EMEP CONTRIBUTION TO THE PREPARATORY WORK FOR THE REVIEW OF THE CLRTAP PROTOCOL ON PERSISTENT ORGANIC POLLUTANTS

NEW SUBSTANCES:
Model assessment of potential for long-range transboundary atmospheric transport and persistence of Short Chain Chlorinated Paraffins (SCCPs)

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CONTENTS

INTRODUCTION

Short chain chlorinated paraffins (SCCPs) are extremely complex mixtures classified by carbon chain length (C_{10} - C_{13}) and a degree of chlorination (48% – 71% by weight). Technical mixtures of SCCPs were widely used in Europe, America, Asia, Australia and South Africa in metal working fluids, rubber/flame retardants, PVC plasticators, textile polymers (other than PVC), leather fat liquors and in paints and coatings.

Chlorinated paraffins with short and medium chain are part of the OSPAR List of Substances of Possible Concern and of the HELCOM List of Selected Substances for Immediate Priority Action. In addition OSPAR List of Chemicals for Prioriry Action and Water Framework Directive List of Priority Substances in the field of water policy also contains SCCPs [*HELCOM MONAS* 9/2006].

SCCPs are potential candidates for the inclusion into the UN ECE Protocol on POPs. This group of compounds was addressed by the Ad Hoc Expert Group on POPs [*Lerche et al*., 2002]. The European Commission has submitted a proposal for amendment to the Protocol with regard to SCCPs in 2005. A dossier including a risk profile and summary report for SCCPs was prepared by the European Commission, DG Environment [*Risk Profile and Summary Report*, 2005]. Additional information for the evaluation of SCCPs as potential new POPs in accordance with the two criteria: potential for long-range transboundary atmospheric transport (LRTP) and persistence can be provided by modelling. A certain experience in the model assessment of the long-range transboundary atmospheric transport and persistence in the environment for a wide range of typical POPs already included in the Protocol on POPs and some potential new POPs [*Shatalov et al*., 2003; *Dutchak et al*., 2004; *Mantseva et al*., 2004; *Vulykh et al*., 2004, 2005, 2006] is accumulated in the Meteorological Synthesizing Centre-East of EMEP.

In view of variable composition of SCCP technical mixtures (calculated number of congeners, homologues, diastereoisomers and enantiomers exceeds several thousands) three chlorinated n-alkanes were chosen for modelling to represent the fate of SCCPs in the environment. These substances are characterized by different length of carbon chain and different chlorine content. Their formulas and abbreviations are given in Table 1.

Table 1. *Chemical formulas and abbreviations for three SCCP isomers chosen for modelling*

Chemical formula	Chemical name	Abbreviation
$C_{10}H_{17}Cl_5$	Pentachloro-*n*-decan	PeClD
$C_{12}H_{20}Cl_6$	Hexachloro-*n*-dodecan	HxClDd
$C_{13}H_{21}Cl_7$	Heptachloro-*n*-tridecan	HpClTd

The choice of these three SCCP compounds for modelling was based on the results of SCCP measurements in the air in different world regions (Annex A) and literature data on composition of SCCP technical mixtures [*Zencak et al.,* 2003].

For the evaluation of LRTP and persistence of SCCPs, EMEP/MSCE-POP multicompartment hemispheric transport model is used.

To estimate LRTP and persistence for SCCPs, the model calculation of its atmospheric transport from a conventional emission point source located in Europe (5°E; 47.5°N) is made for one-year period. Information on physical-chemical properties and degradation rates of this pollutants used for modelling is presented in Annex B.

To evaluate LRTP of a particular SCCP isomer, two numerical characteristics are calculated. The first one is residence time in the atmosphere (**Half-life in air$_{calc}$ ($T_{1/2}{}^{air}$)**) obtained with allowance of all processes removing the given pollutant from the atmosphere. The second is ***Transport Distance (TD)*** that is the distance from the source at which annual mean atmospheric concentration of a chemical in question drops 1000 times compared with the concentration near the source. Additional information on this criterion for SCCPs is provided by the spatial distribution of air pollution caused by the considered conventional point source.

Persistence in the environment is evaluated by ***Half-life in the environment*** ($T_{1/2}{}^{env}$) estimated for SCCPs on the basis of the model simulation of its atmospheric transport taking into account deposition processes, degradation and exchange of the pollutant between main environmental media.

To diminish uncertainties in evaluating LRTP and persistence of the SCCPs with the help of the model dependent *TD* and $T_{1/2}{}^{env}$, a comparison of their numerical values against those obtained for B[a]P as an adequately studied "benchmark substance" is presented.

In conclusion, the calculated numerical characteristics of LRTP and persistence of SCCPs are given in relation to the indicative criteria outlined in Executive Body Decision 1998/2.

Detailed information on the structure of the model and parameterisation of the media processes can be found in the EMEP/MSC-E reports [*Gusev et al*., 2005] and on the Internet (http://www.msceast.org).

1. LONG-RANGE TRANSPORT POTENTIAL

According to the Executive Body Decision 1998/2 the LRTP criterion for the evaluation of new substances as potential candidates for the inclusion into the Protocol on POPs is characterized by indicative numerical values of their vapour pressure and atmospheric half-life, which should be greater than two days.

The half-life of SCCPs in the atmosphere can be estimated with the help of modelling as residence time in the atmosphere (Half-life in air$_{calc}$ ($T_{1/2}{}^{air}$)) obtained on the basis of simulation of their atmospheric transport taking into account not only degradation process in this medium but also all other removal processes. Advantages of modelling approach are contained in possibility to distinguish the most important processes affecting LRTP of a particular considered pollutant in the atmosphere. Additional information on LRTP based also on the model calculations of atmospheric transport is provided by the spatial distribution of air pollution. The latter allows estimating Transport Distance (TD), characterising LRTP of an isomer of SCCPs as the distance from the source at which annual mean atmospheric concentration drops 1000 times compared with the concentration near the source.

This Chapter contains the main results on evaluation of LRTP criterion for SCCPs with the help of above-mentioned characteristics obtained on the basis of the EMEP/MSCE-POP model calculations performed at the hemispheric level for the above mentioned three SCCP isomers.

1.1. Residence time in the atmosphere

To estimate the residence time in the atmosphere, the model calculation of SCCP atmospheric transport with allowance of such processes as degradation in the atmosphere, partitioning between particulate and gas phases, dry and wet deposition of particles and gas exchange with various types of underlying surface is carried out. Emissions of each isomer to the atmosphere are assumed to be 1 tonne per year from a conventional point emission source located in Europe (5°E; 47.5°N). On the basis of this calculation annual atmospheric balance for the considered SCCP isomer emitted to the atmosphere is estimated. The calculated balance for the removal processes from the atmosphere for three SCCP isomers (PeClD, HxClDd and HpClTd) is given in Figs.1.
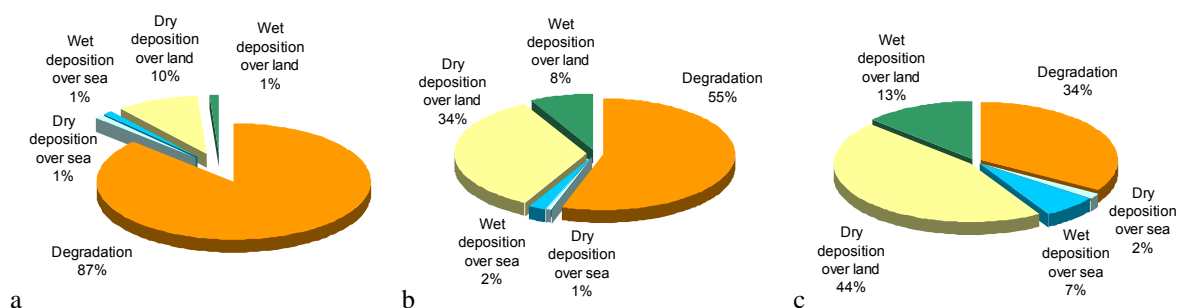

Fig.1. *Calculated annual balance of removal from the atmosphere for PeClD (a), HxClDd (b) and HpClTd (c)*

As seen from the calculated balance, degradation and deposition processes make different contribution to the removal of the SCCPs from the atmosphere depending on a particular isomer.

The main process of PeClD removal from the atmosphere is degradation. Within a year bulk mass of the emitted pollutant (about 87%) is degraded in the atmosphere. Wet and dry deposition to the land amount to 11% of total removal and only 2% is deposited to the sea surface.

For HxClDd, 55% of emitted pollutant are degraded in the atmosphere and 45% are deposited to the different types of underlying surface within a year. Here, the most part of deposited pollutant (42%) falls into soil and the rest (3%) − into seawater.

For HpClTd, degradation process takes about 34% of the total removal from the atmosphere within a year, the most part is deposited to land (57%) and sea (9%).

Thus, the character of the presented balance can be explained not only by the physical-chemical properties of the considered substance (degradation rate constants, subcooled liquid-vapour pressure values and Henry's law constants) but also by the type of underlying surfaces and some meteorological parameters.

Calculated values of residence time in the atmosphere (Half-life in air$_{calc}$ ($T_{1/2}^{air}$)) are presented in Table 2.

Table 2. *Characteristics of LRTP (**Half-life in air**$_{calc}$) calculated for SCCP isomers*

Isomer	$T_{1/2}^{air}$, days
PeClD	4
HxClDd	2
HpClTd	3

The numerical values of this characteristic of LRTP for SCCP isomers meet the existing criterion (atmospheric half-life is greater than two days).

According to the known literature data, half-lives of considered SCCP isomers in the atmosphere calculated on the basis of degradation rate constants due to interaction with OH-radical equal approximately 2 days for all three isomers [*Final Draft, II,* 2003; *Risk Profile and Summary Report,* 2005; *Muir et al.,* 2000].

1.2. Spatial distribution of pollution from conventional emission source

Additional information on LRTP of the considered chemicals is provided by the spatial distribution of air pollution by SCCP isomers estimated by modelling on the basis of their atmospheric transport from the conventional point emission source and atmospheric balance. Concentration fields of SCCP isomers in the Northern Hemisphere and in the EMEP domain are given in Figs 2 − 4 below. For convenience, air concentrations are presented in the relative units i.e. as ratios of the concentration calculated in the particular point to the concentration near a source (basic value).
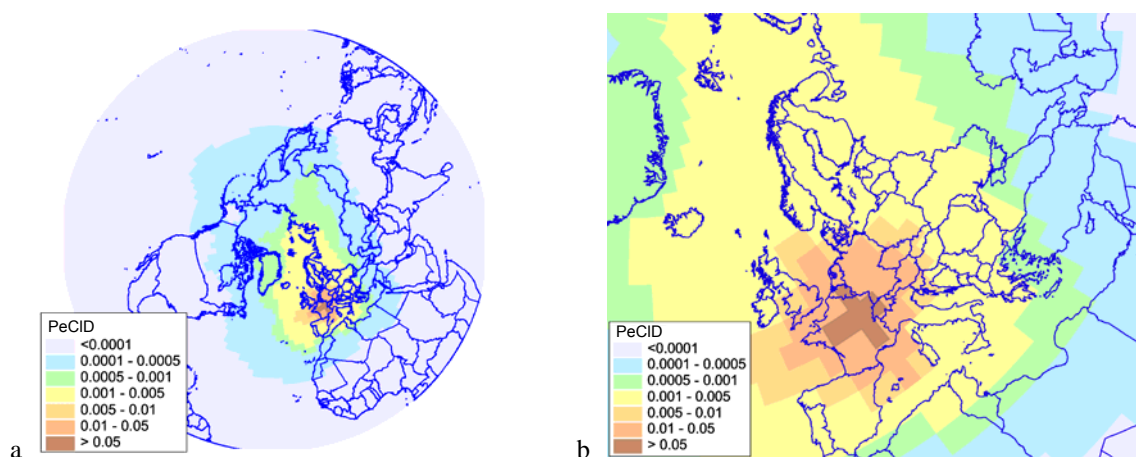

Fig. 2. *Spatial distribution of **PeClD** concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain*

The European **PeClD** source shows noticeable influence within the European region (Fig. 2a). The long-range atmospheric transport of this pollutant contributes also to the contamination of the Atlantic region.

The pollution by PeClD from the point source covers the whole territory of the EMEP domain (Fig. 2b). For this isomer the areas where concentrations drop down less than 1000 times reach the

Scandinavian Peninsula and Barents and White Sea regions. These areas also include the Mediterranean Sea and partly northern Africa. The levels of air concentrations over the major part of European countries vary from 0.005 to 0.01 of the basic value. The levels of air concentrations amounting from 0.01 to more than 0.05 of the basic value are mostly characteristic of France, Switzerland, Belgium and the Netherlands.
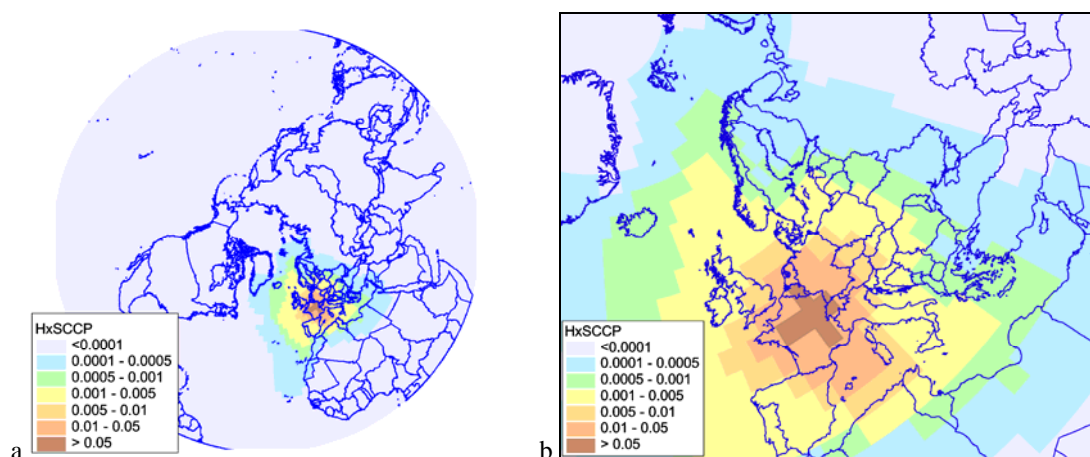

Fig. 3. *Spatial distribution of* **HxClDd** *concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain*

According to the calculation results, for **HxClDd** there is no noticeable long-range atmospheric transport from the European region (Fig. 3a). However, the areas with concentrations equal to 0.001 of the basic value cover an essential part of the EMEP region (Fig. 3b). Areas with high air concentrations (> 0.05 of the basic value) are located near the source. Concentrations from 0.01 to 0.05 cover neighboring regions (northern Italy, Germany, France and part of the Mediterranean Sea). Relatively low contamination levels (0.001 – 0.005 of the basic value) takes place in central and southern parts of Italy, Spain, the UK, Poland, Scandinavian countries, etc.
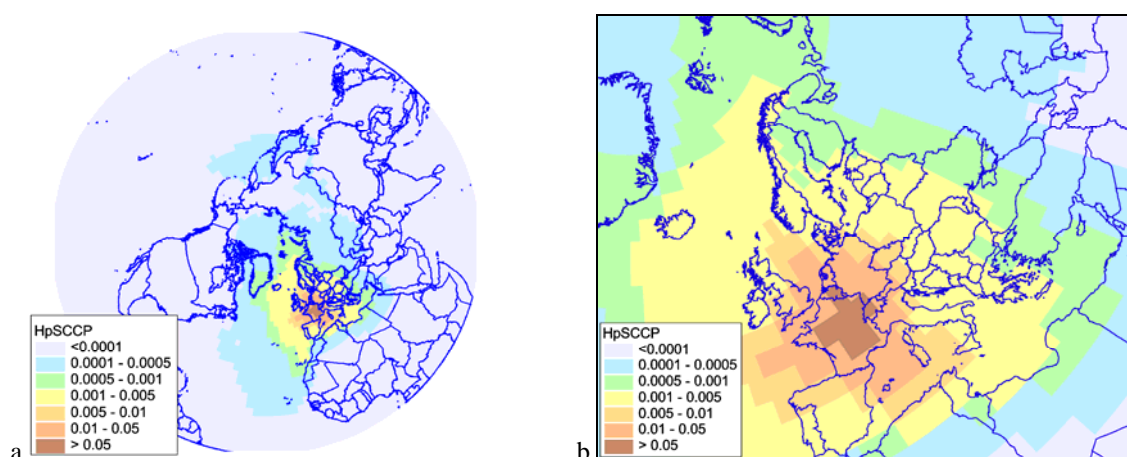

Fig. 4. *Spatial distribution of* **HpClTd** *concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain*

Higher ability to the long-range atmospheric transport is characteristic of **HpClTd** (Fig. 4a). The European source can affect the contamination levels over longer distances. This can be explained by higher fraction of particle-bound form of this isomer and, as a consequence, less degradation rate in the atmosphere. As seen from Fig. 4 b concentrations lower than 1000 times than the basic value almost reach the Greenland coast. Within the EMEP region areas with concentrations 100 times less than basic one is much wider than for HxClDd and cover southern part of the UK, northern Italy, Germany and considerable parts of Mediterranean and North Seas.

As follows from the above results, the long-range atmospheric transport of SCCPs is affected not only by degradation rate constant but also by the form in which the given isomer is present in the atmosphere (gaseous or particle-bound) since particle-bound form degrades in the atmosphere rather slowly. For this form the process of removal from the atmosphere will be governed by deposition velocities to various types of underlying surface.

1.3. Transport Distance

At present several model approaches to the evaluation of LRTP of a pollutant by means of different numerical characteristics have been developed and introduced in [*Scheringer and Berg*, 1994; *Scheringer*, 1996; *Bennett et al*., 1998; *van Pul et al*., 1998; *Wania*, 1998; *Rodan et al*., 1999; *Beyer et al*., 2000; *Beyer et al*., 2001; *Beyer and Matthies*, 2001; *Leip and Lammel*, 2004, etc]. For example such characteristics are spatial range, spatial scale, transport distance, characteristic travel distance, travelling distance, and so on. In this assessment in addition to the atmospheric residence time of SCCP isomers, another characteristic demonstrating LRTP of the considered substance is provided by the model estimate of its *Transport Distance* (TD). Numerical values of TD are defined with the help of Eq. 1 as the average distance from the source at which annual mean atmospheric concentration of a chemical in question drops 1000 times compared with the concentration near the point source (as an example See Fig. 5):

$$TD_{0.001} = \sqrt{\frac{S_{0.001}}{\pi}} \qquad (1)$$

where $S_{0.001}$ is the area covered by air concentrations dropped less than 1000 times.

It should be noted that such an approach is similar to that suggested in [*Rodan et al*., 1999].
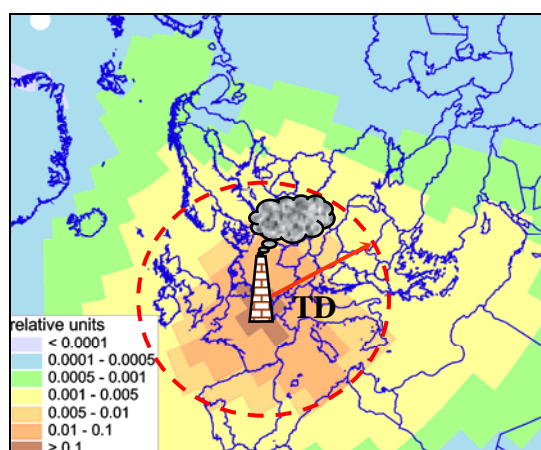

Fig. 5. *Definition of the transport distance*

The value of *TD* depends on all of the processes removing the pollutant from the atmosphere such as deposition to the underlying surface (land, sea) and atmospheric degradation. It was found that for different SCCP isomers processes of degradation and depositions to different types of underlying surfaces contribute differently to its removal from the atmosphere and produce corresponding effect on the calculated value of *TD*. The calculated value of TD for SCCP isomers presented in Table 3.

Table 3. *Characteristics of LRTP (**Half-life in air_{calc}** and **Transport Distance**) calculated for SCCP isomers*

Substance	$T_{1/2}^{air}$, days	TD, km
PeClD	4	2609
HxClDd	2	1756
HpClTd	3	2180

The highest PRTP is characteristic of PeClD, the lowest − for HxClDd. However, the presented numerical characteristics of all considered LRTP for SCCP isomers meet the LRTP criteria of Executive Body Decision 1998/2.

2.   PERSISTENCE

The behaviour of a substance in the environment to a large extent is determined by its persistence not only in the atmosphere but also in other environmental media. Its redistribution between air and soil, seawater, sediment, vegetation etc is important for its ability to cause adverse effects to the environment and to be accumulated in the food chain. In this process the main characteristics of a substance is its half-life in the medium under consideration.

In compliance with the Executive Body Decision 1998/2 the persistence of "new substances" in terms of their possible inclusion into the Protocol on POPs is demonstrated by indicative numerical values of their half-life in water, which should be greater than two months, or half-life in soil, which should be greater than six months, or half-life in sediments, which should be greater than six months also.

According to the parameterization of the three SCCP isomers used for modelling half-life in water is 3 months and half-lives in soil and sediments are 6 months for all of them. Thus, these substances meet the persistence criteria.

However, in addition to these parameters characterizing the persistence for particular media, multimedia model calculations allow estimating complementary characteristics of persistence in the whole environment - overall residence time or overall environmental persistence [*Scheringer*, 1996; *Webster et al*., 1998; *Gouin et al*., 2000, etc]. In this assessment such characteristic as *Half-life in the environment ($T_{1/2}^{env}$)* is estimated for the considered pollutant on the basis of the model calculations of its atmospheric transport taking into account deposition processes, degradation and gaseous exchange between main environmental media.

The model assessment of persistence in the environment for SCCP isomers is demonstrated by the numerical value of $T_{1/2}^{env}$ calculated with the help of Eq.2 as an inverse value of weighted mean of degradation rate constants k_j in the environmental media (atmosphere, soil, seawater, vegetation, sediments) with weights being the fractions f_j of a pollutant accumulated in *j*-th medium:

$$T_{1/2}^{env} = \ln2 \Big/ \sum k_i \cdot f_i \tag{2}$$

Here fractions f_i are evaluated on the basis of the model calculations.

Thus, the value of *Half-life in the environment* is affected by the distribution of the total environmental content of SCCP isomers between main environmental media (air, soil, water, sediment and vegetation) and the values of its half-life in each particular medium due to degradation process.

The distribution of SCCP total content in the environment between main environmental media (annual media balance) and relative fractions of the pollutant degraded in each media during a year (annual degradation balance) were obtained on the basis of simulations for one-year period. It should be noted that seawater includes pollutant content in sediments, and only degradation in forest litter is considered as degradation in vegetation. The distribution of total environmental content of PeClD, HxClDd and HpClTd between environmental media is compared with its relative fractions degraded in each media during a year in Fig.6.
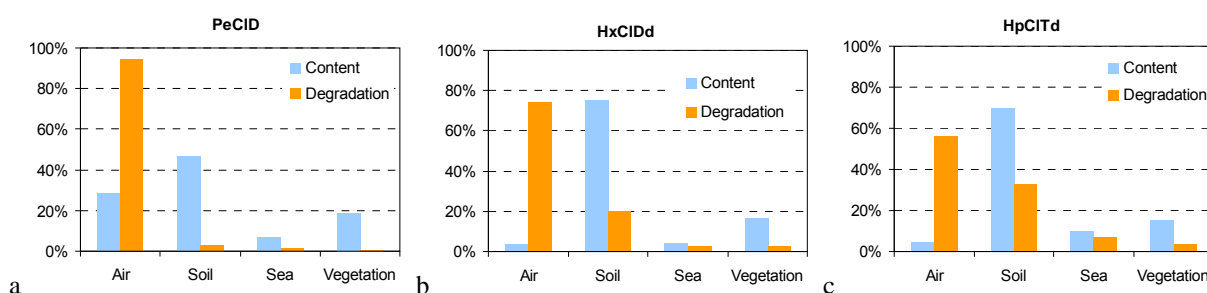

***Fig. 6**. Annual degradation and media balances for SCCP isomers*

All three considered SCCP isomers tend to be accumulated in soil though in different extent. For PeClD the fraction of environmental content in soil amounts to 46.6%, for HxClDd − 75.4%, and for HpClTd − 69.7%. But the degradation of all three isomers takes place mainly in the atmosphere. The contribution of atmospheric degradation to total degraded mass equals 94.4% for PeClD, 74.6% for HxClDd and 56.3% for HpClTd. The contributions of soil degradation for two latter isomers are also considerable − 20.3% for HxClDd and 33.0% for HpClTd. Slightly more than 20% of total environmental content for the three SCCP isomers are accumulated in vegetation. However, due to the absence of degradation rates in literature degradation in vegetation was not taken into account in modelling.

To evaluate the ability of the considered pollutants to be persistent in the environment, the values of **Half-life in the environment** for SCCP isomers were estimated on the basis of calculated media balances and the values of half-lives in the considered environmental compartments. Obtained estimates of $T_{1/2}^{env}$ are presented in Table 4.

***Table 4**. Characteristics of Persistence (Half-life in environment) and half-life of SCCP isomers in different environmental media used for modelling of atmospheric transport*

Substance	$T_{1/2}^{env}$, days	Half-life, days		
		Air	water	soil
PeClD	6.8	2	60	180
HxClDd	42.6	2	60	180
HpClTd	33.9	2	60	180

According to the calculated value of *Half-life in the environment*, persistence of SCCP isomers in the environment can be characterised as relatively low. The highest persistence is characteristic of HxClDd, the lowest – for PeClD. At that the obtained value of $T_{1/2}^{env}$ is considerably lower than those of half-life due to degradation process in soil and seawater and higher than that for degradation in the atmosphere. Due to relatively high ability of SCCP isomers to accumulate in soil, this pollutant may course long-term adverse affect through this medium.

3.   BENCHMARK APPROACH

Since the numerical values of $T_{1/2}^{air}$ and $T_{1/2}^{env}$ of particular chemicals are model dependent, one of the possible ways to diminish uncertainties in evaluating new substances proposed by *Scheringer* [1997] and *Beyer et al.* [2000] and discussed at the OECD/UNEP Workshop on the Use of Multimedia Models for the Estimation of Environmental Persistence and Long-Range Transport (Ottawa, Canada, 2001) was to use a "benchmark" approach. This approach suggests that model results on LRTP and persistence are used to compare the pollutants under study with some adequately studied "benchmark substance" with known values of the considered parameters.

This procedure enables assessment of "new substance", by considering their ranking in terms of persistence or LRTP among the well-known benchmark chemicals. Examples of chemicals ranking and classification approach are described by *Matthies et al.* [1999], and *Bennett et al.* [2001]. Relative approach may also be applicable when the desired outcome is the screening of a large set of existing chemicals, to establish priority classes of substances for further assessment or action.

The comparison of calculated characteristics of LRTP and persistence for SCCP isomers against those obtained for a benchmark pollutant is presented in this subsection. Benzo[a]pyrene (B[a]P) is used as a benchmark substance in this assessment. For B[a]P dry and wet depositions of particulate phase mainly determine its ability to the long-range transport. Characteristics of its behaviour in the environment are well studied and clearly meet the UN ECE criteria for POPs. It is already included in the Protocol on POPs and is considered as pollutant of regional concern. All calculations were performed for one-year period from a conventional point source with one and the same location in Europe and one and the same emissions intensity.

The considered SCCP isomers and B[a]P have been ranked in ascending order according to their values of *Transport Distance* (Fig. 9a) and *Half-life in the environment* (Fig. 9b).
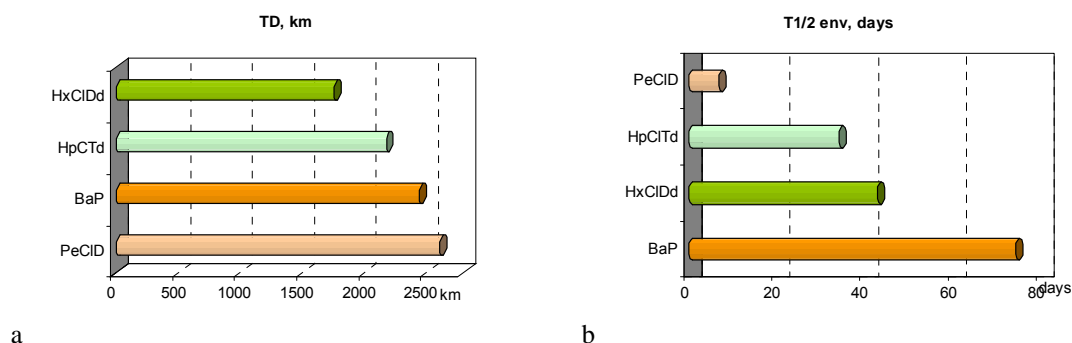

Fig. 9. *Transport distance* and ***Half-life in the environment*** *calculated for SCCP isomers and B[a]P*

According to the model calculations of **TD**, only one of the three SCCP isomers − PeClD has TD value larger than that of B[a]P. However, the rest two isomers show TD values only slightly less than that of B[a]P. Hence, short chain chlorinated paraffins can be classified as pollutants of regional concern.

The ranking of the considered isomers and benchmark pollutant with respect to $T_{1/2}^{env}$ values to some extent differs from that obtained on the basis of TD. It is found that all three considered SCCP isomers are less persistent in the environment than B[a]P. However, the persistence of the two heaviest isomers (HxClDd and HpClTd) has the values of environmental half-life comparable with that of B[a]P by the order of magnitude. Thus, from the viewpoint of environmental persistence SCCPs can be classified as pollutants of regional concern.

4. CHARACTERISTICS OF SCCP LONG-RANGE TRANSPORT POTENTIAL AND PERSISTENCE IN RELATION TO THE INDICATIVE CRITERIA OUTLINED IN EXECUTIVE BODY DECISION 1998/2

As it was stated above this model assessment was carried out for three SCCP isomers chosen as a representative of all possible SCCPs (see Annex A). Physical-chemical properties of SCCPs presented in [*Risk Profile and Summary Report*, 2005] are given in Table 5 in relation to the LRTP and persistence criteria outlined in the Executive Body Decision 1998/2 with addition of the MSCE-POP model estimates. Data on physical-chemical properties of three SCCP isomers used in the model calculations are given in the Annex B (Tables B1).

Table 5. *Comparison of LRTP and persistence of SCCP isomers and criteria of Executive Body Decision 1998/2 based on data [Risk profile and Summary Report, 2005] and with additions of MSCE-POP model estimates*

Criterion	Criterion values	Meets the criterion (Yes/No)	Characteristics of SCCP isomers			Remarks
			PeClD	*HxClDd*	*HpClTd*	
Potential for Long-Range Transboundary Atmospheric Transport						
Vapour pressure, Pa	<1000	*Yes*				Presented in *Risk profile and Summary Report, 2005*
Half-life in air, days	>2	Yes	2	2	2	
Half-life in air$_{calc}$, days		Yes	4	2	3	$T_{1/2}^{air}$ calculated by MSC-E
Persistence						
Half-life in water, months	> 2	Yes	>2	>2	>2	Presented in *Risk profile and Summary Report, 2005*
Half-life in soil, months	>6	Yes	>6	>6	>6	
Half-life in sediment, months	>6	Yes	>6	>6	>6	
Half-life in the environment, months	-	-	<1	1.4	1.3	$T_{1/2}^{env}$ calculated by MSC-E

The results of the model assessment demonstrate the considerable long-range atmospheric transport potential and relatively low persistence of SCCP isomers.

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TECHNICAL MIXTURES AND LEVELS OF SCCPS MEASURED IN ENVIRONMENTAL SAMPLES

Environmental releases of chlorinated paraffins can occur anywhere along the life-cycle chain from manufacture, transport, use, to disposal. However, it is widely agreed, because manufacture and transfer occur within closed systems, that the most likely source of releases comes from use and disposal in dispersive use applications such as metalworking. The most ecologically significant impacts occur when SCCPs are released to water and sediment. Because of their low solubility in water, they are thought to be transported in water by adherence to particles and are strongly adsorbed to sediment. [*CHLORINATED PARAFFINS*: A STATUS REPORT].

The available data on the environmental concentrations of SCCPs are presented below.

Air concentrations

Air concentration levels of SCCPs were found in different regions including those located far from emission sources such as the Arctic (see Table A1). SCCPs were not found in the analysis of archive samples from Alert site.

Table A1. Levels of SCCPs in air

Sampling location	Sampling data/period	SCCP (ΣC_{10}-C_{13}), concentrations, pg/m^3	References	Remarks
Spitsbergen, Norway	1999	9-57	*Borgen et al.*, 2000; cited from *Zencak Z.*, 2004	
Egbert, Sothern Ontario, Canada	1990	$\frac{65\text{-}920}{540}$	*Tomy*, 1997; cited from *Peters et al.*, 2000	Archived air samples; 4 month period, Gas+particles
Alert, Canada	1992	$\frac{<1.7-67}{20}$	*Peters et al.*, 2000	Archived air samples; September – December (4 month period), Gas+particles
Alert, Canada	1993-1994	2.0	Canadian Arctic Contaminants Assessment Report II, 2003	Archived air samples, gas phase
Station near Lancaster, UK	1997-1998	$\frac{<D.L-1085}{319\pm318}$	*Peters et al.*, 2000	May 1997- April 1998; High Vol air sampler; Gas+particles
Hazelrigg, UK	2003	$\frac{<180\text{-}3400}{1100}$	*Barber et al.*, 2005	April- May 2003, High Vol air sampler; Gas+particles;

The data presented in Table A1 give general impression of contamination levels of polychlorinated n-alkanes with short chain in the atmosphere but do not allow evaluating the distribution of isomers/congeners.

Water concentrations

Monitoring data for SCCPs in water are limited. The literature data on SCCP contamination levels in water concern total content (ΣC_{10}-C_{13}). Researchers have reported detection of SCCPs at low ng/L levels in natural water bodies including in remote regions. SCCPs have been reported in filtered

Canadian river water at 18.6 to 49.7 μg/l In the United Kingdom, higher measurements of 4 μg/L in marine water and 4 μg/l in fresh water have been reported [*CHLORINATED PARAFFINS: A STATUS REPORT*].

In aquatic systems, where SCCPs are generally associated with sediment or suspended particles because of their low solubility, chlorinated paraffins have the potential for bio-accumulation in aquatic organisms.

Very high levels have been measured in sediment adjacent to manufacturing facilities but these are generally old and not considered relevant to modern day operations [*ICES MCWG Report 2005*].

Soil concentrations

No data on the occurrence of chlorinated paraffins in soil have been reported.

Choice of isomers for modelling

The choice of SCCP isomers for modelling is based on available data on homologue group profiles in technical mixtures and in the atmosphere.

Unfortunately, the results of investigation of SCCP chemical composition of emissions to the atmosphere are absent. However, there exist data on relative fractions of isomers in three technical SCCP mixtures with different degree of chlorination − 51% Cl, 55.5% Cl and 61% Cl [*Zencak et al.,* 2003]. Among polychlorinated paraffins with 10 – 13 carbon atoms in the chain, 32 isomers different by both chlorine and carbon content were identified. The plots illustrating the composition of the three technical mixtures are shown in Fig. A1a.
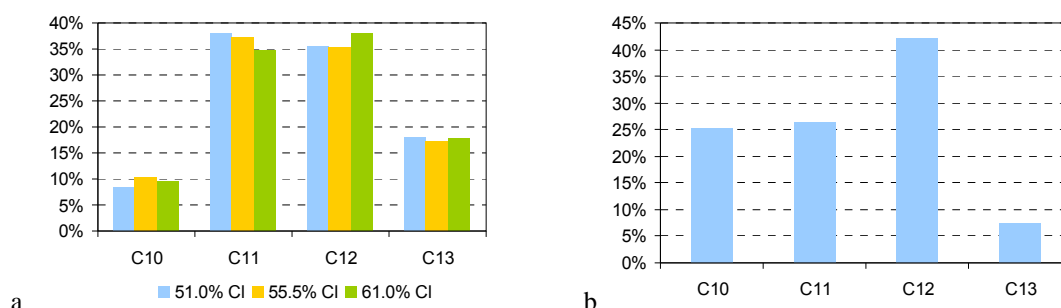

Fig.A1. *Compositions of three technical mixtures of polychlorinated paraffins (a) and homologue group profile of SCCPs in the air concentrations (b)*

Physical-chemical properties needed for modelling of C11 homologues of SCCPs have not been found in the literature. However, about 60% of mass in all three mixtures consist of chlorinated n-alkanes with chain length C_{10}, C_{12} and C_{13}.

The analysis of SCCPs focused at the examination of homologue group profile of polychlorinated n-alkanes with short chain in the atmosphere was carried out in the GB [*Peters et al.,* 2000]. However, only 7 samples were used in the examination. The obtained profile is shown in Fig. A1b.

In the atmosphere, homologue group with 12 carbon atoms is dominating. The three groups (C10, C12 and C13) cover about 75% of total SCCP content. Three of isomers ($C_{10}H_{17}C_5$, $C_{12}H_{20}C_6$ and $C_{13}H_{21}C_7$) representing groups C10, C12, C13 were chosen for modelling.

PHYSICAL-CHEMICAL PROPERTIES OF SCCP ISOMERS USED FOR MODELING

The full set of physical-chemical properties and degradation rates of SCCP isomers selected for the model parameterisation on the basis of data available in literature is presented in Table B 1.

Table B1. *Parameters of SCCPs for modeling of atmospheric transport*

Parameter Base values at 25 °C	Numerical value			References and remarks
	$C_{10}H_{17}Cl_5$	$C_{12}H_{20}Cl_6$	$C_{13}H_{21}Cl_7$	
Henry's law constant for freshwater, Pa m³/mol	12.0	5.0	1.5	Calc – solubility on bases I*snard and Lambert,* 1989; vapour pressure on bases *Drouillard et al.*, 1997
Henry's law constant for seawater, Pa m³/mol	12.0	5.0	1.5	
Henry's law constant temperature coefficient, K	–	–	–	
Washout ratio	1.0×10^5			Calc on bases *van Pul et al.*, 1998
Subcooled liquid -vapour pressure, Pa	5.1×10^{-3}	2.3×10^{-4}	2.3×10^{-5}	Calc on bases *Drouillard et al.*, 1997
Temperature coefficient of subcooled liquid -vapour pressure, K	–	–	–	
SCCP – OH-radical interaction rate constant, cm³/s	5.22×10^{-12}	–	4.96×10^{-12}	Final Draft II, 2003
Degradation in air constant, s⁻¹	4.18×10^{-6}	4.01×10^{-6}	3.97×10^{-6}	For $C_{12}H_{20}Cl_6$ taken from *Muir et al.*, 2000, for the rest – calculated
Half-life in air, days	2	2	2	Calc
Degradation in water constant, s⁻¹	1.37×10^{-7}	1.37×10^{-7}	1.37×10^{-7}	*Muir et al.*, 2000
Half-life in water, days	60	60	60	
Degradation in soil constant, s⁻¹	4.46×10^{-8}	4.46×10^{-8}	4.46×10^{-8}	*Muir et al.*, 2000
Half-life in soil, days	180	180	180	
Molar volume, cm³/mol	356.0	425.2	496.6	Calc *Mackay et al.*, vol.II, p.10
"Octanol-water" partition coefficient, K_{ow}	1.0×10^6	5.89×10^6	1.37×10^7	*Muir et al.*, 2000
"Octanol-air" partition coefficient, K_{oa}	2.7×10^8	2.93×10^9	2.34×10^{10}	Calc
Temperature coefficient of K_{OA} coefficient, K	–	–	–	
Molecular diffusion coefficient, m²/s				Calc on bases *Schwarzenbach et al.*, 1993
in water	4.17×10^{-10}	3.75×10^{-10}	3.54×10^{-10}	
in the air	4.32×10^{-6}	3.93×10^{-6}	3.73×10^{-6}	
"Organic carbon-water" partition coefficient, K_{oc}, m³/kg	4.1×10^2	2.41×10^3	5.66×10^3	Calc on bases *Karikhoff*, 1981

The data on SCCP physical-chemical properties in literature are quite limited. The reason can be explained by difficulties in separating individual isomers from SCCP mixtures. Experimental data on temperature dependencies of physical-chemical parameters are also absent. In our investigation most parameters obtained by calculations based on different regression relations.