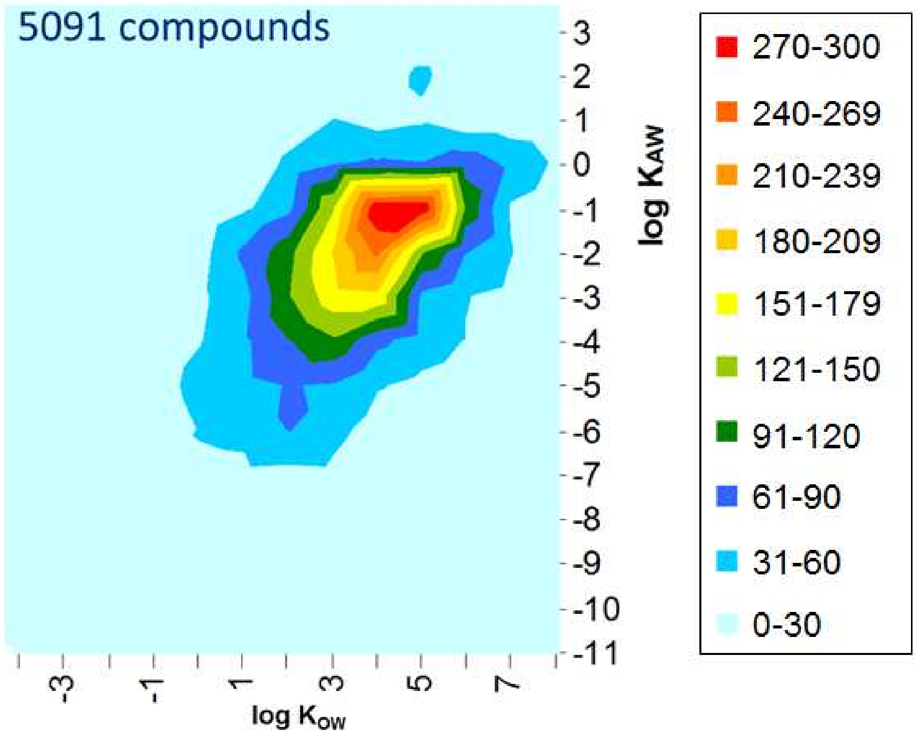

**Figure 1: Chemical space plot of 5091 organic non-ionized compounds contained in the Canadian Domestic Substance List. Partition coefficients $K_{OW}$ and $K_{AW}$ were estimated with the software package EPISuite. Colours represent the number of substances within a specific combination of partition coefficients scaled to the maximal occurring number of compounds (red region).**

Simulations with EPI Suite v4.0 also resulted in estimates for half-lives in water, sediment and soil and for the bioconcentration factor (BCF) for each of the listed compounds. Comparison of these values with respective criteria defined in the REACH regulation for persistence (P) and bioaccumulation potential (B) leads to a first classification of all substances according to P and B. Information on substance toxicity (T) is available in the CDSL. Thus, the 5091 substances can be classified into 159 substances which are PBT and 4932 compounds which are not PBT. Among these,

- 74 are PB¬T,
- 1000 are P¬BT,
- 3418 are P¬B¬T,
- 4 are ¬PBT,
- 2 are ¬PB¬T,

- 91 are ¬P¬BT and
- 343 are ¬P¬B¬T.

**Identification of non-PBT-L substances based on the half-life criterion in air.** When the LRTP half-life criterion in air is applied to the list of 5091 organic non-ionized compounds, 621 substances turn out to be characterized by a half-life in air ($t_{1/2(air)}$) > 2 days and are thus assumed to be prone to LRT. The distribution of these compounds in a chemical space plot (Fig. 2) in comparison to the CSP of all organic, non-ionized compounds (Fig. 1) shows a slight shift towards substances with a higher log $K_{AW}$ and a lower log $K_{OW}$. This means that the screening based on the half-life criterion favours compounds which show an increased partitioning into the air compartment and are less sorbed to particles. Classification into sub-categories according to the P, B, and T criteria results in a list of 27 PBT compounds and 594 non-PBT compounds which can be further specified into:

- 3 PB¬T,
- 60 P¬BT,
- 511 P¬B¬T,
- 20 ¬P¬B¬T compounds.

Thus, the half-life screening method identified in total a first list of 594 compounds of the CDSL that are not PBT and thus not regarded as substances of very high concern according to the REACH regulation, but are characterized by LRTP (non-PBT-L substances).

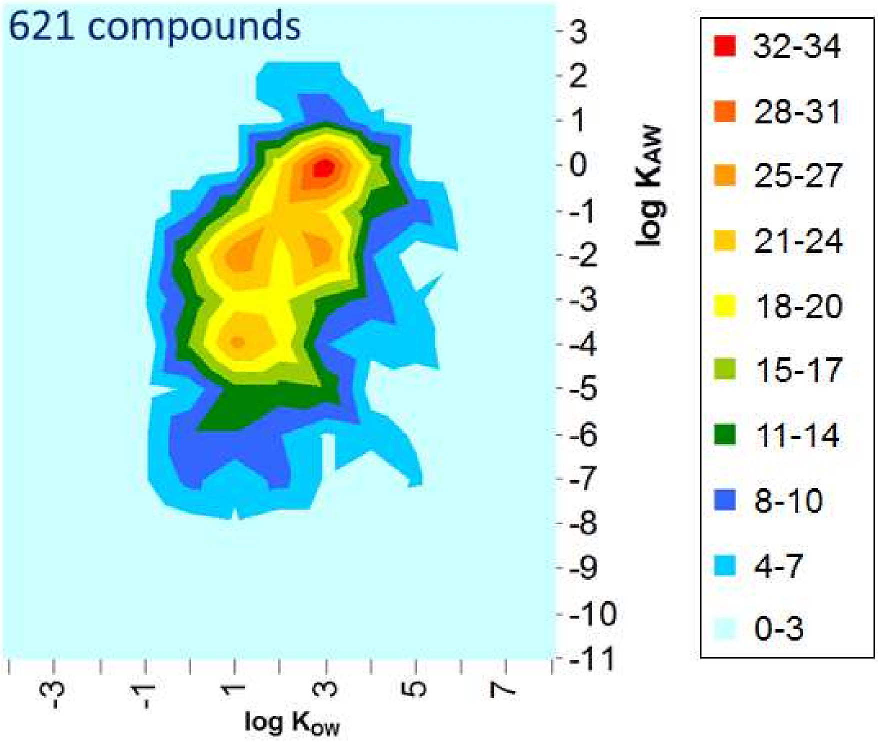

**Figure 2: Chemical space plot of 621 organic non-ionized compounds contained in the Canadian Domestic Substance List and showing LRTP according to the half-life criterion in air defined in the Stockholm Convention. More details are given in the caption of Fig. 1.**

**Identification of non-PBT-L substances with a multimedia model.** Screening the 5091 organic, non-ionized substances identifies 196 compounds showing high LRTP (category A and B of the ELPOS model) with 8 PBT substances and 188 substances which are not PBT (non-PBT). As far as the partitioning behaviour is concerned, the CSP (Fig. 3) reveals a higher abundance of the 196 LRTP compounds characterized by distribution coefficients ranging from – 1 to 6 (log $K_{OW}$) and from – 5 to 2.5 (log $K_{AW}$). Most of the compounds indicating LRTP according to the simulation results are characterized by a log $K_{AW} \leq 1$ which supports the screening criterion of Muir and Howard (2006). Analysing the 188 non-PBT substances for subcategories reveals that 58 of these substances belong to category A with 4 being persistent and toxic but not bioaccumulative (P ¬B T), and 54 being persistent but neither bioaccumulative nor toxic (P ¬B ¬T). Category B even includes 130 substances, but again these compounds are either P ¬B T (20 substances) or P ¬B ¬T (110 substances). Thus, the list of non-PBT-L substances resulting from the screening with the multimedia model approach only contains substances which are persistent and not bioaccumulative. In comparison to the non-PBT-L substance list based on the half-life criterion, investigations with the multimedia model lead to a shorter list of 188 substances in total. This discrepancy results from model assumptions taking partitioning and degradation behaviour of the simulated substances into account. Of these 188 substances, 162 compounds can also be found on the longer list of 594 substances, i.e. 162 substances are identified to be prone to LRT by both of the methods, the half-life criterion and the multimedia model approach. Consequently, the model-based approach is more focussed as far as an aim-oriented screening on critical compounds is concerned what has already been reflected in the CSP.

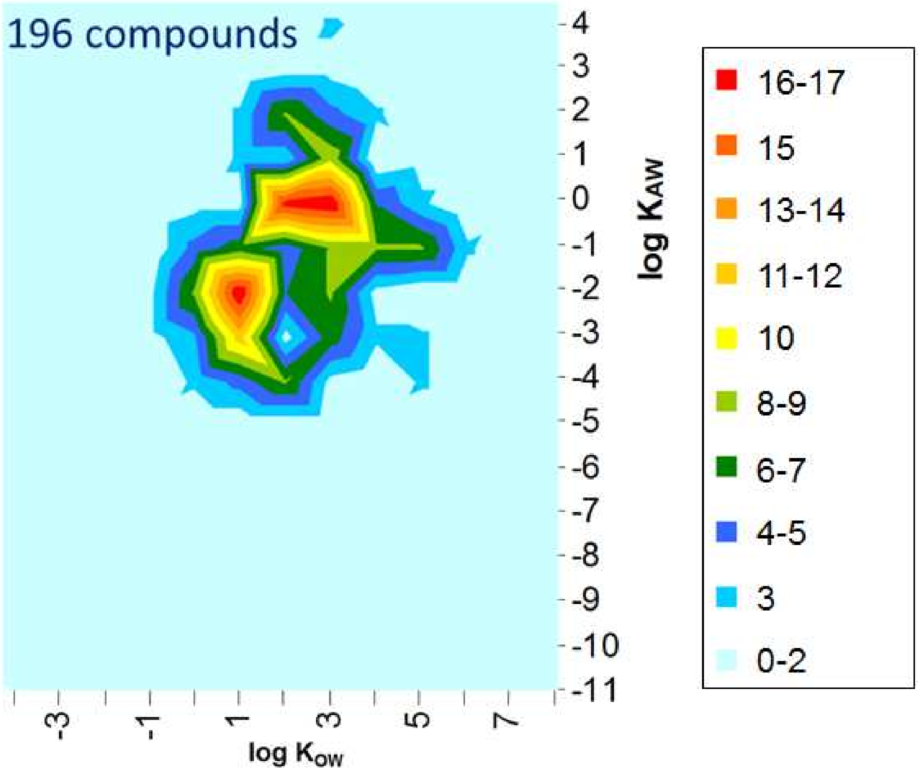

**Figure 3: Chemical space plot of 196 organic non-ionized compounds contained in the Canadian Domestic Substance List and showing LRTP according to simulations with the multimedia model ELPOS. More details are given in the caption of Fig. 1.**

**Comparison with potential Arctic contaminants.** Of the 120 compounds identified by Brown and Wania (2008) to be potential Arctic contaminants, 49 substances can be found within the total set of domestic substances from the CDSL. Thereof, nine substances could not be screened by our method since for two compounds toxicity data were not given and seven substances are characterized by dissociation constants leading to a neutral fraction of less than 95% within the environmental relevant pH range of 4 to

10. Five of the potential Arctic contaminants are persistent and toxic, but not bioaccumulative (P ¬B T) and also show high LRTP according to our model simulations (category A: 2, category B: 3). In addition, they are identified as compounds with high LRTP by the half-life criterion in air. Further six potential Arctic contaminants are classified as P¬B¬T with high LRTP according to model simulations (category A: 5, category B: 1) and the half-life criterion. Important to notice is that all potential Arctic contaminants were identified as such by Brown and Wania (2008) due to their chemical structure related to known Arctic contaminants and not only by their modelling results such that we do not compare the results of two different modelling approaches but the outcome of our modelling approach with a kind of empirical extrapolation. With regard to an evaluation of the model results this procedure is more applied and meaningful than a mere comparison between calculations. If the results of Muir and Howard (2006) are included, the set of substances following the half-life criterion in air can be focussed on a subset of 28 compounds. Thereof, 16 substances are not PBT and were partly also identified by Brown and Wania (2008) to be prone to LRT (3 substances) but also by our multimedia model approach (2 substances) or by both of them (3 substances).

Combining the four substance lists resulting from different methods (half-life criterion, combined method (half-life in air and log $K_{AW}$ ≤ 1 or ≥ 5) by Muir and Howard (2006), multimedia model, and chemical profile of known Arctic contaminants, Fig. 4) leads to a number of 417 non-ionized organic compounds of the CDSL which are only identified by the half-life criterion to be non-PBT-L substances, 26 compounds are only identified as such by the multimedia model approach, and two compounds are only identified by Brown and Wania (2008) to show LRTP but are not PBT. These two compounds whose chemical structure is similar to that of known Arctic contaminants are N-ethyl-1,1,2,2,3,3,4,4,5,5,6,6,7, 7,8,8,8-heptadecafluoro-N-(2-hydroxyethyl)-1-Octanesulfonamide (CAS: 1691992) and 4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-Methanoisobenzofuran-1,3-dione (CAS: 115275). Both, neither the half-life criterion in air nor the multimedia model characterize them to show LRTP. For the latter substance, the estimated half-life criterion in air (1.95 days) just misses the threshold value of 2 days whereas the estimated half-life in air for the first one falls far below that value (0.45 days). Both substances have in common that according to simulation results with the multimedia model ELPOS the calculated CTD does not rank them within the CTD range of compounds with LRTP. This means that

1. If the method of Brown and Wania (2008) clearly identifies substances with LRTP by comparing the chemical with known Arctic contaminants then both, the half-life criterion and the multimedia model fail.
2. If comparison of the chemical structure with known Arctic contaminants is not sufficient to identify the compounds which show LRTP, then the cross section of the three non-PBT-L compounds derived from the three screening methods may give strong evidence that these substances are prone to LRT but are not PBT.

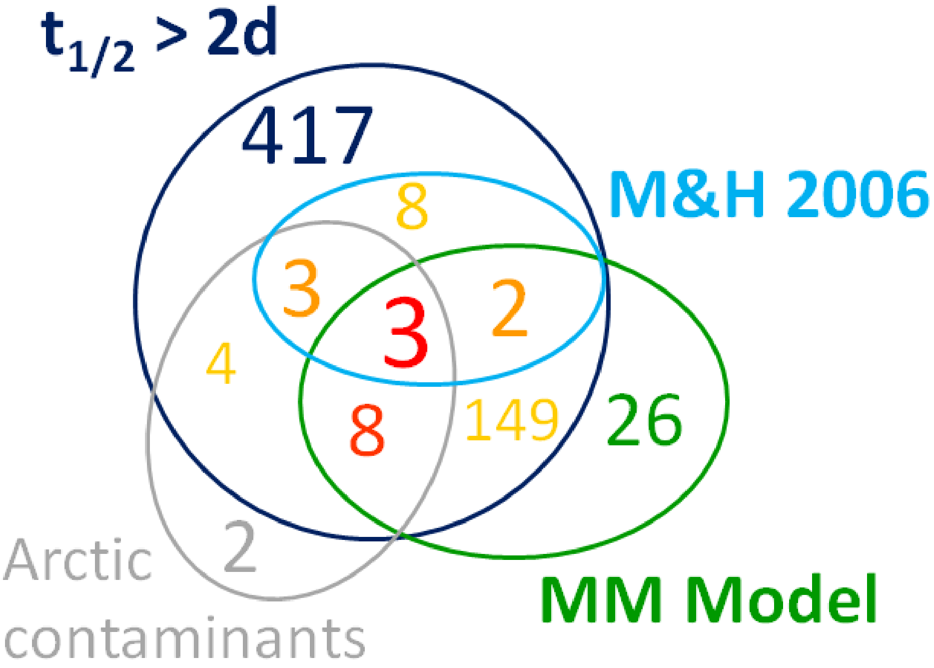

**Figure 4: Combination of four sets of compounds assumed to be prone to LRT but are not PBT derived from the half-life criterion ($t_{1/2}$ > 2 d, dark blue circle), from the advanced half-life approach including a log $K_{AW}$ condition (Muir and Howard (2006), $t_{1/2}$ > 2 d and log $K_{AW} \leq 1$ or $\geq 5$; M&H 2006, light blue circle), from simulations with the multimedia model (MM model, green circle) and from the chemical structure of known Arctic contaminants (grey circle) as given by Brown and Wania (2008).**

**Table 1: Substances fulfilling all of the three screening criteria indicating LRTP (half-life criterion, multimedia model, chemical profile of known Arctic contaminant) and their physico-chemical properties according to estimations by EPISuite. The three bold substances indicated with an asterisk (*) are identified by combination with the log $K_{AW}$ condition, log $K_{AW} \leq 1$ or $\geq 5$ (Muir and Howard, 2006), to be prone to LRT.**

| CAS | Name | MW [g mol$^{-1}$] | Log $K_{OW}$ | $K_{AW}$ | PBT classification |
|---|---|---|---|---|---|
| 1897-45-6 | 2,4,5,6-tetrachloro-1,3-Benzenedicarbonitrile (chlorothalonil) | 265.91 | 3.66 | 7E-06 | P¬BT |
| 58-89-9 | 1,2,3,4,5,6-hexachloro-Cyclohexane (lindane) | 290.83 | 4.26 | 0.011 | P¬BT |
| 87-61-6 | 1,2,3-trichloro-Benzene | 181.45 | 3.93 | 0.097 | P¬BT |
| 120-82-1 | 1,2,4-trichloro-Benzene | 181.45 | 3.93 | 0.097 | P¬BT |
| 634-66-2 | 1,2,3,4-tetrachloro-Benzene | 215.89 | 4.57 | 0.072 | P¬BT |
| **87-84-3*** | **1,2,3,4,5-pentabromo-6-chloro-Cyclohexane** | **513.09** | **4.71** | **4E-05** | **P¬B¬T** |
| **117-08-8*** | **4,5,6,7-tetrachloro-1,3-Isobenzofurandione** | **285.9** | **4.65** | **8E-05** | **P¬B¬T** |
| **30554-72-4*** | **tetrabromodichloro-Cyclohexane** | **468.64** | **4.62** | **1E-04** | **P¬B¬T** |
| 115-25-3 | octafluoro-Cyclobutane | 200.03 | 2.29 | 3275 | P¬B¬T |
| 1929-82-4 | 2-chloro-6-(trichloromethyl)-Pyridine | 230.91 | 3.35 | 7E-04 | P¬B¬T |
| 108-77-0 | 2,4,6-trichloro-1,3,5-Triazine | 184.41 | 1.73 | 2E-05 | P¬B¬T |

Some of the investigated compounds are identified as non-PBT-L substances by two of the methods, i.e. 8 by the advanced half-life approach, i.e. half-life criterion combined with the log $K_{AW}$ criterion (Muir and Howard, 2006), 149 by the half-life approach and by the multimedia model approach and 4 compounds by the half-life approach and by the screening on the chemical profile of known Arctic contaminants. As far as the advanced half-life approach is concerned, 3 compounds agree with the results of Brown and Wania (2008) and 2 compounds are identified to show LRTP in combination with multimedia model results. Finally, a set of 11 substances fulfils all of the three criteria indicating LRTP with a focus on 3 compounds if the advanced half-life approach is assumed. These substances together with their estimated basic physico-chemical properties are given in Table 1.

In order to evaluate the screening results for these eleven compounds, a literature research was conducted on parameter values and monitoring data to underline that estimated parameters of the technically identified substances can be confirmed or that these compounds have also shown LRTP under environmental conditions, i.e. have been found in remote regions.

*Chlorothalonil* is used worldwide as a fungicide. Measured values of its log $K_{OW}$ range from 2.64 to 4.38 (Caux et al. 1996) and thus confirm the value estimated by EPISuite. However, experimental data on half-lives in water (3 – 6 days) and soil (30 – 60 days) (Caux et al. 1996) are contradictory to estimated half-lives and indicate microbial degradation within a few days. This is also confirmed by low concentration data in surface waters and groundwater. Nevertheless, atmospheric long-range transport was identified to contribute to chlorothalonil concentrations in rain water (Caux et al. 1996) and simulation results for experimental half-lives with the multimedia model ELPOS indicate LRTP. Therefore, the PBT classification of the substance based on estimated half-lives may be wrong as far as persistence is concerned, the general result of LRTP of a non-PBT compound, however, remains valid for chlorothalonil.

*1,2,3,4,5,6-hexachloro-Cyclohexane* (Lindane or γ-HCH) has been broadly used as insecticide but production volumes are declining worldwide. According to the Risk Profile of the Persistent Organic Pollutants Review Committee (chm.pops.int/Implementation/NewPOPs/TheNewPOPs/tabid/672/Default.aspx) in 2006 Lindane is persistent, bioaccumulative and toxic following acute and chronic exposures. In addition, monitoring data indicated substance concentrations in all environmental compartments as well as long-range transport to remote regions. Thus, Lindane was listed as a new POP in Annex A of the Stockholm Convention in 2009. Our screening results indicate that Lindane was not bioaccumulative and would thus not fall under the PBT criteria according to REACH. Laboratory data also vary significantly over several orders of magnitude (e.g. Geyer et al. 1997, Berny 2002). It is thus important to highlight that our screening method identifies in this case a possible SVHC, which is already listed as POP, but would not necessarily be recognized as a PBT compound.

Both *trichlorobenzenes* (TCBs) are used as intermediates in the production process of pesticides and dyes and were formerly also applied as dye carrier and corrosion inhibitor (Hansen et al. 2003). Literature data collected for an European risk assessment of TCB on half-lives in surface waters (2–3 days), sediments (>200 days) and soil (300 days) support the persistence assumption of the compounds (Hansen et al. 2003). Monitoring data in herring of the North Sea and the Baltic Sea but especially in Arctic foxes support our results of TCBs being prone to LRT (Strachan et al. 2001). This is confirmed by the results of the EU Risk Assessment Report (Hansen et al. 2003).

*Tetrachlorobenzene* is, like chlorothalonil, mainly used as an intermediate for pesticides. Lipid concentrations have already been reported in Alaskan salmon of the North Pacific and indicate transport to remote regions[8]. Similarly, LRTP of tetrabromodichlorocyclohexane can be assumed since it belongs to the top ten brominated compounds and to the top 50 priority compounds surveyed in the Great Lakes[9].

*4,5,6,7-tetrachloro-1,3-isobenzofurandione*, finally, was identified by all investigated screening methods to be prone to LRT and is, in addition, not PBT. It is used as an intermediate substance for dyes and medicines, but also as flame retardant, e.g. in plastics and textiles. Nevertheless, there was no monitoring data available to support our screening results.

These examples show that a combination of screening methods is helpful to prioritize potential substances of very high concern in regard to PBT and LRTP characteristics. Subsequent analysis producing experimental and monitoring data can focus on the respective compounds and support or reject the assumption of a SVHC.

### 5.1.3. *References*

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[9] http://epa.gov/greatlakes/p2/

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## 5.2. Proposal of substances for consideration in the Environmental Specimen Bank

One of the main objectives of the research project is the identification of five substances that may be considered for inclusion in the Environmental Specimen Bank. These substances should not belong to the PBT compounds but raise concern due to their LRTP. The investigations presented above show that three substances are of high priority according to different screening criteria indicating LRTP (atmospheric half-life, log $K_{AW}$, chemical profile of known Arctic contaminants, multimedia-model). These are 1,2,3,4,5-pentabromo-6-chloro-cyclohexane (CAS 87843), tetrabromodichloro-cyclohexane (CAS 30554724) and 4,5,6,7-tetrachloro-1,3-isobenzofurandione (CAS 117088). In addition, we propose 1,2,3,4,5,6-hexachloro-Cyclohexane (lindane), the tri- and tetrachlorobenzenes, because experimental and modelling investigations of these compounds have revealed that they are prone to LRTP and have thus already been identified to be chemicals of high concern (compare above).

This seven substances, which are a subset of the 11 substances in Table 1 above, are listed again in Table 2.

**Table 2: Substances recommended for inclusion in the Environmental Specimen Bank. The three substances in bold are the ones in the central part of Figure 4. For details on how the substances were selected, see Table 1 above.**

| CAS | Name | MW [g mol$^{-1}$] | Log $K_{OW}$ | $K_{AW}$ | PBT classification |
|---|---|---|---|---|---|
| **87-84-3** | **1,2,3,4,5-pentabromo-6-chloro-Cyclohexane** | **513.09** | **4.71** | **4E-05** | **P¬B¬T** |
| **117-08-8** | **4,5,6,7-tetrachloro-1,3-Isobenzofurandione** | **285.9** | **4.65** | **8E-05** | **P¬B¬T** |
| **30554-72-4** | **tetrabromodichloro-Cyclohexane** | **468.64** | **4.62** | **1E-04** | **P¬B¬T** |
| 58-89-9 | 1,2,3,4,5,6-hexachloro-Cyclohexane (lindane) | 290.83 | 4.26 | 0.011 | P¬BT |
| 120-82-1 | 1,2,4-trichloro-Benzene | 181.45 | 3.93 | 0.097 | P¬BT |
| 634-66-2 | 1,2,3,4-tetrachloro-Benzene | 215.89 | 4.57 | 0.072 | P¬BT |

# 6. APPENDIX: CONTRIBUTIONS TO CONFERENCES

## 6.1. *ABSTRACT SUBMITTED TO GDCH/SETAC-GLB MEETING, SEPTEMBER 2010*

### Entwicklung von Kriterien für das Ferntransportpotential von organischen Substanzen im Wasser

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*Hintergrund und Ziel* Nach der Stockholm-Konvention für persistente organische Schadstoffe (POPs) ist bei der Bewertung von Chemikalien das Ferntransportpotential (LRTP) eine kritische Eigenschaft. Neben Messungen in vom Emissionsort entlegenen Gebieten, wie z.B. der Arktis, gelten Substanzeigenschaften zu Umweltverhalten und entsprechende Modellierungen als Hinweis auf einen potentiellen Ferntransport. Für den Transport in der Luft gibt es dazu bereits das in der Konvention festgelegte Halbwertszeit-Kriterium von 2 Tagen. Viele Substanzen werden jedoch hauptsächlich mit dem Wasser transportiert. In der europäischen Gesetzgebung (REACH) ist Ferntransport sogar bisher gar nicht explizit erfasst. Daher haben wir verschiedene Ansätze untersucht, um analog zum Ferntransport in der Luft Kriterien für den Ferntransport im Wasser abzuleiten, so dass Schadstoffe, die in das Wasserkompartiment verteilt werden, gezielt nach ihrem LRTP bewertet werden können.

*Material und Methoden* Mittlere Fließgeschwindigkeiten großer Ströme in Europa werden herangezogen, um ein Halbwertszeit-Kriterium für LRTP in Wasser abzuleiten. Zur Berücksichtigung der Verteilung von organischen Substanzen in der Umwelt werden mit Hilfe des Modells ELPOS Substanzeigenschaften identifiziert, durch die der charakteristische Ferntransport (CTD) im Wasser die CTD in der Luft übersteigt. Eine Berechnung der CTD im Wasser für die als POP identifizierten Substanzen dient zur Bestimmung einer Grenze für Ferntransport für organische Stoffe, die hauptsächlich im Wasser wieder gefunden werden.

*Ergebnisse und Diskussion* Basierend auf mittleren Fließgeschwindigkeiten von 0.8 m $s^{-1}$ (Elbe) bis 2.8 m $s^{-1}$ (Donau) lässt sich ein Halbwertszeit-Kriterium für LRTP in

europäischen Fließgewässern ableiten. Dies führt darauf, dass Substanzen mit einer Halbwertszeit im Wasser von mehr als 10 Tagen einem Ferntransport im Wasser unterliegen. Dies entspricht einem Radius von ca. 1000 km und damit auch dem Halbwertszeitkriterium von 2 Tagen für LRTP in Luft. Zur Berücksichtigung der tatsächlichen Verteilung in der Umwelt wurden hypothetische Substanzen mit verschiedenen Eigenschaftskombinationen definiert und mit ELPOS simuliert. Dabei dominiert der Transport mit dem Wasser dann, wenn log KOW<5, log KAW<-4 und $t_{1/2}$(Wasser)>75 d. Dies lässt sich an ausgewählten Pestiziden, wie z.B. Bromuconazol und Dichlofluanid belegen (1). Die Berechnung der CTD im Wasser für identifizierte POPs ergibt eine CTD von ca. 200 km (Lindan). So zeigen auch α-HCH, β-HCH und Chlordecon eine CTD im Wasser nahe der durch die Fließgeschwindigkeit und Gesamtpersistenz definierten oberen Grenze, während z.B. bei BDE-99 der Luftpfad deutlich den Wassertransport übersteigt.

*Schlussfolgerungen* Die verschiedenen Kriterien zur Beurteilung des Ferntransportpotentials organischer Substanzen im Wasser stellen einen ersten Ansatz dar, um Chemikalien zu bewerten, die nicht in der Luft, sondern hauptsächlich im Wasser über weite Strecken transportiert werden. Dabei berücksichtigt die CTD im Gegensatz zum Halbwertszeitkriterium die Umweltverteilung der betrachteten Substanzen. Weitere Untersuchungen sind erforderlich, um Referenzchemikalien für den Wasserpfad festzulegen, um damit analog zum Ferntransport in Luft (2) auch denjenigen im Wasser in die Bewertung einbeziehen zu können.

(1) Matthies, M., Klasmeier, J., Beyer, A., Ehling, C., 2009. Environ. Sci. Technol. 43, 9223-9229.
(2) Klasmeier, J., Matthies, M. et al. 2006. Environ. Sci. Technol. 39, 53-60.

## 6.2. *ABSTRACT SUBMITTED TO SETAC-EUROPE MEETING, MAY 2010*

### Are marine plastic particles transport vectors for organic pollutants to the Arctic?

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*Introduction*

Ever since plastics are commonly developed in the 1950s worldwide production has expanded within the last few decades up to 245 million tonnes in 2008. Properties like versatility, low weight, chemical- and light- resistance turn plastics into one of the most drastic and observable impact factors on the marine environment. Besides mechanic impacts of plastics on organisms a relationship between chemical burden and plastic ingestion has already been indicated. Further studies underline that organic chemicals like polychlorinated biphenyls (PCBs) are adsorbed from surrounding seawater [1]. In addition, several additives are contained within the plastic matrix. Bound to the plastics chemical compounds escape a fast degradation and may thus become “persistent” and subject to long range transport (LRT). However, the significance of plastic particles as transport vectors of organic pollutants within ocean currents to remote regions like the Arctic (i.e. LRT) remains uncertain and qualitative. Thus, the objective of our study is to roughly quantify the pollutant amount transported to the Arctic by plastics and to discuss its subsequent availability for uptake by organisms relative to other abiotic modes of transport (via air and ocean currents). Substances are chosen exemplarily to underline that the relevance of specific abiotic transport routes depends on the chemical properties and partitioning behaviour. Uptake of contaminated plastic particles into marine organism, transfer into food chains and subsequent transport with migrating animals might be another important (biotic) transport route but is not considered here and subject of another study.

*Materials and methods*

Transport of pollutants with plastic particles depends on (i) the amount of plastic debris in oceans, (ii) the specific surface per mass of plastic particles, (iii) the sorption of pollutants to plastic surface, and (iv) the velocity of ocean currents leading to the Arctic.

In a first step, the flux of plastics can be estimated using reports on plastic amount per km2 of ocean surface and knowledge on water volumes transported to the Arctic via the main ocean currents. In a second step, the pollutant flux attached to the plastics is estimated. Two approaches can be compared. On the one hand, the pollutant flux is based on pollutant concentrations measured on the plastic particles. On the other hand, the same flux can be estimated by measurements of the pollutant concentration in the ocean and respective partition coefficients between seawater and plastics. This procedure allows a check on consistency of the underlying data. Wania [2] estimated gross transport rates of three classes of selected persistent organic pollutants (POPs) across 60° Northern latitude into the Arctic in order to assess the relevance of LRT via different transport routes. These calculations are chosen as reference to classify the significance of LRT by plastics.

### *Results and discussion*

Selected substances. The selection of investigated substances is based on several aspects: (i) availability of concentration data in marine plastic debris, (ii) available knowledge on adsorption behaviour to plastics from the surrounding ocean, and (iii) contrasting environmental partitioning. Reports on pollutant concentrations on plastics and respective adsorption data are the most numerous for PCBs [e.g. 4]. An important category of plastic additives includes the brominated flame retardants, such as PBDEs, which mainly partition into air and are hardly water soluble. Surfactants like perfluorooctanoic acid (PFOA) are acids partitioning into water and designed to adsorb to e.g. textiles.

Plastic mediated pollutant flux to the Arctic. The plastic flux to the Arctic was estimated to comprise several thousand tonnes per year. This calculation is based on average plastic amounts floating on the world's ocean surface reported by the UNEP and the APEC [5]. Variation, however, is very high and results from different aspects like spatial heterogeneity, temporal variability and different sampling methods. Annual PCB and PBDE fluxes were then assessed to be in the order of several hundreds of grams to some kilograms per year. For reasons of consistency, calculations for PCB are compared to an estimated pollutant flux based on partition coefficients Ke between ocean water and plastics. Again, reported values include several orders of magnitude. Investigated sorption of PCBs to plastics varies between log $K_e$-values of 3 to 6 [6]. Thus, the combination of these data with an average PCB concentration of $15 \cdot 10^{-9}$ mg L-1 in sub-polar waters as proposed by Wania [2] results in a PCB flux of less than 1 g to hundreds of grams per year. Partition coefficients between ocean water and different plastic materials are not available for PBDE, yet. Thus, a consistency check as presented for PCBs is not possible. Even less data is available for PFOA: Ocean concentrations range from $52 \cdot 10^{-7}$-$439 \cdot 10^{-7}$ mg $L^{-1}$ and organic carbon normalized partition coefficients ($K_{OC}$) cover $10^1$ to $10^3$ L $kg^{-1}$ [3]. Assuming sorption to plastics to be two orders of magnitude stronger than to organic carbon as observed for PCBs [1] a PFOA flux of up to a few kilograms can be expected. Nevertheless, sorption of surfactants strongly depends on the accessible surface area and cannot necessarily be described by volume based partition coefficients. Thus, further research is needed on surface dependent sorption behaviour of surfactants to plastic particles.

Significance of various pollutant transport routes. Although these rough estimations include a large uncertainty as far as plastic amounts and scattered concentration data are concerned the resulting orders of magnitudes for each of the calculated pollution fluxes allow a comparison of various transport routes. Assuming an average PCB concentration of $15 \cdot 10^{-9}$ mg $L^{-1}$ in the ocean, transport of PCBs with ocean currents results in an annual PCB flux which exceeds the flux with plastic particles by two to four orders of magnitude. Mass fluxes of PCBs and PBDEs with atmospheric currents are the largest ones exceeding plastic mediated transport by four to six orders of magnitude. For PFOA, the mass flux with plastics to the Arctic is four to six orders of magnitude smaller than with ocean currents. Further knowledge on surface dependent sorption coefficients to plastic particles will improve estimations for surfactants. However, mass fluxes are not sufficient to assess the relevance of transport routes and the resulting environmental risk as far as availability for uptake by organisms is concerned. For many pollutants which are prone to LRT via atmospheric currents it is not known how they finally enter the aquatic food chain. Plastic particles, in contrast, have been shown to be swallowed by accident and to accumulate from prey to predator. Thus, they are pollutant vectors transported directly into the food chain.

### *Conclusions*

For risk assessment of chemicals according to their LRT potential it is not only necessary to quantify transported mass fluxes. It is even more important to identify transport routes which may directly serve as pollutant vectors into organisms and into food chain, e.g. plastic particles. Plastic mediated transport may especially gain importance for substances which are not transported in air, e.g. due to respective partitioning properties or rapid degradation by OH radicals. Future research should therefore focus on refining the mass balance for plastics (as mentioned before) under special consideration of concentrations in and sorption to plastic material of substances which are mainly partitioned into water and not transported by atmospheric currents.

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## 6.3. SESSION PROPOSAL FOR SETAC-EUROPE MEETING, MAY 2011

### Plastic pollution - polluted plastics: Fate, effects and life cycle assessment

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Pollution of the environment by plastic polymers is now drawing wide attention from the media, governance bodies and the environmental science community. Between 50 and 80% of marine waste is estimated to be out of plastic and has been detected on beaches, on the ocean surface and on seabed all over the world [1]. Moreover, weathered by sunlight, wave action and abrasion plastics are fragmented into particles smaller than 1 mm. These microplastics also result from the use of small plastic particles as abrasive scrubbers in cleaning products and from resin pellets as raw material. Besides uptake and accumulation of plastics along the food chain a relationship between chemical burden and plastic ingestion has already been indicated in seabirds proving that plastic particles represent an additional exposure pathway for organic pollutants to marine organisms [2]. Further studies, also on plastic as passive samplers, underline that organic pollutants are absorbed from surrounding seawater with sorption coefficients two orders of magnitude higher than for suspended particles. Moreover, several additives are already contained within the plastic matrix, are thus transported directly into the food chain and may leach into the surrounding environment. This complex pollution issue also specifically calls for a Life Cycle approach as improvements in the environmental performance of plastics can be achieved in the production, use and waste treatment phases.

This session shall continue the fruitful discussions during the first plastic session at SETAC 2010 in Seville and focus on fate, effects and life cycle assessment of plastics. Investigations on spatial and temporal variability of plastic distribution are as well important as insights on interactions between (micro)plastics, organic pollutants and organisms from a cellular level up to the food chain level. In addition, plastic product design studies, policy measures, consumer behaviour and waste management are key factors reducing the impact of plastics on the environment. Therefore, the aims of the session are, on the one hand, to present specific scientific data and knowledge, and on the other hand, to create a holistic perspective on the plastics environmental issue. Central questions may be:

- Which plastic-related issues have the highest impact on ecosystem scale (e.g. entanglement and starvation of organisms by macroplastic debris, or the toxic effects of plastic additives)?
- To what extent does leaching from plastics into the environment lead to environmental pollution and adverse effects by plastic additives worldwide?
- How can the emerging knowledge on additives and littering be incorporated into life cycle assessment studies to fully account for the environmental consequences of plastics?

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## 6.4. *ABSTRACT SUBMITTED TO SETAC-EUROPE MEETING, MAY 2011*

### Organic pollutants with long-range transport potential in oceans are persistent

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*Introduction*

The aim of current chemical regulations on an international level is to protect environment and human health against adverse effects induced by pollutants. Thus, the Stockholm Convention on Persistent Organic Pollutants (POP Convention) assesses chemicals based on different substance properties like persistence, bioaccumulation potential and toxicity [1]. In addition, substance transport over long distances with atmospheric or ocean currents or migrating animals leads to an exposure of especially sensitive ecosystems like the Arctic and is thus declared to be of high concern. This long-range transport potential (LRTP) can be supported by measurements of the respective pollutant in remote areas, by substance properties describing the environmental fate or by modelling results indicating LRTP. The POP Convention defines that substances showing LRTP with atmospheric currents are characterized by a half-life of more than two days in air. In this way, a concrete assessment criterion is given for substance transport in air. However, many chemicals are primarily emitted into and, consequently, transported with surface waters [2]. In order to integrate systematically these compounds into assessment of transport behaviour approaches for criteria to assess the LRTP of organic compounds in water were developed and discussed. The objective includes the development of a half-life criterion in analogy to the CTD in air as well as the application of a multimedia model and the usage of the characteristic travel distance (CTD). Thus, partitioning and degradation behaviour of the investigated substance shall be considered when assessing LRTP in water.

*Materials and methods*

A half-life criterion characterizing LRTP in water was developed in analogy to the half-life criterion for transport of organic substance in air. From wind velocities on a regional scale (continental wind velocity) and on a global scale (mean global wind velocity) in combination with the 2-day criterion, distances representing long-range transport were calculated; these were then converted into water-related half-lives by dividing them by flow velocities of large European rivers and major ocean currents. To account for partitioning and degradation of organic substances in all environmental compartments, the CTD was calculated with the multimedia model ELPOS [3] for hypothetical substances that are characterized by different values for partition coefficients and degradation rate constants in air, water, sediment and soil. Modelling results were applied to identify parameter combinations inducing a dominating substance transport with water in comparison to air. By means of substances included in Annex B of the POP Convention in May 2009, the validity of LRTP boundaries derived for airborne chemicals was evaluated for substances mainly transported in water.

### *Results and discussion*

#### *Derivation of half-life criteria*

The half-life criterion of two days in air to characterize LRTP with atmospheric currents means that at least 50% of a substance is transported at least 700 km on a regional scale if a continental wind velocity of 4 m/s is assumed [4, 5]. In combination with a mean global wind velocity of 18 m/s in the free troposphere [6], the 2-day criterion leads to a distance of 3 000 km. On a regional scale mean flow velocities of large European rivers range from 0.7 m/s to 1.0 m/s and result in a half-life criterion in rivers of 8 to 12 days. In contrast, flow velocities of ocean currents running into the Arctic lead to half-life criteria of 40 to 130 days on a global scale. This means that on a regional scale the half-life criterion (10 days) characterizing LRTP in water is below the persistence criterion of 40 days in fresh water [7]. Consequently, substances that are not classified as persistent, may undergo long-range transport on a regional scale. In contrast, on a global scale the criterion for LRTP in oceans (90 days) is already covered by the persistence criterion in oceans (60 days).

#### *Application of the multimedia model ELPOS and CTD*

The CTD describes the distance a substance can travel until 37% of its initial concentration remains. The crucial extension in comparison to the half-life criteria is that partitioning and degradation behaviour are considered when determining the CTD with a multimedia model. In addition, the CTD is a relative measure. Based on POPs mainly partitioning into air as reference chemicals, a CTD boundary has already been derived to identify further substances with high LRTP [8, 9]. This model-based approach is also applied by the OECD-Tool [5] and accepted by the POP Review Committee of the Stockholm Convention for assessment of potential POPs. Simulations of hypothetical compounds with the multimedia model ELPOS indicate that the CTD in water exceeds the CTD in air by more than one order of magnitude if log $K_{OW} < 4$ and log $K_{AW} < -4$. With increasing persistence in air the log $K_{AW}$-boundary decreases and thus a stronger shift of the partitioning behaviour towards the water compartment is required to compensate for the faster transport and higher CTD values in air. Simulations continuously decreasing the half-life in water ($t_{1/2}$(w)) revealed that $t_{1/2}$(w) has to exceed 10 days by far in order to still account for log $K_{OW}$–log $K_{AW}$ combinations showing a CTD in water larger than a CTD in air. Thus, the evaluation of LRTP based on the multimedia model and the CTD approach means that also those substances which are not registered as persistent compounds may be prone to a more efficient transport in water than in air. The respective boundaries for log $K_{AW}$ and log $K_{OW}$ may differ in models other than ELPOS due to different dimensions of the environmental compartments and set-up of environmental processes. Nevertheless, substance transport in water is dominant for those compounds which are characterized by large half-lives in water and low $K_{AW}$. Simulations of the new POPs (included in May 2009) with ELPOS show that at steady state lindane, chlordecone and perfluorooctanesulfonic acid (PFOS) mainly partition into the water compartment in comparison to the air compartment. However, only PFOS is characterized by a higher CTD in water than in air. Monitoring data indicate that PFOS is prone to LRTP [e.g. 10]. This is supported by model simulations showing that PFOS behaves similarly to reference POPs. Thus, the CTD boundary which was previously derived from airborne chemicals can also be applied to substances mainly transported in water.

### *Conclusions*

Derived half-life criteria characterizing LRTP of organic substances in water depend on whether the transport occurs in rivers or in ocean currents. If emission compartment, partition and degradation behaviour shall be considered, the CTD-approach based on multimedia models, which already proved of value for the assessment of LRTP in air, can be applied. Both criteria, however, reveal that substances emitted into rivers may reach the assimilated ocean without being identified as a substance of high concern. Therefore, clarification from a scientific and a regulatory point of view is necessary.

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## 6.5. *ABSTRACT SUBMITTED TO ICCE MEETING, ZURICH, SEPTEMBER 2011*

### Identification of Substances with Potential for Long-Range Transport as Possible Substances of Very High Concern

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In the European chemicals legislation REACH (2006) a substance is considered of very high concern if it is persistent, bioaccumulative and toxic (PBT). A substance’s long range transport potential (LRTP) and the subsequent hazard to remote regions are not explicitely included but can give cause for serious concern. To identify compounds, which would not be classified as PBT substances but are prone to LRTP (non-PBT-L substances), we screened the Canadian Domestic Substance List (CDSL), which contains 22,438 compounds in use on the Canadian market.

The CDSL was stepwise analyzed and searched for organic compounds, which are to more than 95% in the neutral form at an environmentally relevant pH range of 4 to 10. For the latter compounds we applied the SPARC Online-Calculator v4.5 to estimate dissociation constants from molecular structure. The identified compounds were run through EPI Suite v4.0 such that physical and chemical substance properties were quantified by the implemented estimation methods. Next, the list was edited in two ways to identify compounds with LRTP. On the one hand, the half-life criterion for long-range transport in air as defined in the Stockholm Convention was applied (half-life in air > 2 days). On the other hand, all compounds were simulated with the multimedia model ELPOS v2 which calculates relative indicators for persistence (overall persistence Pov) and LRTP (characteristic travel distance CTD) (Matthies et al. 2009). The results were compared with the implemented and well-established set of reference chemicals indicating POP-like behaviour (Klasmeier et al. 2006).

Applying the half-life criterion of 2 days in air as an indicator for LRTP, we identified 621 substances which are prone to LRT; 594 of these are not PBT. In contrast, investigations with the ELPOS lead to a shorter list of 188 substances, which are not PBT but show LRTP (non-PBT-L substances). This discrepancy results from more realistic model assumptions taking partitioning and degradation behaviour of the simulated substances into account. All 188 non-PBT-L compounds are persistent, but not bioaccumulative. However, in order to decide if these substances are of very high concern the list has to be evaluated with experimental or monitoring data from literature. In this way, substance properties estimated with EPI Suite have to be proven, indications for LRTP resulting from model simulations can be confirmed and data on possible adverse effects can give hints on the exposure of sensitive remote regions.

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# 7. Summary of the Workshop: „Long range transport – New findings & integration into REACH" March 27th 2012

**Institute of Environmental Systems Research, University of Osnabrück**

## 7.1. *Objectives*

Aims of the European chemicals legislation REACH[10] are on the one hand, "free circulation of substances on the international market" and, on the other hand, a "high level of protection of human health and the environment" in accordance with the precautionary principle.

For chemicals identified as substances of very high concern (SVHC) due to their intrinsic properties, an authorization might be required for production and use. These SVHCs include chemicals which are:

(iv) carcinogenic, or mutagenic, or toxic to reproduction (CMR), or

(v) persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB) or

(vi) substances of "equivalent concern" as identified from scientific evidence, such as those having endocrine disrupting properties or those having PBT-like or vPvB-like properties.

The criteria for the PBT and vPvB assessment are defined in Annex XIII of the REACH-regulation. However, a substance's long range transport potential (LRTP) and the subsequent hazard to remote regions are not explicitly included in the REACH legislation. The revised Annex XIII (2011) offers the possibility to use all available sources for an assessment concerning the P, B and T dimensions, but consideration of LRTP is not explicitly required. Under the Stockholm Convention on Persistent Organic Pollutants[11], long-range transport in air, with ocean currents, and in migrating animals is considered a critical substance property in addition to persistence, bioaccumulation and toxicity. Besides measurements in remote regions, e.g. the Arctic, substance properties describing environmental fate as well as modelling results are considered as indicators

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[10] Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH). Official Journal of the European Union L396 (http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L: 2006 :396:0001:0849:EN:PDF)

[11] Stockholm Convention on Persistent Organic Pollutants. United Nations Environment Programme, Geneva, Switzerland (http://chm.pops.int/)

for LRTP under the Stockholm Convention. However, currently it is not clear how information on LRTP can be used under REACH. Substances with LRTP cross international boundaries and may be transported to particularly sensitive ecosystems such as the Arctic. Based on the precautionary principle as embedded in the REACH legislation and based on the responsibility of each Member State to ensure that activities within their control do not impact the environment of other Member States, inclusion of substances with LRTP in the SVHC list is desirable. Therefore, the objective of this workshop was to present new scientific findings on long-range transport in the environment and to develop, in discussions among authorities and scientists, specific options for including LRTP as critical substance property in the SVHC identification according to REACH.

## 7.2. *Presentations*

On March 27, 2012, the final workshop of the project “Advancements of Concepts for Identification of Substances of Very High Concern (SVHC) in Terms of the REACH Regulation” was held at the University of Osnabruck. The workshop title was „Long range transport – New findings & integration into REACH“ and the workshop was attended by representatives of various governments of EU Member States, of the European Chemicals Agency, ECHA, and of research institutions (see list of participants at the end of this document). At the workshop the key findings of the project were presented:

| | |
|---|---|
| 9:00 | Welcome (Prof. Matthies) |
| 9:10 | Introduction (Dr. Schulte) |
| 9:20 | Relevance of long-range transport in the environment (Dr. Scheringer) |
| 9:50 | Comparison of different transport pathways to remote regions (Prof. Matthies) |
| 10:30 | Coffee break |
| 10:45 | Evaluation of monitoring data from remote locations, comparison of monitoring data and model results (Dr. Scheringer) |
| 11:30 | Selection of non-PBTs with LRTP (Dr. Zarfl) |
| 12:15 | Lunch break |
| 13:15 | Integration of LRTP into SVHC identification (Ackermann, UBA) |
| 14:00 | Discussion |
| 15:30 | Closing |

C. Schulte introduced into the regulatory background and recent developments in PBT-assessment under REACH. M. Scheringer outlined the relevance of the long-range transport of chemicals in the environment in chemicals assessment and presented different ways in which this indicator can be interpreted. M. Matthies presented findings on the relevance of different transport pathways (air, water, plastic particles present in water, migratory species) for different types of chemicals. A main finding was that for sufficiently water-soluble chemicals riverine transport may be highly effective, but would not be captured by the current half-life criteria (chemicals that are clearly below the half-life criteria in water may still long-lived enough to undergo long-range transport in rivers). In the next block, M. Scheringer used monitoring data for polychlorinated biphenyls measured at the Arctic stations, Zeppelin and Alert, as a reference point for model results for the LRT of PCBs. He focused on two models, a Lagrangian Particle Dispersion Model (FLEXPART) and a multimedia mass-balance model (BETR-Global) and identified various aspects where one or the other model showed better agreement with the field data. C. Zarfl, finally, presented results from a systematic search for chemicals with high LRTP in lists of chemicals, including the Canadian Domestic Substances List (CDSL) and the list of chemicals currently registered under REACH. Application of a series of filters for LRTP evidence led to a list of 11 substances of the CDSL with high LRTP that are not PBT (see chapter 5.1 of the main text of the final project report). Using the same approach for filtering the list of 3,908 registered substances under REACH (list_substances_phasein_en.xls)[12] 12 substances could be identified with high LRTP that are not PBT substances (see Table 1). All identified non-PBTs with LRTP of both lists are persistent, but not bioaccumulative and need further elaboration on their P, B and T properties. Four substances are on both lists (see Table 1). J. Ackermann, UBA, then continued by presenting various options for integrating the LRTP into the identification of Substances of Very High Concern (SVHC). As examples for the discussion trichlorobenzenes and perfluorohexane sulfonic acid (additional contribution by L. Vierke, UBA) were used.

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[12] http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances; 3rd November 2011

**Table 1: Twelve substances of the list of registered substances under REACH fulfilling all of the three screening criteria indicating LRTP (half-life criterion, multimedia model, chemical profile of known Arctic contaminants). These chemicals were identified by means of the same method as applied to the Canadian Domestic Substances List (CDSL) described in Chapter 5 of the Final Report. Toxicity information for the first four substances was taken from CDSL. The symbol "¬" means "not".**

| CAS | Name | Usage | Log $K_{OW}$ | $K_{AW}$ | PBT classification |
|---|---|---|---|---|---|
| 87-61-6 | 1,2,3-trichloro-benzene | intermediate | 3.93 | 0.097 | P¬BT |
| 120-82-1 | 1,2,4-trichloro-benzene | intermediate | 3.93 | 0.097 | P¬BT |
| 117-08-8 | 4,5,6,7-tetrachloro-1,3-isobenzo-furandione | intermediate, flame retardant | 4.65 | 8.4E-05 | P¬B¬T |
| 108-77-0 | 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) | precursor of triazine herbicides | 1.73 | 2.2E-05 | P¬B¬T |
| 98-56-6 | Parachlorobenzotrifluoride (PCBTF) | intermediate, ink solvent | 1.6 | 1.42 | P¬B? |
| 102-36-3 | 3,4-dichlorophenyl isocyanate | intermediate | 3.88 | 5.2E-03 | P¬B? |
| 307-35-7 | Heptadecafluorooctane-sulphonyl fluoride | raw material for preparation of fluorinated surfactants | 9.62 | 2.7E+03 | P¬B? |
| 2402-79-1 | 2,3,5,6-tetrachloropyridine | intermediate, synthesis of chloropyrifos | 3.38 | 0.35 | P¬B? |
| 5216-25-1 | 4-Chlorobenzotrichloride | intermediate | 4.54 | 7.9E-03 | P¬B? |
| 29091-09-6 | 2,4-dichloro-1,3-dinitro-5-(trifluoro-methyl) benzene | intermediate | 3.88 | 1.6E-05 | P¬B? |
| 34893-92-0 | 1,3-dichloro-5-isocyanatobenzene | intermediate | 3.88 | 5.2E-03 | P¬B? |
| 138495-42-8 | 2H,3H-Decafluoropentane | solvent degreaser | 3.84 | 9.1E+03 | P¬B? |

## 7.3. *Discussion*

The workshop participants extensively discussed the relevance and weight of the LRTP criterion in relationship to the PBT assessment criteria. In existing approaches, e. g. Annex D of the Stockholm Convention, model results and monitoring data are combined for LRTP evidence but there is not a clearly accepted criterion for LRTP. Two possible solutions were discussed: the development of criteria for LRTP (precise definition) and the establishment of guidelines for LRTP (weight-of-evidence). The LRTP indicator represents a dimension of environmental hazard that is complementary to those represented by the three established PBT criteria. When the LRTP dimension is to be included in the assessment scheme for Substances of Very High Concern, SVHCs, there is not a prescribed algorithm for this, but there are several possible combinations of the different criteria. The assessment of these combinations depends on the values and preferences of the assessor with respect to risk and precaution.

As already outlined by C. Zarfl in her presentation and described in the final project report in Chapter 5.1, there are primarily three cases for which the role of the LRTP indicator needs to be discussed in the context of SVHC assessment:

1. chemicals with P, T and LRTP
2. chemicals with P, B and LRTP
3. chemicals with P and LRTP

Property combinations in which the P criterion is not fulfilled are probably less relevant.

As a first step in the identification of SVHCs, it seems plausible that chemicals that are classified as SVHCs because of their environmental hazard should fulfill the P criterion. High persistence of a chemical reflects several unwanted properties that are typical of environmental hazard: a persistent chemical has the time to undergo long-range transport, to bioaccumulate and to exert toxic effects. (Chemicals can be SVHCs without being persistent, for example when they are CMR substances, but this is a different type of SVHCs not covered by the current discussion.)

If the P criterion is fulfilled, but the B or T criterion is not, the LRTP may be considered as a replacement or rather as a completion of the missing B or T property and can be used to support the decision on the SVHC status of a chemical. The first case is that the B criterion is not met: when the P and T criteria are fulfilled and the chemical has a high LRTP, it seems plausible to argue that the chemical can be classified as SVHC, in particular if the B threshold is barely missed (‘borderline’). In this case the combination of P, T and LRTP can be seen as similarly problematic as PBT (chemical has potential for long-term and widespread exposure and for toxic effects). However, ‘borderline’ is not yet defined and has to be evaluated in a weight-of-evidence approach. The second case is that the P and B criteria are met, but not T, and the LRTP is high. In this case the high bioconcentration factor of the chemical (B is met) implies a considerable baseline toxicity that makes the chemical “almost T”. Because, in addition, the LRTP is high, it is again plausible to argue that such a chemical may be an SVHCs (chemical has potential for long-term and widespread exposure, for bioconcentration and exerts significant baseline toxicity).

The third group of chemicals includes substances that have high LRTP and meet the P criterion, but neither B nor T. When a strong version of the precautionary principle is applied, it can be argued that the combination of P and LRTP even in the absence of B and T is a source of high concern. This is because there is always uncertainty concerning B and T and it is not possible to definitely conclude that the chemical has no B and T properties, even if the testing for B and T has been negative up to this point (possibility of false negatives). If it turns out at a later point in time that B and/or T is fulfilled, for example for biological species or endpoints that are tested for the first time or because the chemical occurs in mixtures or has endocrine effects, the unwanted combination of P, LRTP *and T* will be manifest and the chemical will by cycling in the environment – in other words, exactly a situation will occur that should have been avoided by the very concept of SVHC assessment. The downside of this approach is that it will create an unknown number of false positive cases.

The precautionary approach outlined above is a logically consistent position. The key question is whether or not a relatively strong version of the precautionary principle is considered desirable and if an unknown, but non-negligible, number of false positive cases in the list of SVHCs is considered acceptable. In conclusion, there is a potential role for the LRTP indicator in the identification of SVHCs and it can be argued that a high LRTP can replace missing B or T properties to some extent.

The workshop participants agreed that the LRTP criterion may be relevant or even decisive for SVHC classification in cases where one of the PBT criteria (P, B or T) is slightly below the threshold value defined in Annex XIII of REACH. However, this would have to be based on a weight-of-evidence evaluation and it was agreed that, in a follow-up activity, specific cases should be identified and discussed in detail in order to demonstrate how the LRTP criterion can be used in combination with PBT data for the purpose of SVHC classification. There was agreement that the LRTP criterion adds an important dimension to the assessment because it points out whether a chemical has the potential to be widely dispersed in the environment and to cause wide-range and long-term exposure; in such a case, the human and environmental exposure is irreversible and cannot be controlled or mitigated, which causes health impacts and economic costs. The assessment would have to be based on a weight-of-evidence evaluation and in the current stage of the discussion, finding a conclusive definition for LRTP might be more necessary and helpful than defining cut-off values. It was also agreed that both measurements of a chemical in the environment and results from environmental fate and transport models can be useful input data for an assessment of a chemical's potential for LRT. If measured environmental concentrations are available, in particular in remote regions, emission volume and its temporal and spatial pattern if available should be taken into consideration. No agreement was reached whether article 57 d) or e) of the REACH regulation, i.e. integrate LRTP-compounds as "real" PBT substances, or article 57 f), i.e. LRTP as a criterion for a substance of equivalent concern, are more appropriate.

## 7.4. *Participants*

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