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BETR-World: a geographically explicit model of chemical fate: application to transport of α-HCH to the Arctic

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"Capsule": *A geographically explicit multi-compartment model is applied to the transport of α-HCH to the Arctic, showing Europe and the Orient are key sources.*

Abstract

The Berkeley–Trent (BETR)-World model, a 25 compartment, geographically explicit fugacity-based model is described and applied to evaluate the transport of chemicals from temperate source regions to receptor regions (such as the Arctic). The model was parameterized using GIS and an array of digital data on weather, oceans, freshwater, vegetation and geo-political boundaries. This version of the BETR model framework includes modification of atmospheric degradation rates by seasonally variable hydroxyl radical concentrations and temperature. Degradation rates in all other compartments vary with seasonally changing temperature. Deposition to the deep ocean has been included as a loss mechanism. A case study was undertaken for α-HCH. Dynamic emission scenarios were estimated for each of the 25 regions. Predicted environmental concentrations showed good agreement with measured values for the northern regions in air, and fresh and oceanic water and with the results from a previous model of global chemical fate. Potential for long-range transport and deposition to the Arctic region was assessed using a Transfer Efficiency combined with estimated emissions. European regions and the Orient including China have a high potential to contribute α-HCH contamination in the Arctic due to high rates of emission in these regions despite low Transfer Efficiencies. Sensitivity analyses reveal that the performance and reliability of the model is strongly influenced by parameters controlling degradation rates.

Keywords: Model; Global; Alpha-HCH; Long-range transport; Fugacity

1. Introduction

International initiatives are underway to identify and regulate persistent, bioaccumulative, and toxic contaminants and those with potential for long-range transport (PBT-LRT) (Lipnick et al., 2001). These assessments generally rely on either interpretations from monitoring data or the use of generic or evaluative models, which rank chemicals according to these criteria (van de Meent et al., 2000; Scheringer et al., 2000; Beyer et al., 2000). A complementary activity is to compile a global scale mass balance model to predict the fate of candidate chemicals in the global environment. These models can then be validated by comparing the predicted results with monitoring data. Such models have been described by Wania and Mackay (1999), Strand and Hov (1996) and Lammel et al. (2001).

For regulatory purposes, a credible and defensible method must be used to understand and assess the contribution of different geopolitical areas to the global fate of a contaminant. There is a need to identify areas that have potential to be source regions of contaminant to other remote or sensitive regions. This may facilitate the phase-out of known contaminants at a global scale. For example, it may be possible to demonstrate that a release of 1 kg of a specific contaminant, such as DDT in tropical, malarial regions does not have the same potential for accumulation in Arctic ecosystems as 1 kg released in temperate regions. A further regulatory challenge is to determine if new and previously unstu-

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died or under-studied chemicals have the potential for significant transport from the region of use to sensitive regions. For example, organo-bromine and organo-fluorine compounds are being subjected to increased scrutiny as potential Arctic contaminants.

In this study we focus on the Arctic ecosystem as a receptor. An additional goal of this modelling exercise is to describe the global distillation of chemicals to polar regions described by Wania et al. (1999) and Wania and Mackay (1995, 1999). Accordingly, a dynamic geographically explicit global model (BETR-World model) has been developed to assess and improve our understanding of the long-range transport of persistent chemicals in the global environment. It is based on previous models of Canada and the North American continent developed at the Canadian Environmental Modelling Centre (Mackay et al., 1996; MacLeod, 2002; MacLeod et al., 2001; Woodfine et al., 2001). A combination of the political and climatic zoning is used to define the regions. Because the globe is essentially a closed system, the only losses of chemical considered by this model are burial into inaccessible soil or freshwater sediments, deposition to deep oceans, loss to the stratosphere and degradation to other chemical species.

A two-dimensional segmentation of climate-based land- or ocean-dominated regions is used. This represents an increase in spatial complexity and resolution compared with previous models such as those of Wania and Mackay (1995,1999) and Scheringer et al. (2000). By incorporating geographically explicit emission scenarios for specific contaminants we believe that improved validation against measured concentrations in air, water, soil and sediment may be possible and international efforts to regulate chemicals may be better focused.

Here we outline the development and parameterization of the BETR-World model and apply it illustratively to alpha-hexachlorocyclohexane (α-HCH, CAS# 319846). HCH is a chlorinated pesticide that was used in a wide variety of applications throughout the world. We emphasize that the primary purpose of this study is to describe the structure and tentative results from a geographically explicit global model. Other approaches are possible, such as the meridonally segmented model of Wania and Mackay (1999), the more evaluative model of Scheringer et al. (2000) and the computationally intensive models based on detailed meteorological data described by Lammel et al. (2001). At the present state of the science it is not entirely clear which models will prove most useful for informing the international regulatory process.

2. Model segmentation and parameterization

2.1. Segmentation

The Earth has been divided into 25 regions listed in Table 1 and illustrated in Fig. 1, each region representing an area that is primarily ocean or land. All regions

Table 1
BETR-World regions

Region		Total surface area (km^2)	%Fresh water	%Coastal/Oceanic water	%Land
1	NA—Continental Arctic	5.06×10^6	5	20	75
2	NA—Canadian Provinces	8.04×10^6	8	16	76
3	NA—Continental United States	9.19×10^6	4	15	81
4	NA—SA—Carribean	1.15×10^7	1	54	45
5	SA—Centro	1.31×10^7	2	15	83
6	SA—Arg. Chile	6.58×10^6	2	38	61
7	EU—Europe	9.59×10^6	2	40	58
8	AS—Middle East	2.23×10^7	1	48	51
9	AS—Russia	2.30×10^7	5	11	84
10	AS—Orient	1.80×10^7	2	24	74
11	OC—Oceania	1.66×10^7	0	47	52
12	AF—Northern Africa	2.18×10^7	1	15	84
13	AF—Southern Africa	1.54×10^7	3	26	70
14	AN—Antarctica	1.95×10^7	0	37	63
15	American North Pacific	4.19×10^7	0	98	2
16	OC—Micronesia	4.09×10^7	0	98	2
17	North North Atlantic	1.86×10^7	0	49	51
18	South North Atlantic	1.42×10^7	0	89	11
19	Asian North Pacific	3.60×10^7	0	76	24
20	Indian Ocean	1.37×10^7	0	82	18
21	South Atlantic	2.84×10^7	0	100	0
22	Arctic	1.75×10^7	0	43	57
23	South South Pacific	3.75×10^7	0	77	23
24	Antarctic Sea West	3.19×10^7	0	96	4
25	Antarctic Sea East	4.66×10^7	0	96	4
	Total	5.27×10^8	1%	65%	34%

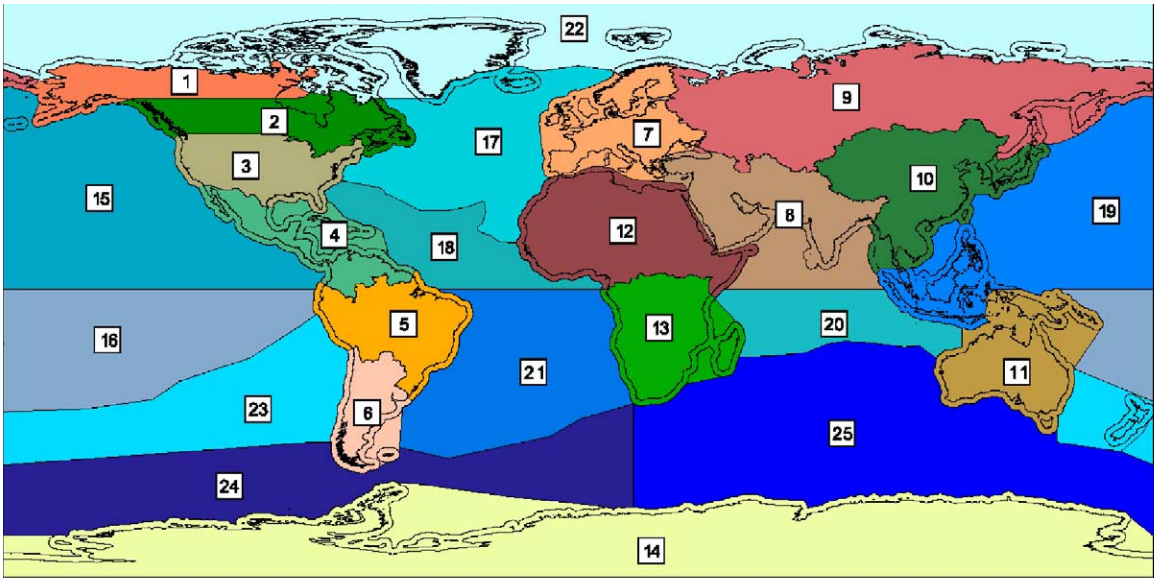


Fig. 1. BETR-World regions.

contain upper and lower atmospheric compartments. The terrestrial segments contain compartments representing soil, vegetation, freshwater and freshwater sediments, as illustrated in Fig. 2. The oceanic segments represent the top 200 m of ocean water and do not have sediment compartments. We believe that the combination of terrestrial/oceanic factors and political factors in this segmentation has merit because chemical use is often regulated by national policy and by being signatories to international policy initiatives such as UNEP Stockholm Convention (UNEP, 1998).

2.2. Parameterization

The 25 regions range in area from 5 to 50 million km^2. The BETR-World regions and the compartments contained within each are parameterized using spatially referenced environmental data sets including climatic, vegetative, soil, hydrologic and oceanographic data. These data were obtained from various reliable sources, usually government or educational institutions.

2.3. Regional characteristics

Parameters that affect residence times and partitioning within each region such as air and oceanic temperature, land, sea and freshwater area and volume, and vegetation indices such as leaf area index (LAI) have been compiled for each region.

The volume of the freshwater compartment in each region was estimated using a dataset distributed by the National Oceanic and Atmospheric Association (NOAA) (Graham et al., 1999). Delineation of major water bodies (lakes and rivers) is derived from the National Geophysical Data Centre (NGDC) 5-min Global DTM (Digital Terrain Model) (Graham et al., 1999). At this resolution, bodies of water greater than 20 km^2 in high latitudes and greater than 85 km^2 in equatorial regions are captured, converted to vector format, and their areas summed within each region. This value is then multiplied by 20 m, the average depth of freshwater bodies suggested by MacLeod et al. (2001) in the BETR-North American continental scale model. Using a conservative estimate of depth of 20 m is appropriate as the spatial resolution used in this exercise restricts the inclusion of small water bodies and wetland areas.

To determine the volume (and mass) of the vegetation compartment within each region, an estimate is made of the percentage of land area covered by vegetation; this value is then multiplied by a leaf “depth” of 0.001 m. The percentage of vegetated cover is derived from the SeaWIFS global LAI (m^2 leaf area/m^2 land area) image (Myneni, 2001).

2.4. Parameterization of intermedia and region to region transport

Intra-regional, inter-compartmental transport rates (i.e. air–water, water–air or soil–water) are functions of the compartmental properties defined above and the physical-chemical properties of the chemical being addressed. The mass transfer coefficients (MTCs) describing air–water, soil–air, soil–water, air–leaf transfer rates (m/h) have been set as a standard across all regions (after Mackay, 2001), except for the rain rate which is calculated using the geometric mean of a global, 1/2-degree resolution gridded coverage of average annual precipitation over each region (Leemans and Cramer, 1991). In previous versions of this model

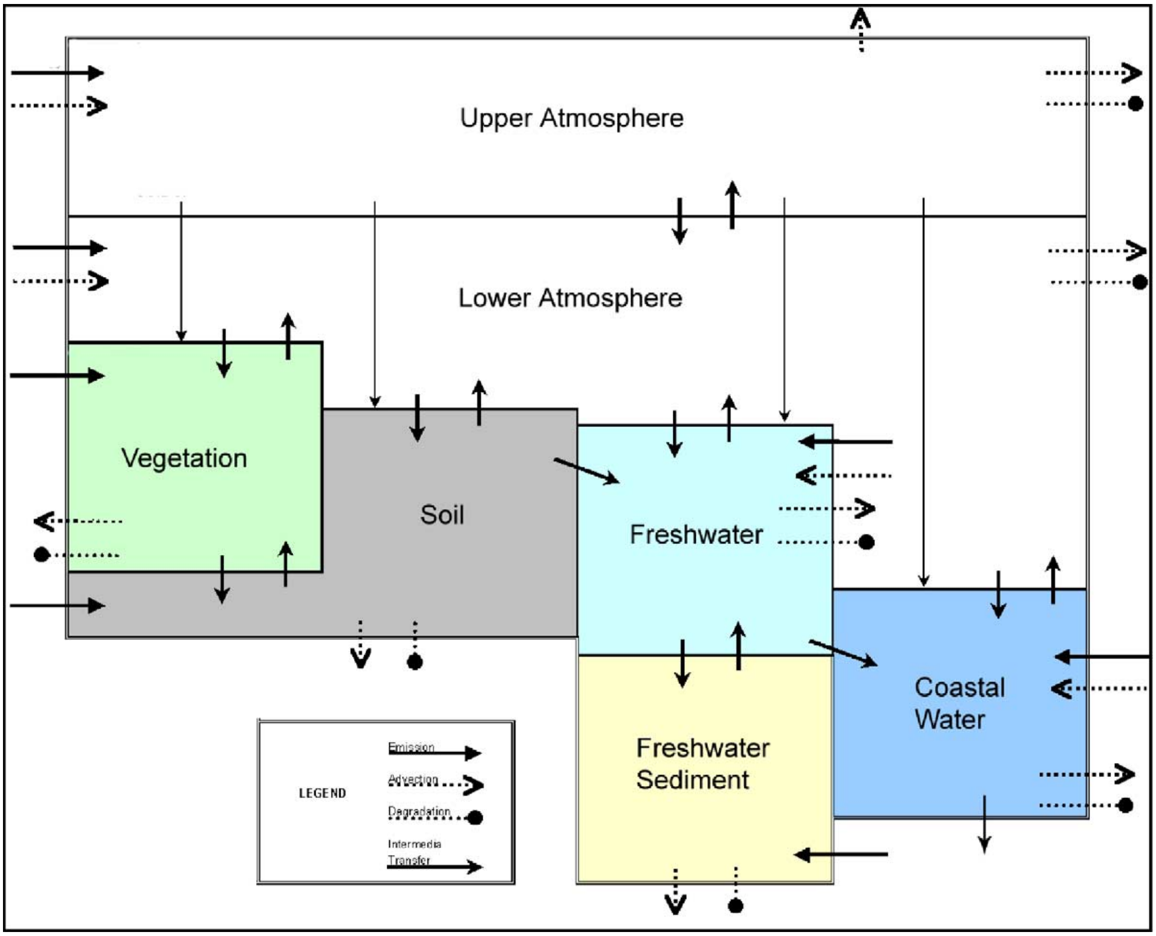


Fig. 2. Generic regional compartments.

framework, oceanic processes have largely been ignored because the coastal or oceanic compartments have played a minor role in the transport of chemicals within or between regions. Increasing the modelled scale to global proportions also increases the proportion of coastal or oceanic water involved in the fate of contaminants in the environment. In an attempt to address this limited representation of oceanic processes an ocean particle settling rate has been included as a permanent loss mechanism in this version of the model. A conservative estimate of the ocean particle settling rate, based on previous studies of organic carbon settling rates is 1.65×10^{-8} m/h (Wania and Daly, 2002) and is set standard across all regions. Table 2 shows the transport velocities used in all regions.

Temperatures and OH^- radical concentrations are specified for all regions and allowed to vary seasonally between winter and summer means. As seen in Table 3, temperatures span approximately 65 °C on a latitudinal scale and approximately 40 °C on a seasonal scale for sub-polar regions 2 and 9. Due to the large variation in temperature over time and space, degradation rate constants are modified in all terrestrial and oceanic com-

Table 2
Transport velocity coefficients and related quantities

Transport velocity parameters	m/h
1 air side air–fresh water MTC	15
2 water side air–fresh water MTC	0.03
3 rain rate	3.93×10^{-5}
4 aerosol depositon	10.8
5 soil air phase diffustion MTC	0.04
6 soil water phase diffusion MTC	1.00×10^{-5}
7 soil air boundary layer MTC	1
8 sediment-water diffusion MTC	1.00×10^{-4}
9 sediment deposition	5.00×10^{-7}
10 sediment resuspension	2.00×10^{-7}
11 soil water runoff	5.00×10^{-5}
12 soil solids runoff	2.00×10^{-8}
13 sediment burial	3.00×10^{-7}
14 diffusion to stratosphere	0.4
15 leaching from soil	1.00×10^{-5}
16 Soil solids convection rate	
17 air side air–veg. MTC	9
18 veg. water uptake velocity	1.00×10^{-4}
19 upper–lower air mixing MTC	5
20 air side air–coastal/oceanic water MTC	30
21 water side air–coastal/oceanic water MTC	0.03
22 ocean particle settling rate	1.65×10^{8}
rain scavenging ratio	2.00×10^{5}
Snow scavenging ratio	1.00×10^{6}
Fraction of rain intercepted by foliage	0.1

Table 3
Winter and Summer (minimum and maximum) temperatures (°C) and hydroxyl radical concentrations (molecules/cm^3)

Region		Winter mean °C	Summer mean °C	Winter [OH$^-$] molecules/cm^3	Summer [OH$^-$] molecules/cm^3
1	NA—Continental Arctic	−31	9	1×10^5	15×10^5
2	NA—Canadian Provinces	−18	15	1×10^5	20×10^5
3	NA—Continental United States	−1	23	5×10^5	25×10^5
4	NA—SA—Carribean	14	22	15×10^5	30×10^5
5	SA—Centro	24	21	20×10^5	20×10^5
6	SA—Arg. Chile	20	8	15×10^5	5×10^5
7	EU—Europe	−3	18	1×10^5	20×10^5
8	AS—Middle East	10	28	5×10^5	25×10^5
9	AS—Russia	−24	15	1×10^5	15×10^5
10	AS—Orient	−8	19	5×10^5	25×10^5
11	OC—Oceania	27	14	20×10^5	15×10^5
12	AF—Northern Africa	19	29	15×10^5	30×10^5
13	AF—Southern Africa	24	18	20×10^5	15×10^5
14	AN—Antarctica	0	−35	5×10^5	1×10^5
15	American North Pacific	4	19	1×10^5	20×10^5
16	OC—Micronesia	14	8	10×10^5	30×10^5
17	North North Atlantic	−5	9	15×10^5	30×10^5
18	South North Atlantic	15	20	20×10^5	10×10^5
19	Asian North Pacific	24	25	10×10^5	30×10^5
20	Indian Ocean	20	15	20×10^5	15×10^5
21	South Atlantic	20	10	20×10^5	15×10^5
22	Arctic	−31	2	1×10^5	15×10^5
23	South South Pacific	25	5	15×10^5	5×10^5
24	Antarctic Sea West	25	5	15×10^5	5×10^5
25	Antarctic Sea East	25	5	15×10^5	5×10^5

partments (compartments 3–7) with respect to region temperature.

In the atmospheric compartments, the dominant degradation process is reaction of chemical with OH$^-$ radicals present in the atmosphere (Brubaker and Hites, 1998). Utilizing modeled OH$^-$ radical concentrations from Wang et al. (1998) we have parameterized the maximum and minimum concentrations for each atmospheric compartment at 850 mb (lower) and 500 mb (upper). These concentrations are varied using a sine function that is in phase with the temperature function as these parameters are both seasonally variable, with the assumption being that the extremes occur in January and July.

Partition coefficients K_{OW}, K_{AW} and K_{OA} and the enthalpies of vaporization and solution are temperature dependent. These, as well as the relationship defining changes in bulk reaction half-lives with changes in temperature suggested by Anderson and Hites (1996) are included in this version of the model. Utilized with the varying temperature, Eq. (1) defines this relationship for the terrestrial and aquatic environments.

$$k_e = k_v \cdot \exp((\Delta E/R) \cdot (1/T_v - 1/T_e)) \tag{1}$$

where k_e is the temperature-modified reaction rate constant (h), k_v is the reference reaction rate constant input to the model (h), ΔE is the activation energy for the chemical in a medium (J/mol), R is the Gas law constant 8.314 J/K mol, T_v is the chemical property temperature (K) (usually 298.15 K) and T_e is the average temperature (K) of the region at that timestep.

Atmospheric degradation rate constants are modified by not only temperature fluctuation, but OH$^-$ radical concentration changes as well. This relationship is described by Eq. (2) (after Wania and Mackay, 2000) and is included in the model:

$$k_e = k_v \cdot [\mathrm{OH}^-] \cdot 1.0 \times 10^6 \cdot \exp((\Delta E/R) \cdot (1/T_v - 1/T_e)) \tag{2}$$

where k_e is the modified reaction rate constant for Upper Air or Lower Air, k_v is the reference degradation rate constant (m^3/molecules.h), [OH$^-$] is the concentration of hydroxyl radicals in the atmospheric compartment, ΔE, R, T_v and T_e are as defined above.

Because the BETR-World model is a set of linked compartments, it can show not only the distribution of a chemical between media within a region, but also to approximate advective and diffusive processes occurring between regions. Mass balances have been compiled for flows of air, water (and contaminant) in all regions. Over the long term, air and water flows into a region must be balanced by equivalent flows leaving the region.

2.4.1. Air balance

Air (and gaseous or sorbed chemical) can enter and leave individual regions by exchange with adjacent regions. The height of the lower air compartment in all regions is set at 1000 m, representing the lower troposphere. An upper atmospheric compartment, set at 2000 m in height allows for treatment of more rapid vertical transport and advection at high altitudes, which can be an important long-range transport process. The upper–lower air mixing mass transfer coefficient is set at 5 m/h for all regions (Seinfeld and Pandis, 1998).

Rates of regional air movement are usually characterized in mass balance models by residence times, namely the ratio of the volume of air in the region (m^3) to average transport to and from (under the steady state assumption) all neighbouring regions (m^3/h). It is estimated as the product of the average wind speed through a region (m/h) and its cross-sectional area (m^2). To link a set of regional models, the proportions of out-flowing air from any region to all others must be specified in addition to the total rate of air movement into and out of a region. A flow matrix for air has been defined from available data, in terms of proportions of air leaving a given region that enters all other adjacent regions. Allowances have been made for two-way exchange of air between adjacent regions using the iterative approach described in Woodfine et al. (2001). A similar approach to the air balance is used for oceanic water and freshwater.

The principal challenge is to parameterize the flow proportions and rates in the air flow matrix. The 2.5-degree Zonal and Meridonal Pressure Data from the NOAA NCEP/NCAR-CDAS (National Oceanic and Atmospheric Association—National Centers for Environmental Prediction/National Center for Atmospheric Research Climate Data Assimilation System) were obtained on a monthly average basis for 1949–2001 (Kistler et al., 2001). Data were then summarized by monthly and annual average wind direction. Using GIS, the centroid of each grid cell was plotted spatially along the regional boundaries. Using this methodology, only the data points within 5 degrees of either side of a regional boundary were used in the calculation of average wind direction. This reduces the data requirements (the dataset was minimized from approximately 10,000 points to 3500 data points) for the model and attempts to address the assumption that the regions are large and assumed to be homogenous and well mixed (Mackay, 2001) by allowing only processes occurring at the regional boundaries to affect transfer rates.

Utilizing an algorithm that applies decision rules pertaining to wind direction to those data points, the proportion of data points that cross each boundary were calculated. The air mass balance for BETR-World is representative of long term annually averaged air movements and it is constant from year to year.

For a given region in the air flow balance, all inflows are defined as the outflows from adjacent regions and the steady state total outflow from the region is therefore also defined. As a result the residence time for air can only be explicitly set for one region in the matrix, and all others are a function of this selected residence time and the connectivity matrix. Once an air flow balance solution has been deduced, it can only be modified by scaling all flows by a constant factor, or by redefining the proportions of flows in the matrix and solving for a new set of steady-state flow rate ratios. The proposed air flow balance between the 25 global regions is the result of setting the residence time of the lower air compartment over the continental United States to 10 days. The resulting hemispheric residence times were calculated and are in good agreement with Seinfeld and Pandis (1998) who suggest that hemispheric residence times are in the order of approximately 1 year.

2.4.2. Freshwater balance

Transfers of water (and hence dissolved chemical) between regions in freshwater (rivers) are quantifiable, but must be balanced with other inputs (e.g. precipitation and groundwater recharge) and outputs (e.g. evapotranspiration and runoff) of water into and out of each region. Because this model functions as a "closed" system, an accounting method was developed and all water volumes and transfers are balanced on a global scale. The water balance has been determined and all inputs and outputs for each region were quantified using the Leemans and Cramer (1991) precipitation data, USGS "HYDRO1K" 1 km resolution hydrological dataset derived from GTOPO30 30 arc-second digital elevation map (USGS, 1999) and world oceanic drifter data from Hansen and Poulain (1996).

Stream-flow records along with a vector representation of rivers are used to determine flow direction and rates between river sub-basins. Using this information, flow rates can be scaled with respect to downstream gauging stations to provide an estimate of the flow rate across regional boundaries.

2.4.3. Oceanic water balance

Estimates of transport velocities of oceanic water across regional boundaries were obtained using Wania and Mackay's (1995) "meridional eddy diffusion coefficients" (m^2/h) with the coastal/coastal, coastal/ocean and ocean/ocean boundary lengths. These eddy diffusion coefficients "lump" advective and diffusive exchange processes between adjacent ocean water regions, and were estimated using previous studies of the average residence time of water in the ocean compartments.

2.5. Mass balance equations

In a typical terrestrial region there are 7 compartments, as illustrated in Fig. 2. Several of the regions are primarily oceanic and therefore have little or no terrestrial volume. A first order differential equation is written for each compartment in each region, resulting in a total of 175 simultaneous differential equations of the form:

$$d(VZf)/dt = E + \Sigma f D_{IN} - f \Sigma D_{OUT} \quad (3)$$

where V is the compartment volume (m^3), Z is the bulk fugacity capacity or ratio of concentration (mol/m^3) to fugacity, f (Pa), t is time (h), E is emission rate (mol/h) to the compartment and the two remaining terms (Σ f D_{IN} and f Σ D_{OUT}) represent the total transport into and out of the compartment, including degrading reactions. A steady state solution is possible if the left side of the equation is zero. To solve the equations an initial condition is defined, all emissions are specified over the time period of interest and the set of equations is solved by numerical integration. This yields all fugacities over the time course from which concentrations, masses and fluxes can be calculated.

The effect of seasonally fluctuating temperatures on Z and D-values is included in the model by adjusting these values continuously. When these changes are made, as the mass and concentration of chemical is conserved, the fugacity changes.

The physico-chemical properties and thus the partitioning characteristics of a chemical change with temperature. A sine function is used to estimate changes between a winter and summer mean temperature for each region. As temperature decreases, the fugacity capacity of air decreases relative to the fugacity capacity of water and soils. This results in an increase in partitioning to water and soil from air, i.e. there is enhanced “condensation” of chemical from the atmospheric compartments. Degradation is also slowed at lower temperatures therefore reaction rates are lower in colder regions. As a result chemical tends to be better “preserved” in the Arctic and can reach higher concentration in environmental media (Mackay and Wania, 1995).

Although there is no perennial snow or ice compartment in the model, the effects of snow scavenging, which is approximately 5 times more effective than rain scavenging, are modelled if the atmospheric temperature falls below 0 °C (Wania et al., 1998).

2.6. *Case study α-hexachlorocyclohexane*

2.6.1. *Chemical properties*

Technical HCH has been used worldwide as an insecticide for agricultural and non-agricultural applications. The primary agricultural uses of technical HCH include application for the control of a wide array of insect crop pests, for seed protection and for poultry and livestock treatment. Non-agricultural uses include rodent bait, termite control in wood structures and in malaria-control operations in India (Wania et al., 1999; Li, 1999a). Technical HCH is composed of a group of 5 to 8 isomers, including α- (55–80%), β- (5–14%), γ- (8–15%), δ- (2–16%), ϵ- (3–5%) (Metcalf, 1955). α-HCH, the dominant isomer in the mixture is of interest for use in this study as it has been found in detectable concentrations worldwide (Wania and Mackay, 1999; Li, 1999a). In this study, the proportion of α-HCH in technical HCH emissions and monitoring data has been defined as 67.5%.

Properties of α-hexachlorocyclohexane (α-HCH) employed are those from Mackay et al., 1992. These include intermedia partitioning information and reaction half-lives (Table 4).

2.6.2. *Emission estimates*

Developing comprehensive estimates of chemical emissions to the global environment is an important and challenging problem. Several agencies, such as the Canadian Global Emissions Interpretation Centre (CGEIC) and the UNEP Pollutant Release and Transfer Registers (PRTR), assess current and historical emission patterns on a global scale. The dynamic simulation of the transport of α-HCH requires that a function be devised that describes changes in emission rates over time and space. To achieve a reasonable estimate of these changes, data from several sources were utilized (Wania et al.,1999; Li, 1999a, Li, 1999b, Li et al., 2000). Wania et al. (1999) summarized historical global α-HCH emissions within the climatic zones defined within their 1-dimensional global distribution model. They estimated that a total of 6.8×10^9 kilograms of α-HCH has been used between 1948 and 1997, with peak usage occurring during the mid to late 1970s. Table 5 summarizes and compares modelled and reported usages

Table 4
Physico-chemical properties of α-hexachlorocyclohexane at 25 °C

Molar mass	290.85
Melting point (c)	157
Aqueous solubility (g/m^3)	1
Vapor pressure (pa)	0.003
Log k_{ow}	3.81
Vegetation reaction half-life (h)	1420
Fresh water reaction half-life (h)	3360
Coastal/oceanicwater reaction half-life (h)	3360
Soil reaction half-life (h)	1690
Sediment reaction half-life (h)	55 000
Enthalpy of vaporization (from water to air) (K/mol)	55 000
Enthalpy of solution (from octanol to water) (j/mol)	−20 000
Degradation rate constant by oh radicals (m^3/molecules h)	4.9×10^{-15}[a]
Activation energy of deg. by OH radicals (J/mol)	8314[a]
Activation energy for vegetation (J/mol)	30 000[b]
Activation energy for freshwater (J/mol)	30 000[b]
Activation energy for coastal/oceanicwater (J/mol)	30 000[b]
Activation energy for soil (J/mol)	30 000[b]
Activation energy for freshwater sediment (J/mol)	30 000[b]

[a] Wania et al. (1999).

[b] Breivik and Wania (2002).

Table 5
Distribution of global usage of α-HCH by BETR-World model regions as defined by Li (1999a), this work and Wania et al. (1999)[a]

Wania et al. (1999) Region names	Region	Li (1999a) summarized by usage density			Dynamic total			Wania et al. 1999 (%)
		kg	%	Σ	kg	%	Σ	Σ
North Boreal	2	2.23×10^{6}	<0.1	*6.6*	4.25×10^{7}	0.7	*6.7*	*3.2*
	9	4.28×10^{8}	6.6		3.82×10^{8}	6.0		
North Temperate	3	1.67×10^{8}	2.6	*66.8*	1.67×10^{8}	2.6	*65.7*	*49.4*
	7	8.26×10^{8}	12.6		5.01×10^{8}	7.9		
	10	3.37×10^{9}	51.6		3.51×10^{9}	55.2		
North Sub-Tropical	4	1.45×10^{8}	2.2	*14.4*	3.59×10^{8}	5.7	*14.2*	*28.3*
	8	7.97×10^{8}	12.2		5.39×10^{8}	8.5		
North Tropical	12	3.62×10^{8}	5.5	*5.6*	6.48×10^{8}	10.2	*10.7*	*16.5*
	19	1.69×10^{6}	<0.1		3.41×10^{7}	0.5		
South Sub-Tropical, Tropical	5	2.93×10^{8}	4.5	*6.7*	1.57×10^{8}	2.5	*2.8*	*2.6*
	6	1.18×10^{8}	1.8		8.74×10^{6}	0.1		
	11	4.87×10^{6}	0.1		4.37×10^{6}	0.1		
	13	1.97×10^{7}	0.3		4.37×10^{6}	0.1		
	Total	6.53×10^{9}			6.35×10^{9}			

[a] Regions not listed have zero usage.

by Li (1999a) and the BETR model parameterization and results.

As these regions are both politically and climatically based, the compilation of peak and total usage data by country, as varying temporally by climatic zone will provide the best estimate of spatial and temporal variability of emissions for the dynamic simulation of the fate of α-HCH. For input into BETR-World, the assumption is that 5% of the emission occurs to the lower air compartment, 92.5% of the emission occurs to the soil compartment, and 2.5% of the emission is to the freshwater compartment. These assumptions are based on a typical agricultural application of technical HCH (Wania and Mackay, 1999).

By assigning the BETR-Regions into the Wania and Mackay (1999) climatic zones (Table 5) it is possible to compare the emission curves for the total emission of the regions classified into the five climatic zone classifications by which emissions were modelled. The curve for the North Temperate climatic band shows that this zone experienced the highest overall usage, in magnitude and duration of usage. Regions in the North Sub-Tropical zone experience peak usage in the early 1980s where regions in the North Tropical zone experienced a slower rise to peak usage in the late 1970s extending until about 1985. The North Boreal regions show a consistent, but low level of usage between the mid 1960s and mid 1970s. The Southern Hemispheric regions experienced peak usage in the 1980s and contribute a relatively minor emission of α-HCH to the global environment.

The total global cumulative emission estimate used in this study is approximately 6.35×10^{9} kg or 6%, less than the Wania et al. (1999) and Li (1999a) figure of 6.8×10^{9} kg. This underestimation is attributed to methods applied in the parameterization of the emissions scenarios, however, as seen in Table 5, the proportion of chemical emitted in each region is generally consistent with the literature (Fig. 3).

2.7. *Steady state and dynamic simulations*

The approach taken here is first to describe the results obtained by running the model in dynamic mode from an initial date of 1947 to 1997 using the yearly emission data. We compare the estimated concentrations with monitoring data and with results from the Wania–Mackay model (1999), which also simulates of global fate of contaminants. Exact comparison between these two models is not possible because the segmentation is different, however it is possible to compare the global-scale summary mass balance as presented by Wania and Mackay (1999) and as reproduced using the BETR-World model.

Second, we examine steady state results. The reason for this is that dynamic results can be difficult to interpret because of the simultaneous changes in concentrations and emissions with time. We suggest that more insight into the broad features of chemical fate can be obtained by examining a set of steady-state results. This shows more clearly the processes which are of greatest significance and allows us to focus on the specific issue of transport to the Arctic. Steady-state model calculations are used to examine, in more detail, the source regions which have the greatest potential to contaminate the Arctic.

Third, we devise a method of characterizing the potential for transport from source to sensitive receptor regions using a "Transfer Efficiency". Finally, a preliminary sensitivity analysis is described.

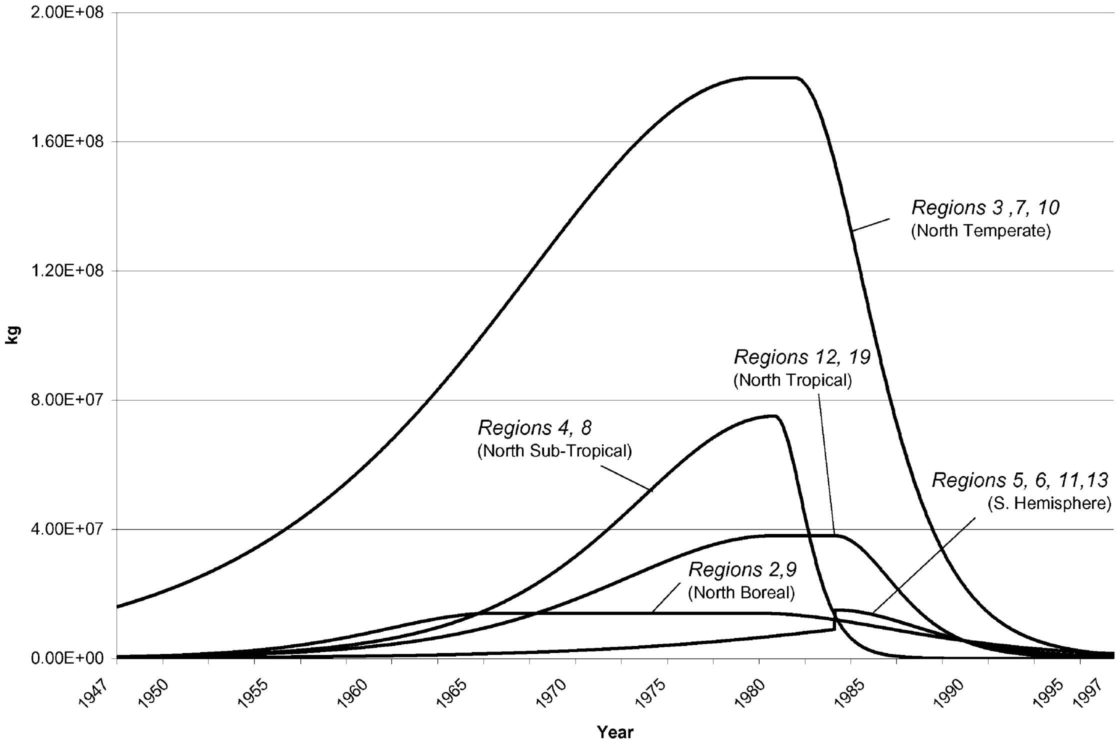


Fig. 3. Total global emissions of α-HCH modelled by the BETR-World model by climatic band.

3. Results

3.1. Predicted environmental concentrations

The model provides information such as compartmental fugacity, Z-value, inventory and concentration at time intervals specified by the user. Perhaps the most useful information with respect to risk assessment and policy development are predicted environmental concentrations. Spatial representations of resulting concentrations in air (ng/m^3) and in coastal/oceanic and freshwater (ng/l) in 1980 (a time of high levels of usage and contamination) are illustrated in Fig. 4a and 4b.

Fig. 4a shows estimates of α-HCH concentration in the lower air compartments of the model. Concentrations over much of the earth are low, between 0 and 1 ng/m^3. Higher, though still classified as "low" (Li, 1999) concentrations (1–10 ng/m^3) of lower air compartments over continental regions of Central America, Northern Africa, Europe and Southern regions of Asia reflect the spatial pattern of emissions, with higher air contamination over areas with very high emissions. It is noteworthy to mention that all model regions experience some level of atmospheric contamination.

Fig. 4b illustrates the spatial pattern of contamination in fresh and coastal/oceanic waters. The shading of terrestrial regions represents the level of contamination of only the surface water fraction of those regions and the shading of primarily coastal/oceanic regions are representative of levels in that medium. The extreme levels ($>$1000 ng/l) predicted in the Islands of the Asian-North Pacific are likely an artifact of the small volume of freshwater which receives input from the relatively large volume of soil (see Table 1) and the lack of significant runoff to coastal waters. Very high levels (100–1000 ng/l) in freshwater systems in Europe reflect the relatively high emission rates experienced in this region leading up to and during 1980. An important finding is that there is a detectable level of α-HCH in Arctic freshwater systems (Canadian Arctic Archipelago and Greenland), indicating that atmospheric transfer to soils and freshwater ecosystems is being captured by the model. Predicted concentrations in coastal water in the Region2—Canadian provinces is in the 1–10 ng/l range, while freshwater in this and in central South American regions have "low" levels of contamination (0–1 ng/l). Measured concentrations in freshwater systems for this time period in the Canadian Provinces region range from 0.25 ng/l in the Attawapiskat River in Ontario (Lockhart et al., 1992) to 1250 ng/l in the Great Lakes region (Hoff et al., 1996). Large volumes of freshwater and relatively low emission rates likely contribute to the lower prediction by the model. Both of these regions have the highest ratio of surface water to surface area (Canadian Provinces, 8%, Central South America, 2.5%), for their respective hemispheres.

An extensive database consisting of reported concentrations of α- and technical HCH in air, freshwater, coastal/oceanic water, soils and sediments has been compiled. The dynamic solution yields results that are consistent with measured environmental concentrations in northern regions such as the Arctic (Region 22), North American Continental Arctic (Region 1) and Europe (Region 7) (Fig. 5). Measured environmental concentrations are after those reported in AMAP (1998); Bidleman et al. (1990); Gaul (1989); Halsall et al. (1998); Hargrave et al. (1997); Hinckley et al. (1991); Holubeck et al. (2001); Iwata et al. (1993); Li (1999a); Salomons et al. (1988); Wania et al. (1999).

As illustrated by Fig. 5, the average annual predicted concentration in coastal/oceanic water of the three northern regions is in general agreement with values as reproduced from measurements in those regions. The predicted concentrations in lower air and coastal compartments of Region 1—Continental Arctic are in line

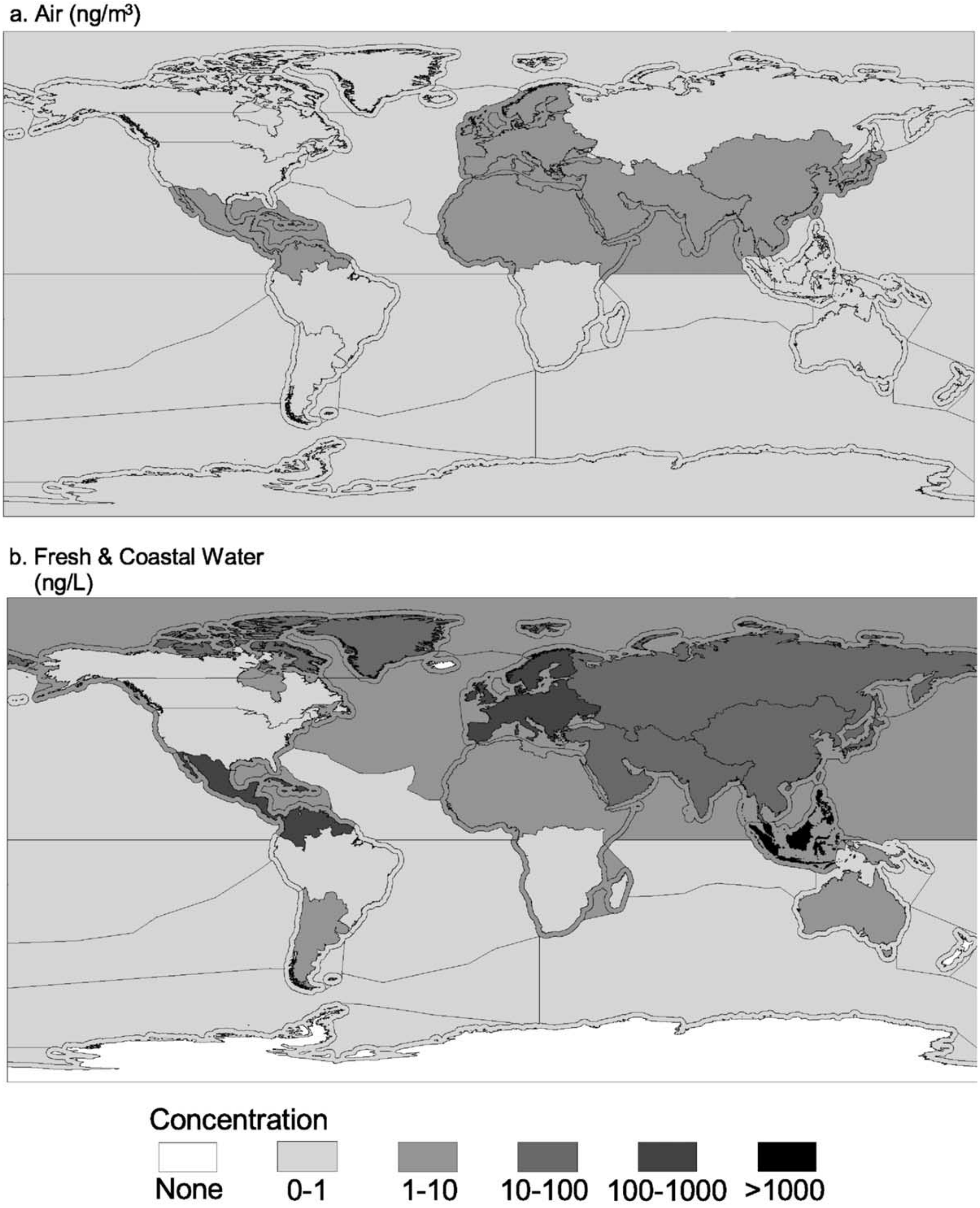
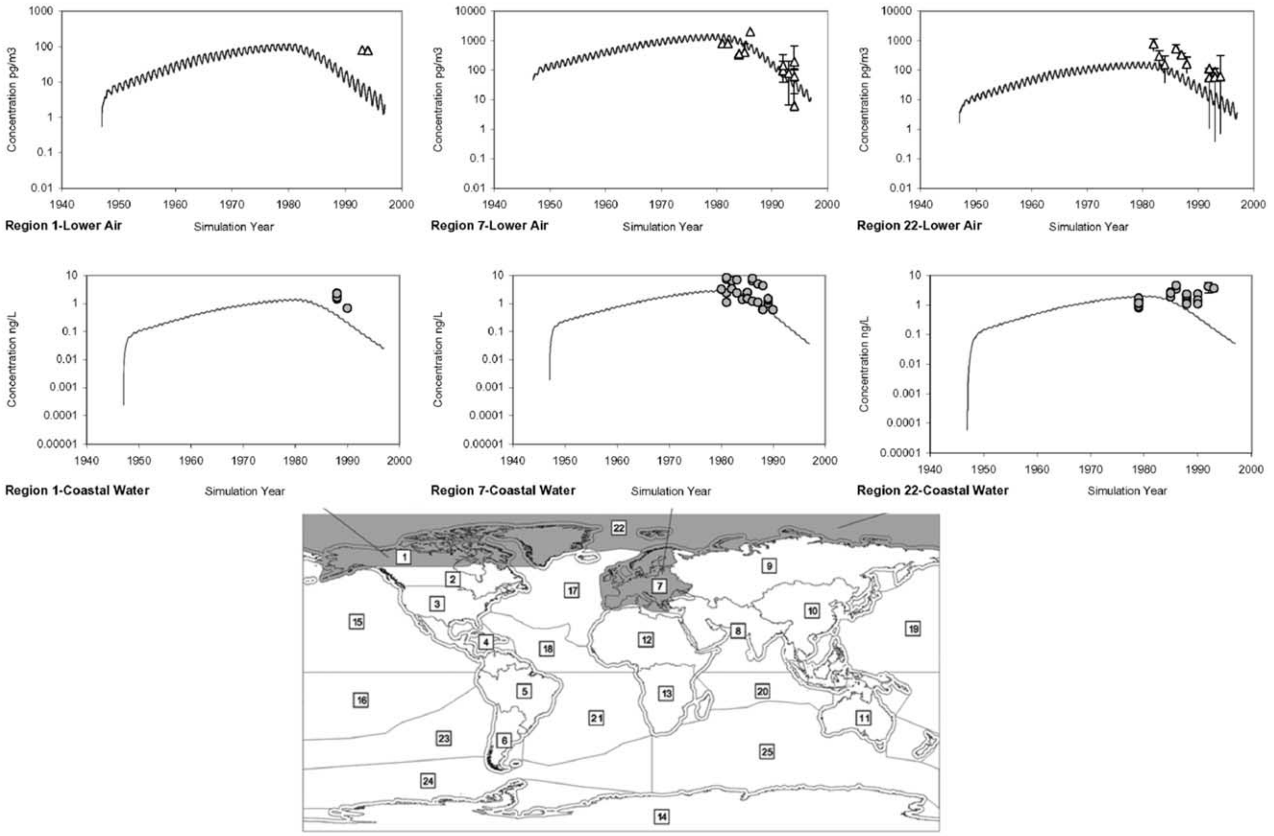


Fig. 4. Predicted concentrations in 1980 of α-hexachlorocyclohexane in a. lower air and b. fresh and coastal/oceanic water compartments using the BETR-World Model.


Region 1-Lower Air

Region 7-Lower Air

Region 22-Lower Air

Region 1-Coastal Water

Region 7-Coastal Water

Region 22-Coastal Water

Fig. 5. Average annual predicted vs. measured concentrations in air, freshwater and coastal/oceanic water compartments in the Canadian Arctic (Region 1), Europe (Region 7) and the Arctic (Region 22).

with the few measured locations, however no conclusion about trends may be drawn in this region yet. In Region 7—Europe, the model captures trends in the measured concentrations in air and coastal waters in the 1980s through the mid-1990s. The measured data in Region 22 show a decreasing trend in atmospheric concentrations and a time lag of about 5 to 10 years in the wide range of peak concentrations and decline in coastal/oceanic water concentrations. The atmospheric trends are described by the model in these regions, however, the lag in decline of coastal/oceanic water concentrations in the Arctic has not been adequately captured by the model. This discrepancy is likely due to an overestimation of degradation rates in coastal/oceanic water, thus the predicted concentration in the modelled environment responds more quickly to changes in emissions than those in the actual environment.

3.2. Comparison with Wania and Mackay Model

The dynamic version of the model was run using the Li (1999a) emission data that had been reparameterized for the 25 model regions (as described above). These estimates are lower (approximately 6%) than those used by Wania and Mackay (1999), however the proportions emitted to each climatic zone are consistent (Table 5). The discrepancy likely arises from the underestimation of peak emissions in the various regions. However, because the model calculations are linear (Mackay, 2001), the results may be examined proportionally.

The results of the BETR-World model show that more than 99% of the total emissions have been degraded or permanently removed to deep ocean, soil or freshwater sediments. This is consistent with the Wania and Mackay results (1999). Fig. 6a and b show a direct comparison between the two models by evaluating global summaries of each of the models. The figures show the proportion of the total emission of α-HCH (as a percentage) as inventory in 1997 and as total transported in and between each of the 5 compartments over the full modeled time period. For this analysis, the vegetation compartment in the BETR-World model has been included with the soil compartment, and transfers and storage in these two compartments have been combined.

Preliminary analysis reveals that the models are generally consistent. However, there appears to be less volatilization to atmospheric from freshwater compartments, and more with the coastal/oceanic compartments in the BETR-model than in the Wania and Mackay model. The media temperatures are generally consistent between the models, however the BETR-World model uses only one varying temperature for all media in each region, where the Wania and Mackay model allows temperature to vary across media within each zone.

The half-lives of chemical in each compartment were modified with temperature (and OH^- radical concentration in the atmosphere) in both models. Table 6 compares the range in half-lives in various media for Temperate, Subtropical and all regions.

The atmospheric reaction half-lives reported by Wania et al. (1999) are similar to those used by the BETR-World model. In coastal/oceanic water and ter-

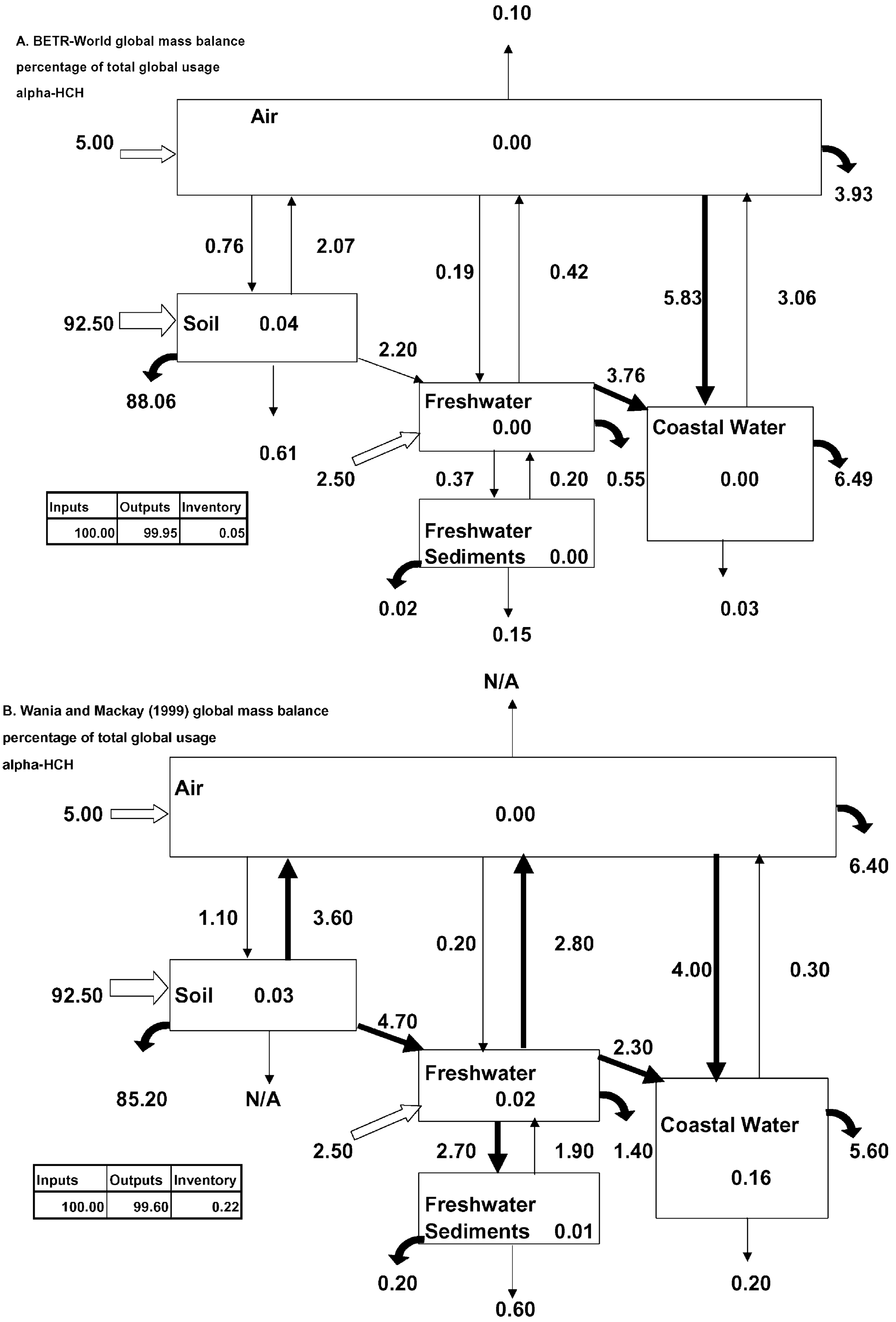


Fig. 6. Regionally averaged global mass balance in units of percentage of total global emission of α-HCH from 1947 to 1997 from a: the BETR-World model and b: Wania and Mackay (1999).

Table 6
Comparison of modelled reaction half-lives (days) in two latitudinal bands and overall with reported values from Wania et al. (1999)

Latitude	Air		Freshwater		Coastal water		Soil		FW Sediment	
	Modeled	*Wania*	Modeled	*Wania*	Modeled	*Wania*	Modeled	*Wania*	Modeled	*Wania*
Temperate	1–36	*17.6*	143–213		143–213		72–107		2238–3486	*Values*
Subtropical	1–6	*6.6*	136–168		136–168		72–84		2214–2743	*not*
Overall	1–60		134–326	*900*	134–326	*120*	67–164	*90*	2192–5335	*reported*

restrial media, where database half-lives were modified by only temperature, the values are also in fair agreement with Wania et al. (1999). As sea and freshwater are treated similarily in the BETR-World model, the ranges in reaction half-lives are the same in these two media, however, the reaction half-life in freshwater is shorter than suggested by Wania et al. (1999). As the global volume of freshwater is small, and at this scale advection plays more significantly as a loss process from the freshwater compartment, it is not considered to be a major deviation from previously modelled results.

3.3. Steady state scenario

The BETR-World model was used to estimate the steady state fate of α-HCH using emission estimates from 1980, obtained from Li (1999a). The region with the highest usage and therefore emission, of α-HCH is region 8, the Middle East Indian Subcontinent Region. This region is responsible for almost half of the total global emission of α-HCH. In contrast, because the use of HCH had stopped in Canada and the USA by 1980, there are no emissions from these regions. The model assumes constant emissions, at these levels, so that inputs equal outputs and transfers within and between regions are constant and balanced.

Mass balance diagrams were compiled to show the inputs and outputs of α-HCH in any region. The results for Region 22-Arctic are shown in Fig. 7. At steady state, the majority (52.8% or 2.1×10^6 kg/y) of the α-HCH reaches the Arctic via inflows of air; meanwhile a significant proportion (46.6%) reaches the Arctic ecosystem through coastal/oceanic water inflows. Table 7 shows the breakdown of transport of chemical to the

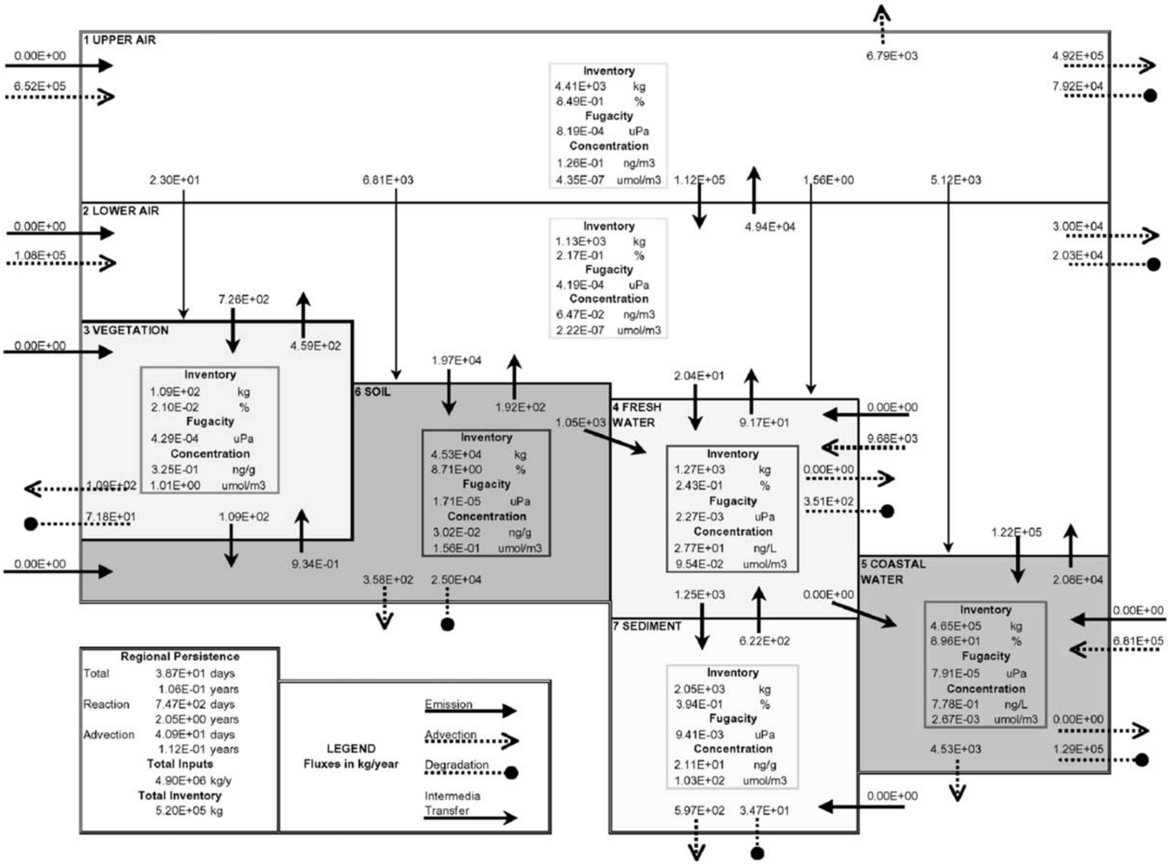


Fig. 7. Mass balance diagram of steady state transfer of α-HCH to Region 22-Arctic.

Table 7
Breakdown of vectors (by percent total transfer to the region) for transport into the Arctic region from adjacent regions at steady state

Adjacent Region	Upper air	Lower air	Fresh–Coastal	Coastal–Oceanic
1 NA—Continental Arctic	3.7%	0.2%	0.0%	0.0%
2 NA—Canadian Provinces	0.8%	0.1%	0.0%	2.8%
7 EU—Europe	11.9%	1.8%	0.0%	23.2%
9 AS—Russia	28.7%	5.3%	0.7%	2.9%
17 North North Atlantic	0.2%	0.1%	0.0%	17.7%
Total	45.2%	7.5%	0.7%	46.6%

Arctic region by adjacent region and by vector. By examining such steady state results the likely major sources and sinks of a contaminant can be determined.

Of the dominant atmospheric transfers, the majority (34.0% of the total influx) comes from Region 9-AS Russia. This indicates the high potential for this chemical to be transported from distant regions through the upper air layer. Further analysis utilizing the steady state scenario follows for the investigation of the potential for transport of a chemical from adjacent and non-adjacent regions to the Arctic region.

4. Transport to the Arctic

A valuable feature of the model is its ability to estimate what we refer to as the "Transfer Efficiency" for each region to a receptor region. This "Transfer Efficiency" is similar to Wania's (2003) Arctic Contamination Potential (ACP) calculated for a series of hypothetical chemicals where the fraction of the total amount present globally that is found in the Arctic surface media after a 1-year release is assessed at 1 and 10 years following the start of the release. The emission of chemical for the determination of its ACP is dependent on global population distributions and time. The "Transfer Efficiency" used here is deduced by emitting a standard and arbitrary amount of chemical systematically into each single region, in turn (MacLeod et al., 2002). The model is then run to steady state for each of the 25 emissions scenarios (one scenario per region) to compile a Transfer Matrix that estimates the percentage of the emission (for a given region) that reaches a receptor region of interest (such as the Arctic Region). This type of analysis was performed using a 100 kg/year release of α-HCH into the lower air compartment with Region 22-Arctic as the receptor. These transfer data express the "ease" with which a quantity of chemical emitted into one region of the globe reaches another region. The data are, of course, chemical specific. To obtain an estimate of the actual quantities reaching the Arctic it is necessary to multiply the percentages with the quantity used or emitted (kg) at a single point in time, or over a length of time.

The Transfer Efficiencies calculated for α-HCH (Fig. 8b) show a distinct latitudinal gradient. Intuitively, the greater number of "steps" the chemical must take through regions, the less likely it will reach the receptor region. These results suggest that chemical used in Region 17-North North Atlantic is the most likely to reach the Arctic Region (Transfer Efficiency of 18.5%), however it is unlikely that significant amounts of chemical will be applied to this primarily oceanic region. Region 10-AS Orient has an overall Transfer Efficiency of only 3.4%, however, when applied to the total global usage scenario (Fig. 8a), because of high usage in this region, it contributes to about 30% of the total estimated load to the Arctic Region. By combining the three highest ranked contributors (Region 7-Europe, Region 9-Russia and Region 10-Orient), over 66% of the total historical loadings to the Arctic can be explained. The combination of the usage and efficiency of transport controls contaminant input to receptor regions such as the Arctic. Fig. 8a–c displays the relative importance of overall Transfer Efficiencies and proportion of total historical global emissions to contribution of loading of α-HCH to the Arctic Region.

A comparison of the total "historical" loadings of α-HCH with the contribution of one specific, high emission year can be made. The total global emission of chemical is defined as M (kg) each total regional emission is then M_i (kg).

$$M = \sum_{i=1}^{25} M_i \tag{4}$$

First, we apply the calculated Transfer Matrix to the total amount of α-HCH emitted in each region (M_i) over the 50 year dynamic scenario. If we total these values for all regions, we can obtain the total amount of chemical transferred from all regions to the Arctic. This becomes the denominator by which the proportion of contribution to contamination of the Arctic Region by any region, at any time can be determined. The annual regional contribution to contamination of a source region to a receptor region is defined here as Ω_{it}, where the sum of all Ω_{it} is equal to 100%. Ω_{it} is calculated:

$$\Omega_{it} = \frac{TE_i \bullet M_i \bullet \alpha_{it}}{\sum_{i=1}^{25}(TE_i \bullet M_i)} \tag{5}$$

where, TE_i is the Transfer Efficiency for region i, M_i is the total emission to region i, α_{it} is the proportion of chemical emitted in year t in region i, and $\Sigma\alpha_{it}$ is 100% in *each* region. Using this method, we can trace back the relative annual contribution of each region with respect to the total contamination of the Arctic ecosystem.

If we use the 1980 emissions scenario, as defined by Li (1999), when there were no emissions in Canada and the United States and very large emissions in Regions 8

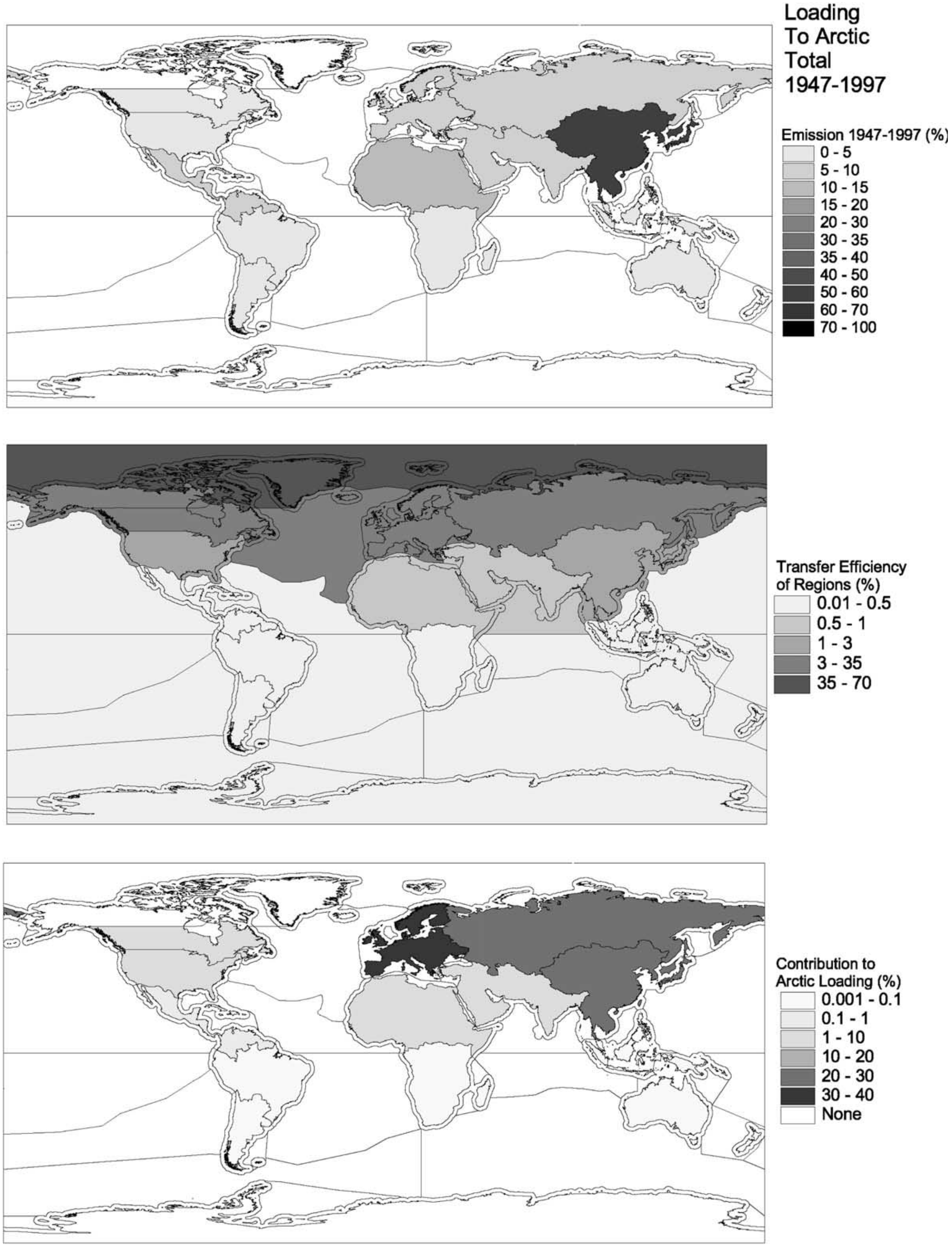


Fig. 8. Potential contribution for transport of α-HCH to the Arctic; a. total historical proportion of usage by region (1947–1997); b. calculated transfer efficiencies; c. contribution to loading of chemical to the Arctic region.

(India) and 7 (Europe), we see that the contribution to total Arctic contamination of this one year is approximately 0.82%. In this year alone, Region 7-Europe contributes approximately 0.61% to the total Arctic burden.

Table 8 identifies Regions 7, 8 and 10 as having a higher than expected role in the contamination of the Arctic (equal emissions over all regions would contribute 0.08% per region per year for 25 regions over 50 years). Utilizing the model in this manner not only allows for the interpretation of transport potential of chemical from specific regions to identified regions of concern, it relieves much of the computational time and detailed emission data requirements necessary in dynamic modelling exercises.

4.1. Sensitivity analysis

The sensitivity of the concentration of α-HCH in the lower air and coastal/oceanic compartments in the Arctic region (Region 22) was addressed. Changes in over 5000 input parameters were made and the effects of each change on the 2 output parameters were monitored. The input parameters can be classified into four types of parameters; *chemical* (such as reaction half-lives, molar mass, K_{ow}), *environmental* (such as environmental temperatures, surface areas, mass transfer coefficients between media), *flow rates* describing advection between compartments in the atmospheric, freshwater and coastal/oceanic compartments and *emission* parameters for each region.

The concentration of α-HCH in Arctic coastal/oceanic water is most sensitive to the coastal/oceanic water reaction half-life and other chemical properties such as reaction activation energy (J/mol) for coastal/oceanic water reaction and property temperature. Reaction half-lives are inherently uncertain and often are only classified into wide ranges. The sensitivity of the model to these inputs may account for the failure to capture the lag in peak concentration in Arctic coastal/oceanic waters. The sensitivity of the model to coastal/oceanic water reaction rates, draws attention to the need to parameterize factors affecting these rates with care.

Lower air concentrations in these three regions are also considerably affected by changes in the hydroxyl radical rate constant. These concentrations are also affected by exchange processes with coastal/oceanic water, and factors such as interfacial area between lower air and coastal water compartment. These exchange processes are more important than flow rates in and out of the lower air compartments are deemed important to parameterize carefully. These parameters are important features affecting environmental (non-chemical specific) potential for long-range transport.

Finally, the magnitude and location of emissions are shown to be important parameters in determining the modelled results. Changes to emissions to bulk lower air in regions 7-Europe, 8-Middle East and Indian Subcontinent and 10-Orient all affect the concentration in Arctic lower air and coastal/oceanic water. As the BETR-World model regions generalize large regions to simplify and accommodate the modelling process, the "homogeneity" criteria of fugacity modelling is met only very loosely. Sensitivity analysis of the model allows us to identify parameters that are important in determining the reliability of the output. This preliminary analysis reveals that data on reaction rate constants, and their temperature dependence are crucial for better understanding long-range transport globally and especially to the Arctic.

5. Conclusions

The BETR-World model has been successfully developed and applied to the global fate of α-hexachlorocyclohexane. It is consistent with both measured concentrations in northern regions and with other modelled results (Wania and Mackay, 1999). This consistency extends to the determination of significant source-to-sink pathways and processes in the long-range transport of chemical to Arctic regions. Higher fidelity of the model to the real environment could be achieved by including snow cover as a storage compartment. Revisiting the hydroxyl radical concentration parameterization and temperature dependencies for environmental reaction rates will also improve model performance. Although the model contains many simplifying assumptions, each increase in the complexity of the model is accompanied by a corresponding increase

Table 8
Contribution to total loading in the Arctic using the Transfer Matrix approach

Region (i)	Transfer efficiency (TE_i)	Total emission, kg (M_i)	Proportion of emission in 1980 ($\alpha_{i,1980}$)	% Contribution to loading ($\Omega_{i,1980}$)
7	10.68	5.01×10^8	1.59	0.61
8	0.75	5.39×10^8	3.49	0.10
9	7.91	3.82×10^8	0.04	0.01
10	1.15	3.51×10^9	0.32	0.09
12	0.84	6.48×10^8	0.27	0.01
Total		5.58×10^9		0.82

in the number of input parameters and descriptive equations. Sensitivity analysis becomes more difficult or even impossible. As indicated by the results presented here for α-HCH in different environmental compartments and in various regions of the globe, the model maintains a relatively simple structure that allows dominant global-scale fate processes to be identified. In our view there is merit in having models at a variety of levels of complexity available to describe the complex interactions between chemicals and the environment. Interpretation of the results of different models will provide insight into the fate and transport processes determining behaviour of environmental contaminants, and provide a framework for interpretation of results from more complex models as they are developed. It is our hope that this successful application of the BETR-World model to the well studied chemical, α-HCH lends credibility to its use for other chemicals and other source-receptor situations.

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