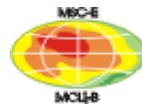


# Summary of Part C: POPs

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# HTAP 2010 Assessment Report

## Part C: Persistent Organic Pollutants

### *Chapter C1: Conceptual Overview*

**T.Harner**, P.Bartlett, R.Guardans, A.Gusev, H.Hung, Y.-F. Li, J. Ma, R.Macdonald, V.Shatalov

### *Chapter C2: Observations and Capabilities*

**H. Hung**, T.Bidleman, K.Breivik, C.Halsall, T.Harner, I.Holoubek, L.Jantunen, R.Kallenborn, G.Lammel, Y.-F. Li, J.Ma, S.Simonich, Y.Su, A.Sweetman, P.Weiss

### *C3. Emissions*

**J.Thepoke and Y.-F. Li**, K.Breivik, H. Denier van der Gon, J.Pacyna, D.Panasiuk, K.Sundseth, S.Tao, A. Sweetman

### *C4. Global and Regional Modeling*

**A.Gusev and M.MacLeod**, V.Shatalov, P.Bartlett, A.Hollander, S.Gong, G.Lammel, J.Ma, K.Breivik

### *C5. Impacts*

**J.Dawson**, K.Hageman, R. Letcher, A. Arif



## Chapter C1: Conceptual Overview

C1.1. Purpose of the HTAP 2010 assessment on POPs

C1.2. International policy on POPs

C1.3. Properties of POPs

C1.4. *Integrated approach for understanding POPs transport: Emissions, observations and models*

C1.5. Interactions between climate and POPs

C1.6. Findings and Recommendations

## Chapter C2: Observations and Capabilities

C2.1. Introduction

C2.2. *Atmospheric observation*

C2.3. Oceanic observation

C2.3. The function of air-surface interaction on LRT of POPs

C2.4. *Air-Surface Interaction, Degradation and Transformation*

C2.5. Chemical Tracers

C2.6. Effects of Climate Variations on LRT and Trends

C2.7. Assessing the Effectiveness of Control Measures – Observational Data and Quality Assurance

C2.8. Findings and Recommendations

## **C3. Emissions**

C3.1. Introduction

C3.2. Emission inventories

C3.3. Uncertainties and verification of emission inventories

C3.4. Emission projections

C3.5. Summary and recommendations

## **C4. Global and Regional Modeling (completed)**

C4.1. Introduction

C4.2. Modelling approaches for the evaluation of POP transport and fate

C4.3. Evaluation of POP long-range transport on global and regional scales

C4.4. HTAP model simulations of POP intercontinental transport

C4.5. Summary and recommendations

## **C5. Impacts (completed)**

C5.1. Overview of impacts of POPs

C5.2. Impact of POPs on ecosystems

C5.3. Impact of POPs on human health

C5.4. Monitoring in human media

C5.5. Implications of HTAP analysis

# **Responses to synthesis questions for POPs**

(as discussed at Chapel Hill Workshop)

Q1. Process Understanding ?

Q2. Source Attribution ?

Q3. Source-Receptor Relationships?

Q4. Future Emission Scenarios?

Q5. Future Climate Scenarios?

Q6. Research Needs?

# Responses to synthesis questions for POPs

## Q1. Process Understanding ?

Emissions (amount and location and residence) time ultimately determine the extent of intercontinental LRT.

- Wide range of pollutants with different physical and chemical properties & persistence.
- Physical and chemical atmospheric processes modify the dispersion on a wider scale:
  - Wind patterns (high level of understanding);
  - OH decay (high level of understanding);
  - Air-particle interaction (medium level of understanding);
  - Surface/air exchange (medium to low level of understanding);
  - Emission inventories (low level of understanding).

## Q2. Source Attribution ?

Varies strongly depending on properties of the substance -ranging from a minor fraction to complete dominance

- For a given substance, strong dependence on emission location and pattern
- Impacts vary strongly depending on toxicity
  - Most important for remote areas like polar regions and cold alpine areas – effects seen on, eg, polar bears, Inuits
  - Arctic ecosystem is particularly sensitive due to nature of food chain

### **Q3. Source-Receptor Relationships?**

### **Q4. Future Emission Scenarios?**

- Policy actions reducing emissions changes intercontinental flows, but the response in changing load and exposure to the environment and humans may be long due to component's persistence.
- Several examples of policy action exist: technical HCH, PCB, etc.

## Q5. Future Climate Scenarios?

- Climate change (temperature) will mainly influence emissions from POPs in products, stockpiles (primary volatilisation) and from POPs already in the environment (secondary volatilisation).
  - Could cause a reversal of direction of net flux –from sink to source. eg, remobilize inventories in glaciers & permafrost
- Other changes in environmental cycling and transport pathways may also occur.
- Alteration of food webs could change exposure levels & patterns.
- The role of extreme events in total transport could become more important.
- Net effect of climate change is not easy to quantify.

## Q6. Research Needs?

- Identify the policy drive
  - Clearly define what the policy relevant science questions are
- Resources to do the necessary analysis
- Integrated monitoring
  - Should include monitoring data in soils & oceans to support estimation of secondary emissions
- Better communication between scientists to ensure transferability of data
  - Emission inventories should/could be reported in a way that can be used directly in models
- Official emission estimates made in different countries should be harmonized and collected into a single inventory
  - Particular problem for dioxins (TEQ versus congeners)
  - Official emission inventories are not assembled with modeling in mind
- Coverage of monitoring networks (spatial and temporal) can be improved to allow better evaluation of models and emissions
  - Need for co-ordinated monitoring

# Summary of Part C (contribution to the Chapter 6)

## Key Findings and Recommendations from Chapters 1-5

Long-range transport as an exposure pathways

Observations

Emission inventories and projections

Modelling

New POPs

Climate change and emission scenarios

## Cross-Cutting Issues

Integrated approach

## Concluding Thoughts

# Q1. POP process understanding

**Meteorological processes**  
**Emissions**  
**POP phys-chem.properties**

**Atmosphere:** Gas/particles partitioning, advective transport, diffusion, degradation

**Exchange between media:** wet deposition (gas + particles), dry particulate deposition, gaseous depositions to the underlying surface (soil, seawater, vegetation), re-emission from the underlying surface

**Soil:**

Partitioning, transport with convective water fluxes, diffusion, bioturbation, degradation.

**Seawater:**

Partitioning, advective transport, diffusion, sedimentation, degradation.

**Vegetation:**

Defoliation, transport to soil, degradation.

# Main POP properties

(~ 1500 toxic substances)

- Henry's law coefficient (temperature-dependent)
- Pressure of subcooled liquid (temperature-dependent)
- Octanol/air partitioning coefficient (temperature-dependent)
- Octanol/water partitioning coefficient
- Degradation rate constants (for air, soil, water, vegetation)
- Molecular diffusion coefficients (in air and water)
- Molar volume
- Aerodynamic diameter of particles
- . . .

## Long-range transport as an exposure pathway

Taking into account the environmental persistence of POPs, long-range transport constitutes an important pathway for human exposure and ecosystem impacts. For many POPs the main route of human exposure is through food.

The extent of long range transport depends critically on the chemical and physical properties of the individual POP, some long-lived POPs are effectively transported on a global scale.

# Long-range transport as an exposure pathway

## *Findings*

The main processes governing intercontinental transport of POPs at relatively short time scales are atmospheric transport, gas-particle partitioning, degradation and deposition.

For POPs which have been cycling in the environment since decades the exchange of POPs between the atmosphere and different types of underlying surface, leading to the accumulation in environmental media and subsequent re-emission, and transport in ocean currents play an important role in determining levels in locations remote from sources.

# Long-range transport as an exposure pathway

## *Findings*

The Joint WHO/Convention TF on the Health Aspects of Air Pollution report (2003) highlighted several POPs that are of concern or are potentially of concern with respect to long-range transport, especially DDT, HCH, dioxins, and PCBs. The TF also stressed the need for a better understanding of the health effects and the long-range transport of other POPs.

The AMAP 2009 assessment of human health in the Arctic concluded that current human exposure to contaminants negatively influences human health. Since most of the POPs in the Arctic are the result of long-range transport, it can be concluded that most of the health effects from POPs in the Arctic are also due to long-range transport.

# Long-range transport as an exposure pathway

## *Findings*

Hexachlorobenzene (HCB) is one of the most stable POPs {EPA, 2002 #4838} and is readily transported globally. A number of potential effects due to low-level exposures to HCB have been identified {TFHealth, 2003 #4835; (AMAP), 2004 #4804}.

Heptachlor is a breakdown product and constituent of chlordane {TFHealth, 2003 #4835}. Long-range transport of both of these are thought to be mainly of concern for infants and those consuming Arctic country diets, {TFHealth, 2003 #4835; Van Oostdam, 2005 #4585}.

Brominated flame retardants, such as polybrominated diphenylethers (PBDEs) and perfluorinated compounds, such as PFOS and PFOA, have been detected in remote areas such as the Arctic.



# Long-range transport as an exposure pathway

## *Findings*

*Source-receptor relationships, source attributed*

Model simulations performed for the selected POPs showed that contribution of intercontinental transport to the pollution levels in the HTAP receptor regions can reach almost 30%.

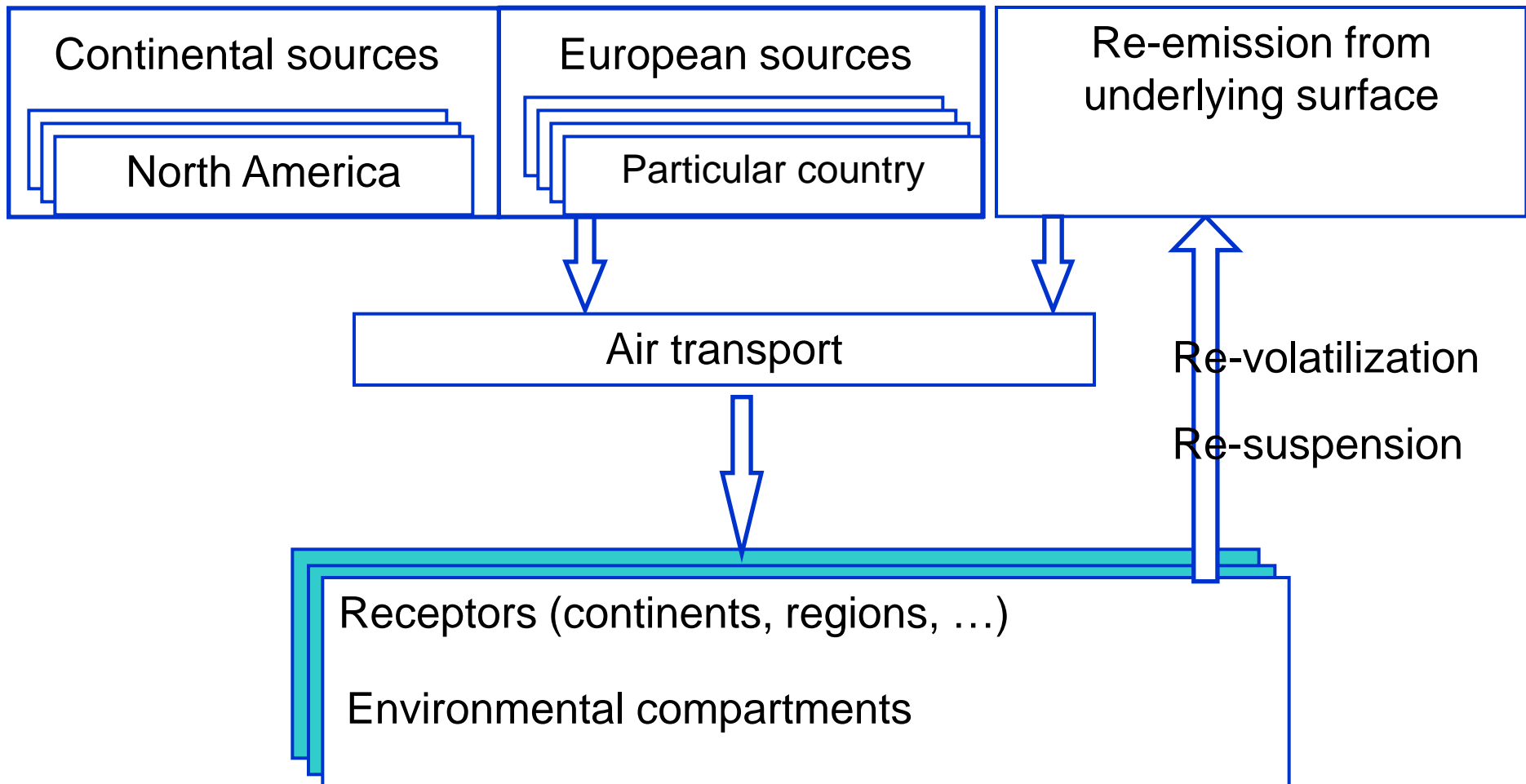
The TF HTAP model intercomparison designed to evaluate and quantify POP intercontinental transport showed concentrations and deposition to be sensitive to changes in POP emissions on the global scale. The contamination levels in the receptor regions are most sensitive to emission reductions in regions with high emission rates; thus, 20% emission reduction in Europe and North America (for PCBs) and in South Asia (for  $\alpha$ -HCH) had the greatest influence on receptor regions, including the Arctic.

# Long-range transport as an exposure pathway

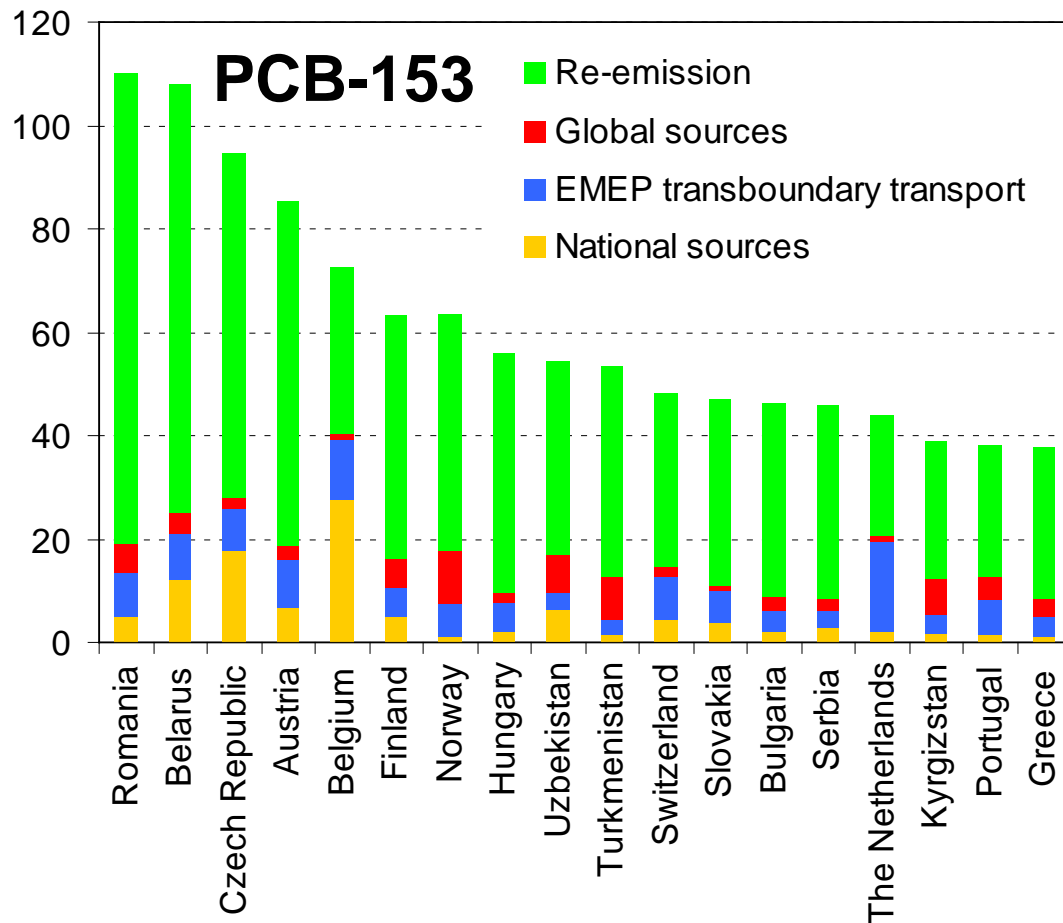
## *Findings*

Evaluation of the source-receptor relationships for POPs is more difficult than for other air pollutants, because of the significance of the secondary emission sources (re-emission, multi-hopping potential).

# Source-receptor calculation scheme



# Source-receptor calculation schemes (contribution to country depositions, 2008)



## Contributions to Europe

Global sources	20 - 30%
Re-emission	40 - 60%
National sources	20 - 40%

# Long-range transport as an exposure pathway

## *Recommendations*

Research by the appropriate national and international bodies into the health effects of legacy and emerging substances for which long-range transport results in significant exposures is needed.

It is a priority to continue to improve our understanding of the fate and transport of POPs through continued efforts in monitoring and process research, modeling, and emissions estimation on global scale.

POPs present global-scale risks that require the Task Force to consider broadening its geographical scope and membership to include regions outside of the UN-ECE.

# Monitoring

Monitoring and measurements have provided important information about the behaviour of POPs in the environment and their transport around the globe. Both intensive field studies and sustained monitoring have helped evaluate the transport and fate of POPs.

## *Findings*

Long-term air monitoring programs provide temporal trends with a time span of approximately 15 years which are important for the analysis of POP long-range transport and the effect of emission changes in different regions of the globe.

The spatial coverage and resolution of air monitoring have increased considerably due to the adoption of passive air sampling methods.

Other than air, there are limited measurements and no organized monitoring of POPs concentrations in other media, e.g. precipitation, dry deposition, ocean, snow, soil and vegetation.

# Monitoring

## *Recommendations*

**Observations of POPs** in air, deposition and other media **will continue** to be a basis for our understanding of prevalence of POPs. That understanding allows evaluation of models for risk assessment and of policy abatement measures.

**Sustained monitoring** of POPs, in media such as air, water, soil, and food, would give a more accurate depiction of the POPs to which humans and ecosystems are actually exposed. Similarly, long-term sustained monitoring in human media, such as blood and breast milk, is needed for an understanding of how POPs impact human health.

**Passive air sampling** programs should be sustained to ensure the ability to develop temporal trends and can be expanded to cover regions where measurements are currently not available.

**Integrated monitoring** of various media within the same vicinity is essential for understanding partitioning processes that influence transport and estimating flux for model validation and parameterization.



# Modelling

At present, there exist a set of POP fate models that describe the system of chemical and environment with widely varying levels of detail. Models are intensively applied within various international bodies (LRTAP Convention, the Stockholm Convention, OSPAR, HELCOM, AMAP, etc.) to support the negotiation process on the evaluation of pollution levels for legacy substances and for inclusion of new ones.

# Modelling

## *Findings*

Model performances based on the developed emission inventories provide consistent information on the pollution variations in space and time, and contributions of particular sources and source categories to the pollution levels.

Nesting approaches developed in a number of contemporary global models permit to link the assessment of pollution on global, regional, and local scales.

Models are useful for analysing future contamination based on the scenarios of future emissions under different regulatory strategies, and possible changes of climate.

# Modelling

## *Findings*

Evaluation of modeling results reveals reasonable agreement between available measurements and model predictions of POP concentrations in the atmosphere. Deviations between the modeled and observed concentrations for most of the studied POPs are typically within a factor of three to four.

Model parameterisation of POP distribution and behaviour in soil, snow and seawater is very uncertain. The same is true for biodegradation. Uncertainties in physical chemical properties (e.g. Henry's Law constants, vapour pressures, octanol-water and octanol-air partition coefficients) of some POP should be further studied.

# Process understanding

(based on monitoring and modelling chapters)

## *Recommendations*

Extend descriptions of soil-air partitioning, taking into account the quality of organic matter, various types of chemical interactions of the chemical substance with organic matter etc.

Apply micrometeorologically based experimental techniques to determine gas exchange fluxes for comparison to model estimates.

Develop techniques to provide better speciation of the “truly dissolved” and “truly gaseous” fractions of semivolatile organic compounds so more accurate gas exchange estimates can be made. Revisit the surface microlayer as an accumulation and exchange reservoir for POPs.

# Processes understanding

## *Recommendations*

Improve estimates of mass transfer coefficients to reduce the uncertainty in gas flux estimates.

Improve measurements and modeling of physical-chemical properties, especially for Henry's Law constants (HLCs). Work to eliminate or minimize experimental artefacts in their determination, expand the data base for HLCs as functions of temperature and salinity and measurements of HLCs for emerging chemicals of concern.

# Processes understanding

## *Recommendations*

In order to understand the impact of climate change on the inter-media exchange and long-range transport of chemicals, there is a need to improve estimates of temperature- and salinity-dependent physical chemical properties, especially for new and emerging chemicals for which such information is lacking.

Further work on the development and improvement of model parameterisation including gaseous exchange between the atmosphere and underlying surface, degradation in all the environmental media and model extension to include water surfaces with broken ice for applications in polar regions.

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# Primary and secondary emissions

Knowledge on primary and secondary sources of POP emissions to the environment are essential for policy activities to reduce the contamination of environment and to understand, quantify, and predict the source-receptor relationships

## *Findings*

For some of POPs (PCBs, HCHs, HCB, PAHs) there are global emission inventories elaborated for particular years or for the whole period of their application including also projections of future emissions. At the same time the development of global scale emission inventories is a challenging work and there are still essential spatial and temporal gaps in information on emission sources.

# Primary and secondary emissions

## *Findings*

POP emission inventories quantify primary emissions only. The emitted POPs tend to accumulate in environmental reservoirs, such as soil and water bodies, and re-emit to the atmosphere forming the secondary emissions, which in future may supersede eventually the primary emissions.

Evaluation of the re-emission can be subject of essential uncertainties as it depends on the historical emissions and requires simulations of long time periods.

# Primary and secondary emissions

## *Recommendations*

Although global primary emission inventories for some of the POPs are available at present, further work on elaboration of emission inventories for other POPs and reducing uncertainties of available inventories is highly appreciated.

Dynamic models, which include both description of relevant air-surface exchange processes and reflecting the life-time of POPs in the environment, need to be applied to estimate secondary emissions contribution.

# Primary and secondary emissions

## *Recommendations*

Characterize technical products of POPs pesticides (e.g., HCH, chlordane, heptachlor, DDT, dicofol, toxaphene) as starting points for understanding emission sources.

Development of emission inventories for POPs requires strengthening of cooperation between different scientific communities as within the TF HTAP and between different conventions.

## Emerging substances, screening

Environmental observations, process-oriented field and lab research and modelling all play important roles in this screening process of new substances.

### *Findings*

Both mass balance models and multicompartment chemistry transport models can be used to support the evaluation of environmental risk associated with new substances. These models evaluate LRTP and environmental persistence of chemicals taking into account main environmental processes such as media exchange and degradation (multimedia approach).

Comparison of ranking of chemicals with respect to their LRTP and persistence in the environment obtained by different models showed reasonable agreement between their predictions.

# Emerging substances, screening

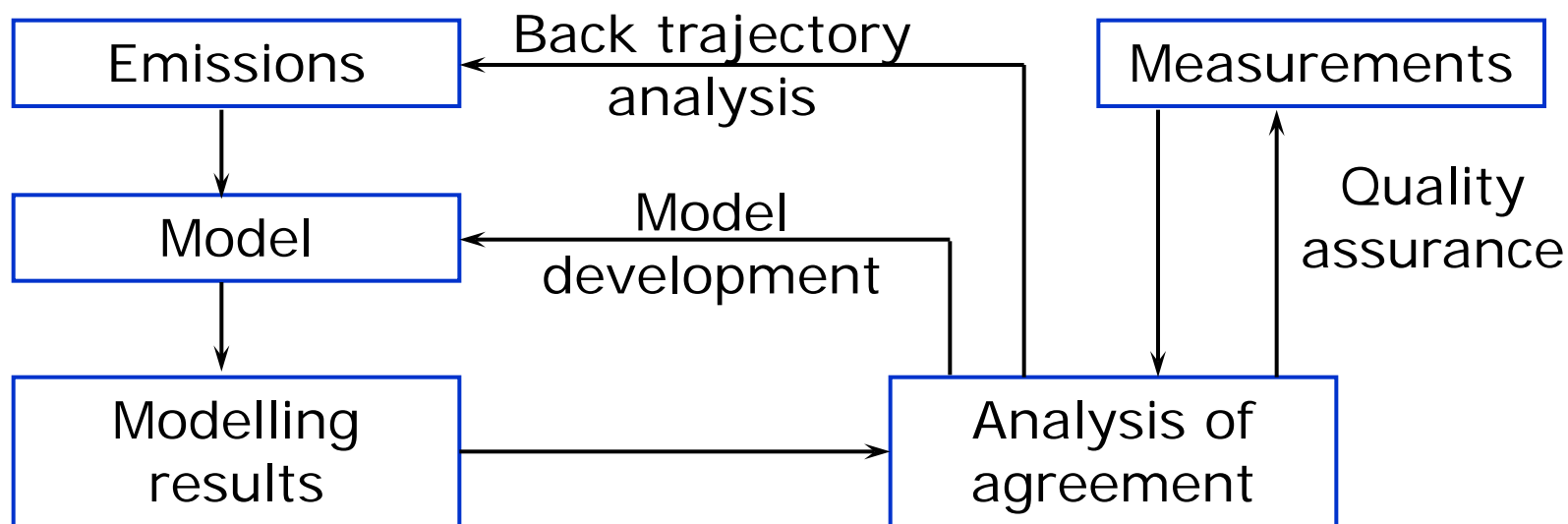
## *Recommendations*

There is a need to conduct process-research and adapt measurement and analytical techniques to target 'new' POPs. Transport models will need to be parameterized for these chemicals and new emission inventories developed.

There is also a need to continue screening efforts (based on monitoring/modelling activities) and research to identify new chemicals with POP-like characteristics for further consideration (PBDE, PFOS, PCP, SCCP ...).

# Integrated approach

An integrated approach to better understand long-range transport and fate of POPs in the environment is based on integrated use and analysis of monitoring, emission, and modelling data for evaluation of POP contamination.



# Integrated approach

## *Findings*

This assessment and several other assessments have demonstrated that an integrated approach can successfully be applied on POPs even if the coverage of emission data, observations and model processes is incomplete.

Observations jointly with multi-compartment models allow assessment of global source strengths for POPs for which inventories are incomplete or erroneous. The complexity of POPs environmental exposure routes to humans and ecosystem requires additional key information in all media.

# Integrated approach

## *Recommendations*

TF HTAP should continue to move in this direction and promote collaboration among these groups of experts and related programs.

Initial steps of this integration include giving attention to the analysis of agreement between spatial and temporal variations of modelled and observed data.

Results of the analysis can characterize the representativeness of the monitoring sites, indicate model errors and the necessity to improve model parameterizations or understanding of processes governing POP fate, and gaps in emission information with respect to its spatial distribution and completeness of coverage of source categories.

# Integrated approach

## *Recommendations*

Further stages of integration can be devoted to the reduction of identified uncertainties.

Additional monitoring experiments and field campaigns can be organised to improve understanding of processes and subsequently to refine models parameterization. Completeness and uncertainties of available emissions should be analyzed and emission scenarios should be elaborated.

# Integrated approach

## *Recommendations*

The occurrence and quantities of POPs in various environmental compartments is not only determined by current levels of emission but also by historical loadings that have accumulated in environmental media and the ability of these chemicals to cycle between compartments and be redistributed.

The development of emission inventories requires the use of multicompartment models that account for primary and secondary emissions.

# Effects of climate change

## *Findings*

Climate change has the potential to affect all POPs pathways in the atmosphere, hydrosphere, cryosphere, biosphere, and soil.

There is evidence that climate change phenomena, e.g. elevated temperatures and sea-ice reduction, and extreme climate events, such as forest fires, flooding and glacial melting, will remobilize POPs previously deposited in sinks, e.g. forest soils and vegetation, ocean and lake sediments and glaciers.

# Effects of climate change

## *Recommendations*

Climate interactions with POPs and the connection between climate and variable meteorology should be considered in the collection and interpretation of data sets to assess spatial and temporal trends for POPs and source-receptor relationships.

In order to understand the impact of climate change on the inter-media exchange and long-range transport of POPs, there is a need to improve estimates of temperature and salinity dependent physico-chemical properties.

For the investigation of the effect of climate change on POP fate in the environment scenarios of future climate change including meteorological data for modelling for a sufficiently large period of time are required.

## Concluding Remarks

National and international regulations have reduced the production, consumption and release to the environment for a number of POPs (like HCHs, DDT and other organochlorine pesticides, dioxins/furans).

Inventories of use and releases of such regulated substances generally confirm the policy effectiveness.

Due to the slow decay rate of POPs these regulated substances will nevertheless remain for a long time in the environment (legacy POPs).

# Concluding Remarks

**Existing air monitoring efforts should be continued to generate long-term trends to assess the effectiveness of international control initiatives**

(Protocol on POPs and the Stockholm Convention).

It is noteworthy that a non-declining atmospheric trend at remote locations may not necessarily indicate ineffectiveness of control. The time required for the target chemical to reach a specific receptor region is influenced by the relative locations of the source and the receptor, the chemical's transport pathways and its physical chemical properties.

**Proper interpretation of temporal trends requires an understanding of these influencing factors which can be estimated using appropriate transport models.**

## Concluding Remarks

For the prediction of POP long-range transport, the coordinated use of multimedia modelling, monitoring of POP content and trends in environmental media, refinement of the understanding of both primary and secondary emissions, as well as POPs degradation and transformation processes, are essential.

Taking into account the complexity of POP pollution evaluation it is important to strengthen co-operation and exchange of information on scientific and research activity between various international programs and bodies.

