SAICM QSP Project
“Training on Risk Assessment of Chemicals at National Level in a Global Context”: Armenia Workshop

Martin Scheringer

International Panel on Chemical Pollution

Yerevan, Armenia
February 24–25, 2011

Goals of the Project

- **Provide training materials** for project partners
- **Implement training activities** in Armenia, Chile, Ghana, supported by IPCP: initiate a process!
- Compare experiences and results from the three countries
- Synthesis, dissemination, lessons learned

Who is the IPCP?

- **Global network** of scientists working on chemical pollution problems: http://www.ipcp.ch
  - Association according to Swiss civil law
  - Members mainly scientists

- Goals:
  - Deliver scientific information about chemical pollution problems to the public, decision-makers, stakeholders...
  - Foster international collaboration and knowledge transfer

Background of the Project

- **Application** to SAICM QSP approved in October 2009
- Project **start**: May 2010
- Inception workshop in Zurich: July 2010
  - presentation of training materials
  - planning of national activities
- **Armenia workshop** is the 2nd national workshop (Ghana: December 2010; Chile: March 2011)
- IPCP project team: Ake Bergman, Heidi Fiedler, Martin Scheringer, Jana Weiss, Carla Ng, Divna Nikolic, Matthew MacLeod

Safety and Environmental Technology Group

Project Workplan

- National workshops: start of **project implementation in the countries** (10 months)
- Reporting ...
- End of the project: synthesis workshop at Stockholm University

Activity	Month																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1. Identification of responsible scientists (countries; IPCP)	■	■																
2. Identify issues of concern at country level (countries; IPCP)		■	■															
3. Identify needs for training (IPCP; countries)		■	■	■														
4. Selection of training materials (IPCP; countries)				■														
5. Kick-off workshop for training (IPCP, Zürich)					■													
6. National workshop to start activities at national level (national principal scientists)						■												
7. Training and application of methods and tools for risk assessment (national scientists; trainers)						■	■	■	■	■	■	■	■	■	■			
8. Conclusions and recommendations from countries (countries; IPCP)																■		
9. Synthesis workshop (IPCP, Stockholm)																	■	
10. Preparation and endorsement of final report (IPCP; national principal scientists; trainers; countries)																■	■	■

Goals of the Workshop

- Present training materials to participants
- Use selected materials in case studies/examples
- Initiate project implementation in Armenia:
  - discuss and agree on short-term, mid-term goals
  - clarify roles and tasks of institutions and people involved
  - discuss budget and resources
  - establish national project team
  - establish/strengthen links to IPCP team members

Structure of the Workshop

- Discussion of project goals and work process in Armenia
- Overview of training materials and hazard and risk assessment methods
- Human Health: WHO Risk Assessment Toolkit
- Environment: property estimation methods, environmental fate modeling
- Hands-on training and feedback
- Plenary: agree on workplan for Armenia

Project Implementation in Armenia

- Overal goal: apply methods for hazard and risk assessment on relevant cases in Armenia:
  - chlorinated dioxins and furans, organochlorine pesticides, others

- What are relevant and feasible case studies?
- Who can work on them in the next 10 months?
- What do you need for this?
- How can we organize the work?

Methods for Hazard and Risk Assessment – Overview of Training Materials

Martin Scheringer

International Panel on Chemical Pollution

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Selection of Training Materials

Compilation of Materials for Training on Risk Assessment of Chemicals

Document for use in the SAICM QSP project

"Training on risk assessment of chemicals

at national level in a global context"

prepared by Divna Nikolic, Martin Scheringer

International Panel on Chemical Pollution, IPCP

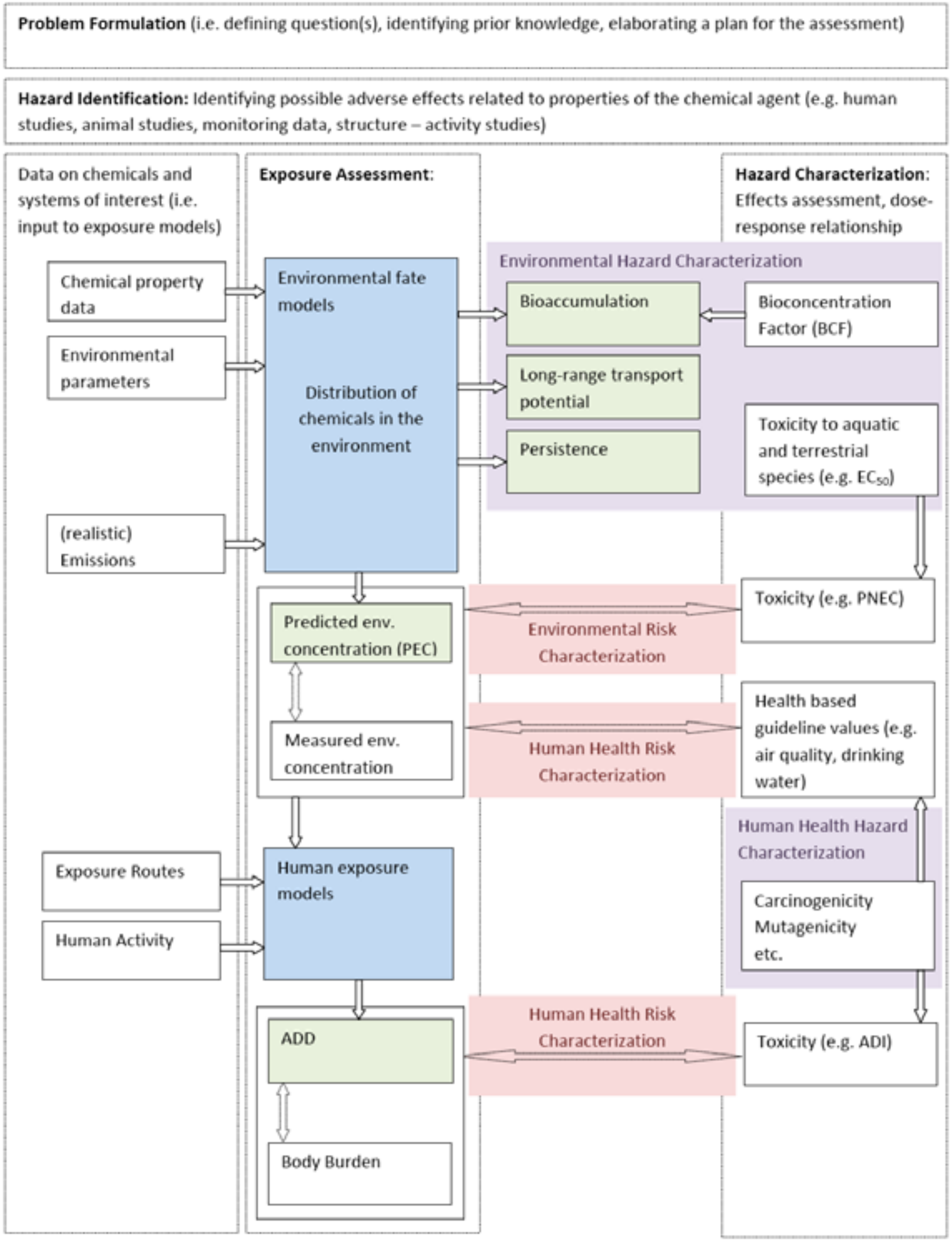
July 2010

The authors thank Matt MacLeod for helpful comments.

Structure of the Document (I)

- Overview of contents
- Brief summary of chemicals assessment (Figure 1):
  - hazard and risk
  - human health and environment
  - measured and modeled data

Graphical Outline of RA Components (Figure 1)



Structure of the Document (II)

- Brief summary of multi-compartment modeling
  - basis for estimating chemical concentrations in various environmental media and in food
- Compilation of training materials
  - Databases for chemical property data etc.
  - Estimation methods for chemical properties
  - Emission estimation tools
  - Environmental fate models
  - Comprehensive toolkits and manuals

Purpose of the Document

- Covers methods, tools, databases from various fields
  - human health, environment
  - hazard, risk
- Not intended to be fully comprehensive; open for updates and amendments

Multi-Compartment Fate Modeling

- In the Training Materials, there is a particular focus on multi-compartment fate modeling, because:
  - fate modeling makes it possible to estimate levels and trends of chemicals in many environmental media and food components
  - fate modeling makes it possible to connect and rationalize data on
    - chemical properties
    - chemical emissions
    - concentrations measured in the field
- But: other techniques and endpoints can and should also be addressed.

A First Example:
Global Distribution of Endosulfan

- **Goals and modeling approach**
- Model input: chemical property data, emission data
- Model results: concentrations, long-range transport, persistence

L. Becker, M. Scheringer, U. Schenker, K. Hungerbühler, Environmental Pollution (2011), in press

Objectives ...

- ... to evaluate persistence and long-range transport of endosulfan in the global environment

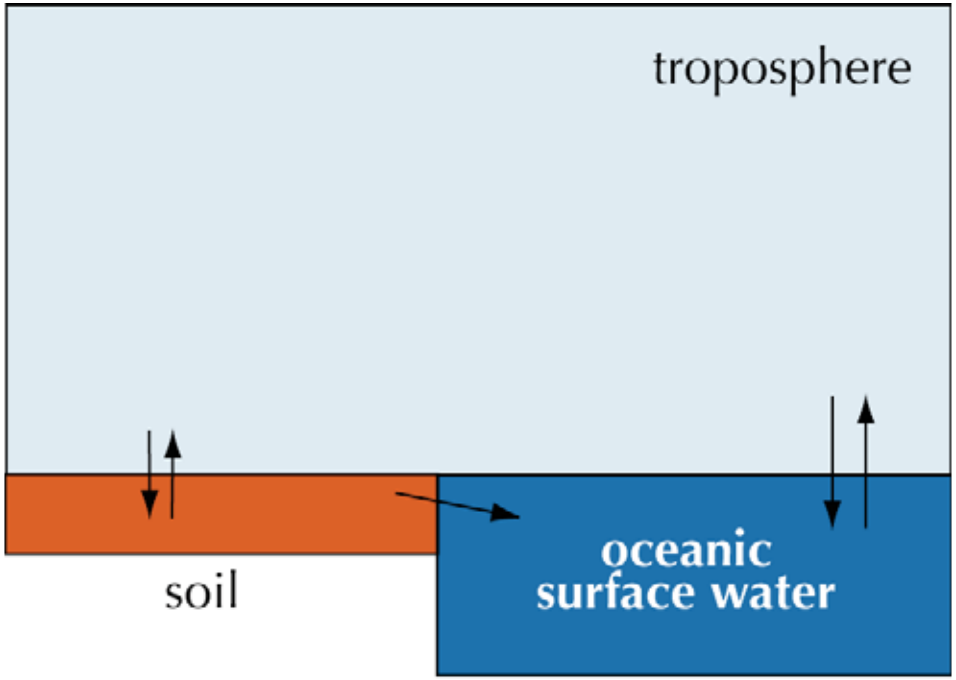
include
α- and β-endosulfan
and endosulfan sulfate

time trends
from measurements
in laboratory test
and field campaigns

field data showing
spatial distribution
of endosulfan

Multimedia Box Models

- Convenient analytical framework for the investigation of environmental processes



Multimedia Box Models

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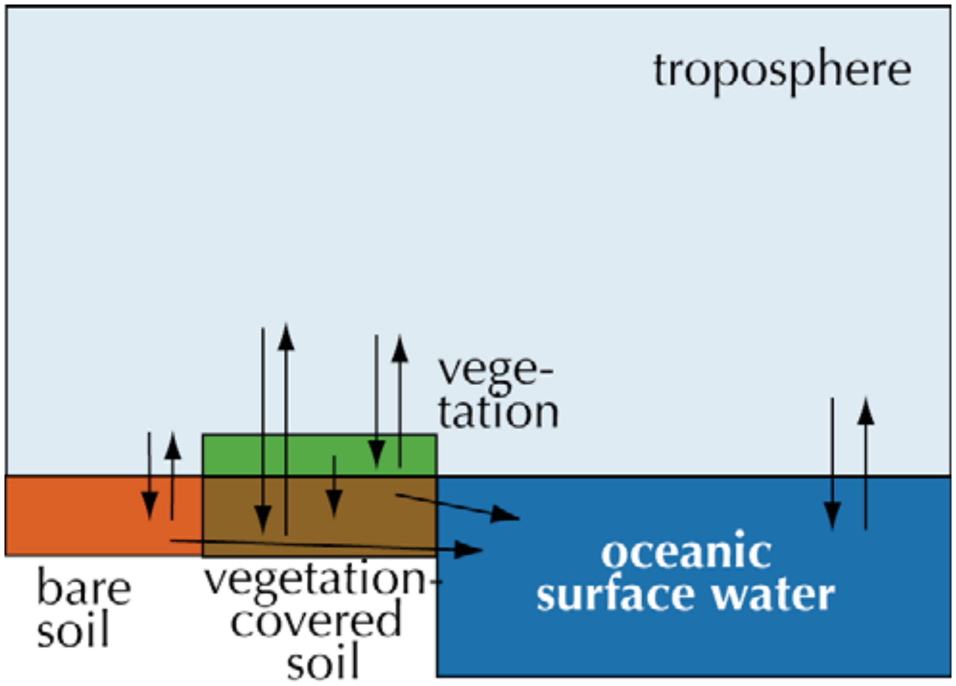

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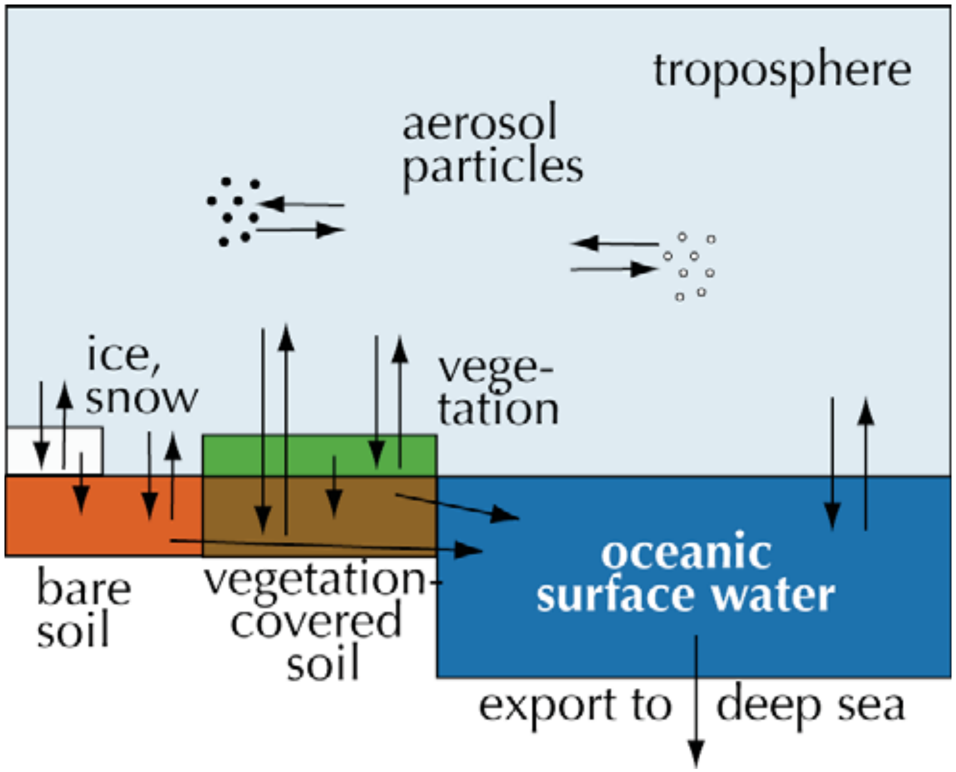
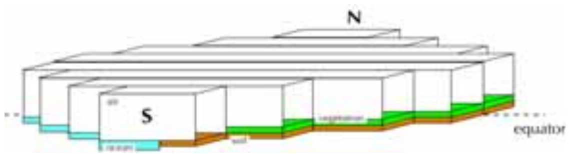


The Environmental Fate Model as an „Integrative Platform“

- Four main components:

model:
description of the
environment,
here: **CliMoChem**



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partition coefficients,
degradation half-lives,
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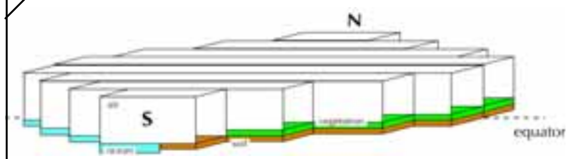
model results:
concentrations,
mass fluxes,
persistence, ...

emission inventory:
spatial and temporal distribution



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model:
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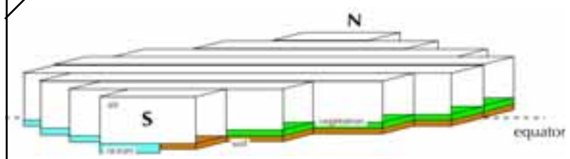
model results:
concentrations,
mass fluxes,
persistence, ...

?

field data:
measured concentrations and mass fluxes

emission inventory:
spatial and temporal distribution



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L. Becker, M. Scheringer, U. Schenker, K. Hungerbühler, Environmental Pollution (2011), in press

Model Inputs: Chemical Property Data

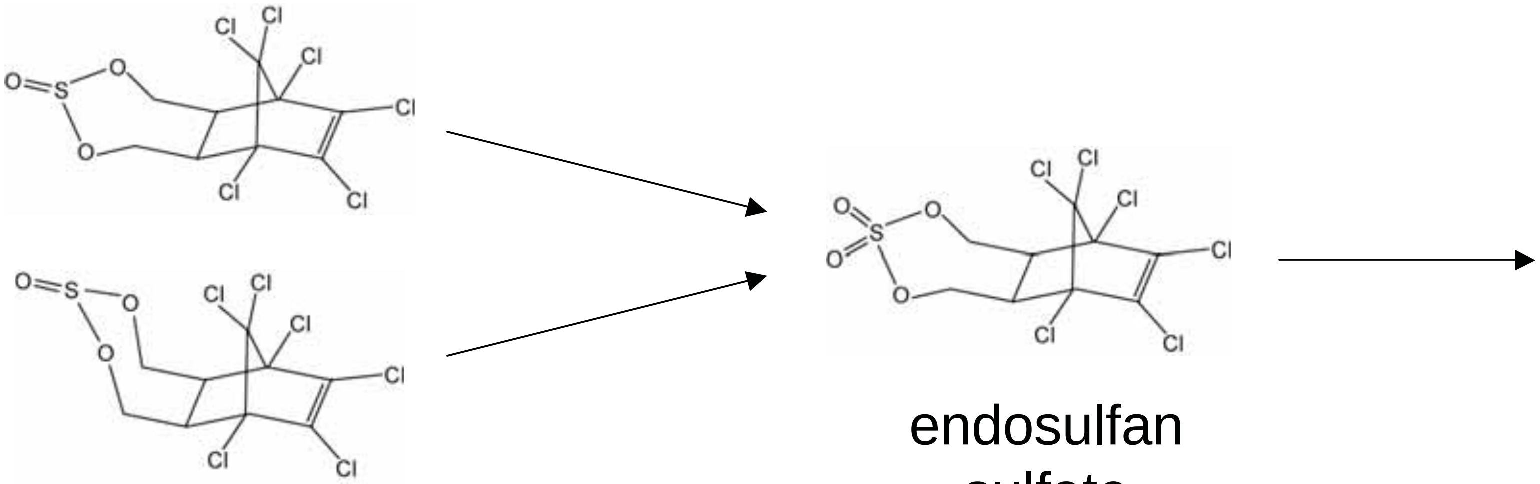
- Partition coefficients and degradation half-lives (days)

	α-endosulfan	β-endosulfan	endosulfan sulfate
log K_{ow}	4.93	4.78	3.71
log K_{aw}	–3.56	–4.75	–4.78
$t_{1/2,\ air}$	6; 10; 18	4.4; 8; 13	4; 7; 12
$t_{1/2,\ water}$	12.6; 22; 38	17.4; 30; 52	58; 100; 173
$t_{1/2,\ soil}$	24; 42; 73	90; 156; 270	180; 312; 540

air: values based on measurements and AOPWIN
water: experimental data for hydrolysis in seawater
soil: selection based on assessment by US EPA R.E.D. (2002)

Model Inputs: Chemical Property Data

- Simplified degradation scheme used in the model:
  - only endosulfan sulfate included as metabolite
  - formation of endosulfan sulfate predominantly in soils



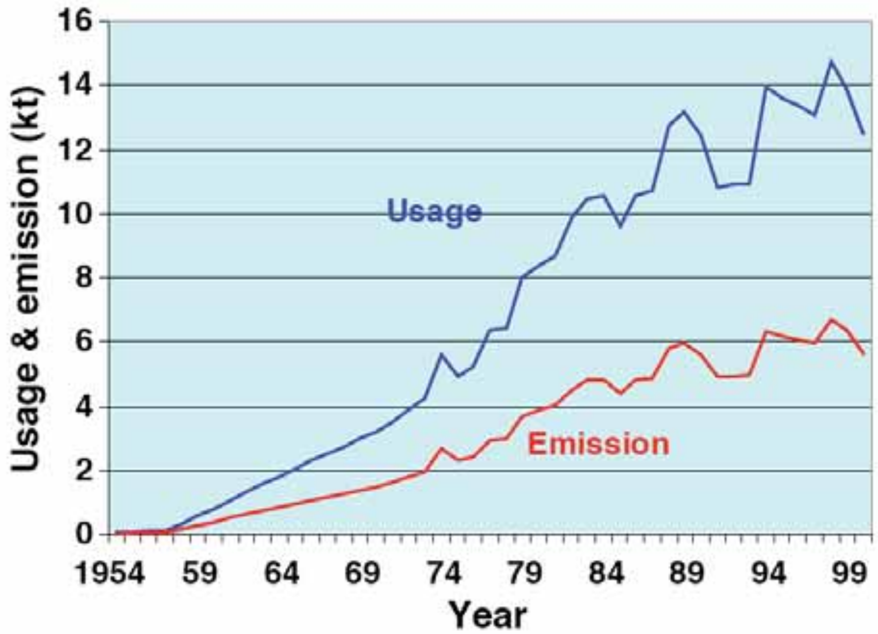
α- and β-endosulfan, released at ratio of 7:3, 10% to air, 90% to soil

endosulfan sulfate

minerali-zation

Model Inputs: Emission Data (I)

- Overall historical emissions (global):[1]

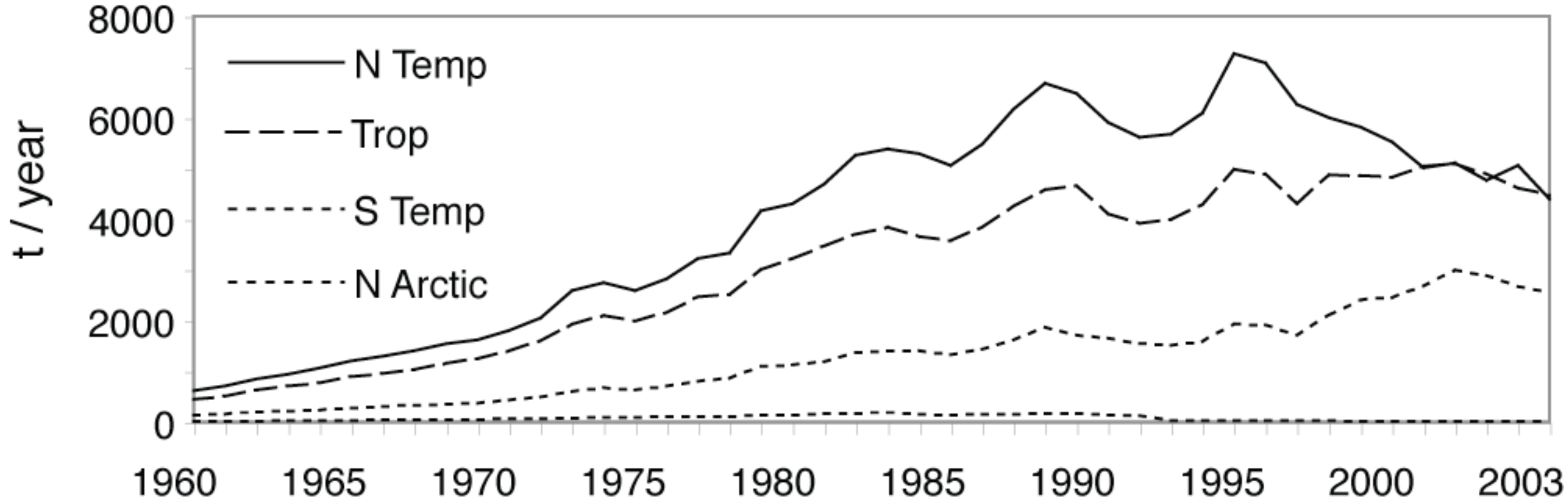


- Total historical usage (here assumed to be released): about 300 000 t

1: Li and Macdonald, Sci. Total Environ. 342 (2005), 87–106

Model Inputs: Emission Data (II)

- Contributions of latitudinal zones:[1]
  - areas of crops under endosulfan treatment: cocoa, coffee, cotton, fruits, soy, tea, vegetables
- Model input:



1: data from FAO; Bayer Crop Sciences

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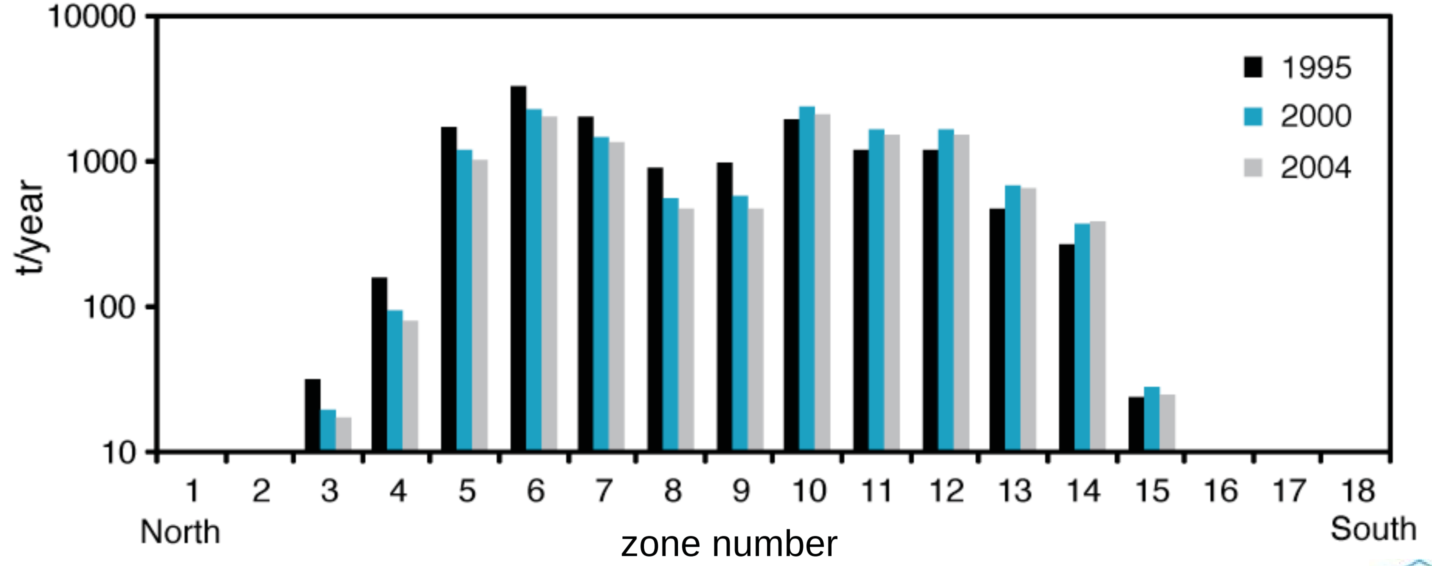
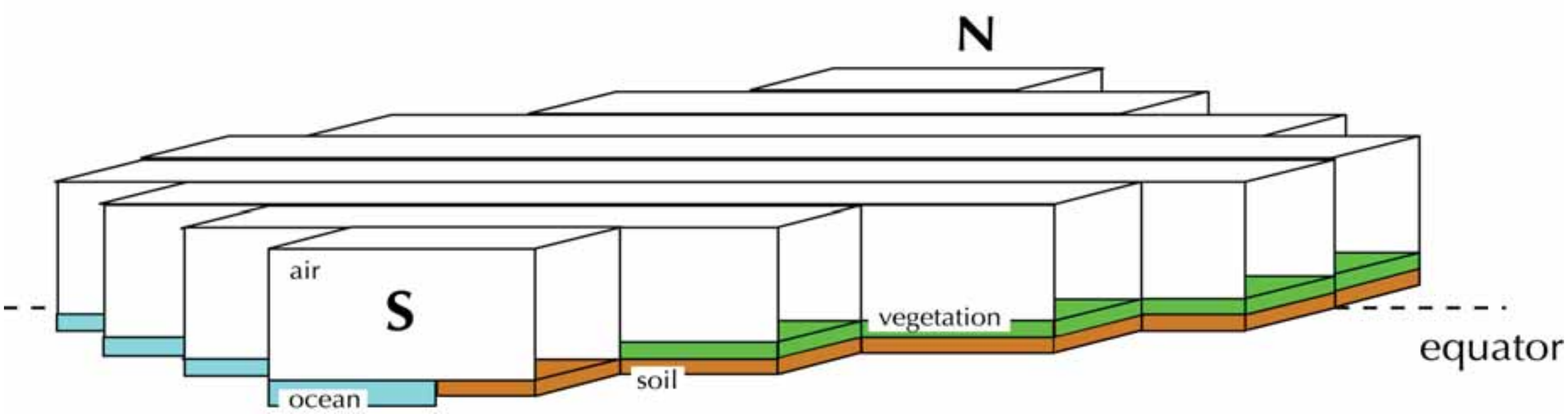


1: data from FAO; Bayer Crop Sciences

Model: CliMoChem[1]

- Structure/cross-section, geometry of the model

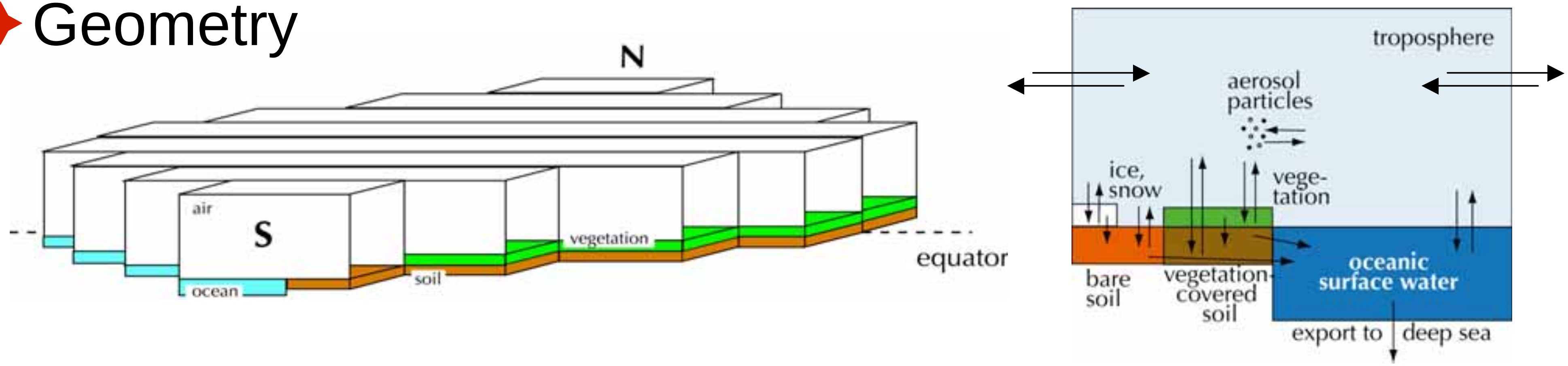


- Model has been validated in studies on PCBs[2], DDT[3], PFOA[4], HCH[5]

1: Scheringer et al., Environ. Sci. Technol. 34 (2000), 1842–1850
2: Scheringer et al., Environ. Pollut. 128 (2004), 177–188
3: Schenker et al., Environ. Sci. Technol. 42 (2008), 1178–1184
4: Schenker et al., Environ. Sci. Technol. 42 (2008), 3710–3716
5: Götz et al., Environ. Sci. Technol. 42 (2008), 3690–3696

The CliMoChem Model

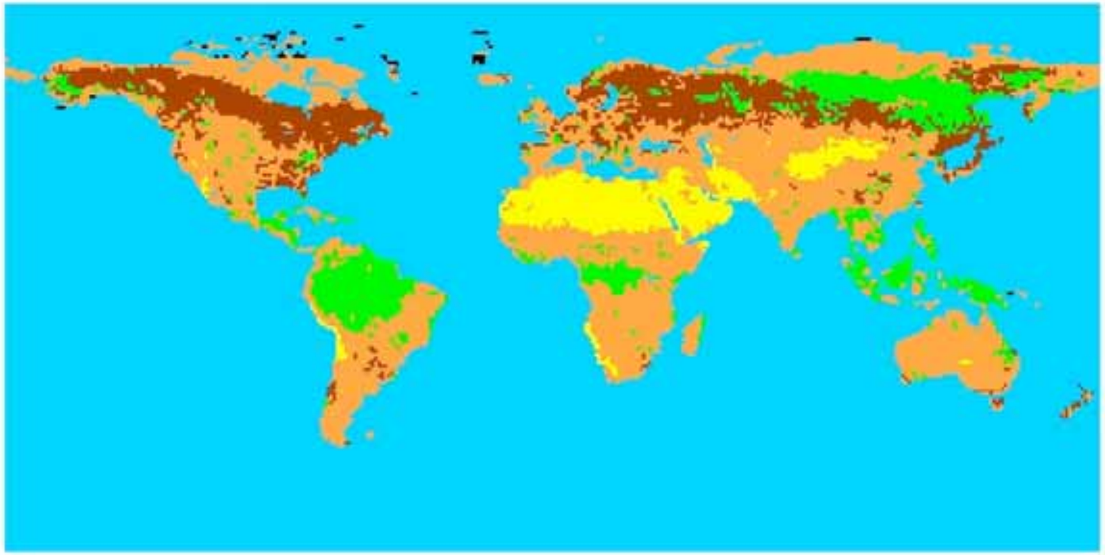
- Geometry



- **Purpose:** mechanistic analysis of long-range transport of persistent organic pollutants
- **Structure:** latitudinal bands; soil, water, air, vegetation, ice/snow; based on remote-sensing data
- **Model applications:**
  - global levels for DDT, DDE and DDD
  - transport of PFOA precursors and deposition of PFOA to the Arctic
  - transport of aerosol-borne pesticides to the Arctic

Vegetation in CliMoChem

- Types of vegetation from DeFries and Townsend, *Int. J. Remote Sensing* **15** (1994), 3567–3586



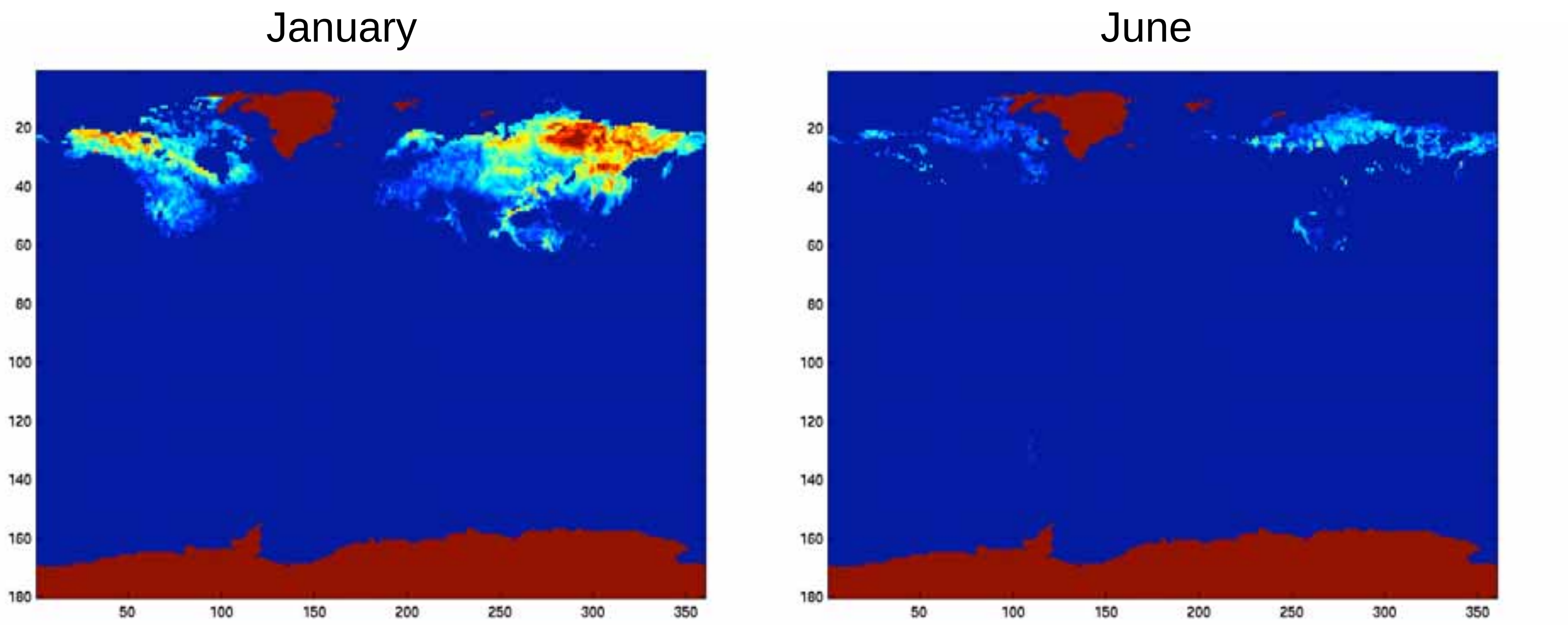
yellow: bare soil
orange: grass land
green: deciduous forests
brown: coniferous forests

- In the model: canopy and organic carbon in soils
  - air-vegetation partitioning: K_{oa}
  - high gaseous deposition velocities (Horstmann & McLachlan)
- Effects: forest filter effect, higher amounts in soils

F. Wegmann, M. Scheringer, M. Möller, K. Hungerbühler, ES&T **38**, 1505–1512 (2004)

Ice and Snow in CliMoChem

- Snow depth from NASA EOS data



- Challenges:
  - Changing snow density and water content
  - Dynamics of snow melt
  - Air-snow phase partitioning

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

J. Stocker, M. Scheringer, F. Wegmann, K. Hungerbühler ES&T **41**, 6192–6198 (2007)

A First Example: Global Distribution of Endosulfan

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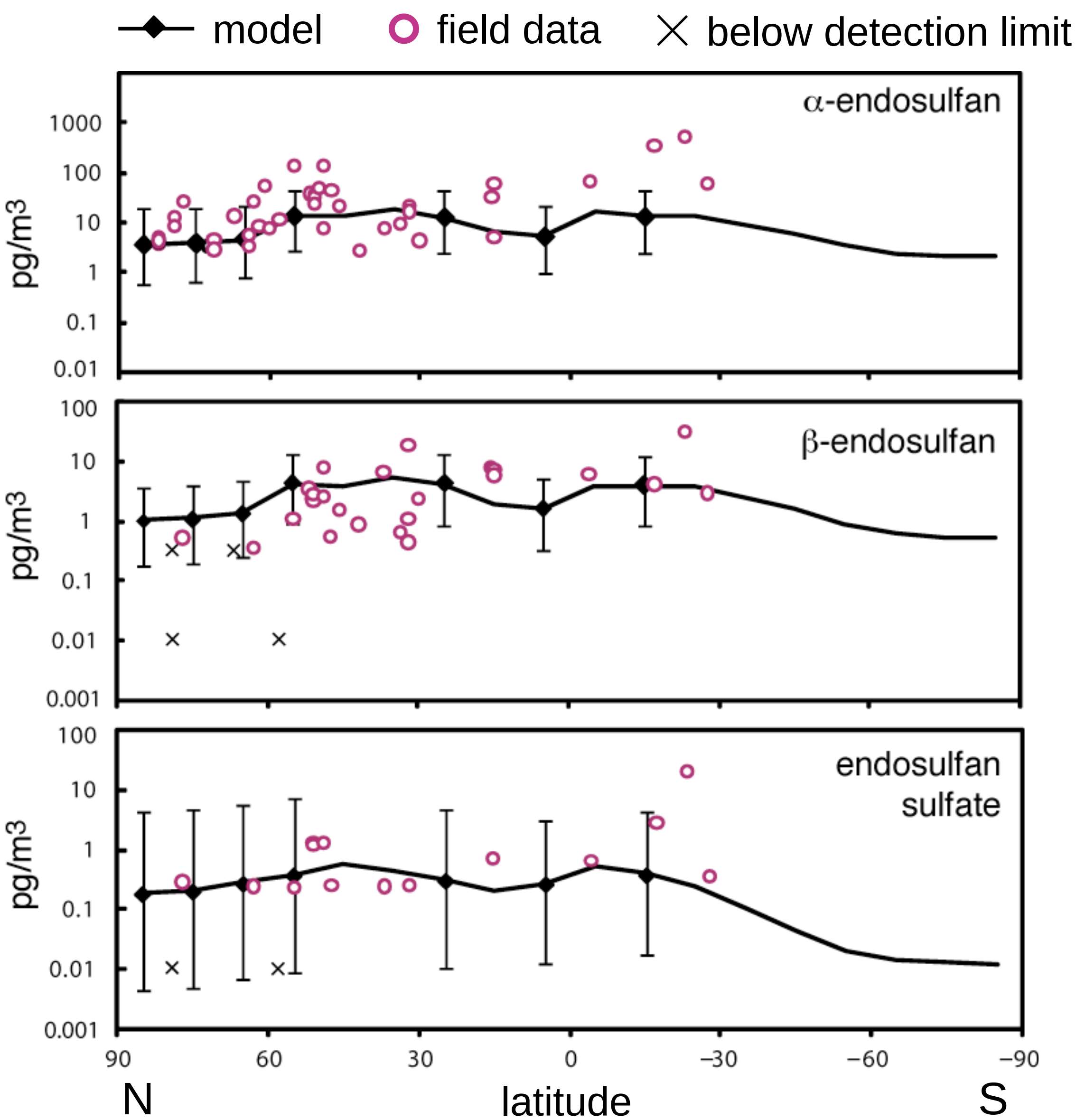
L. Becker, M. Scheringer, U. Schenker, K. Hungerbühler, Environmental Pollution (2011), in press

Results: Concentrations in Air

- Good agreement

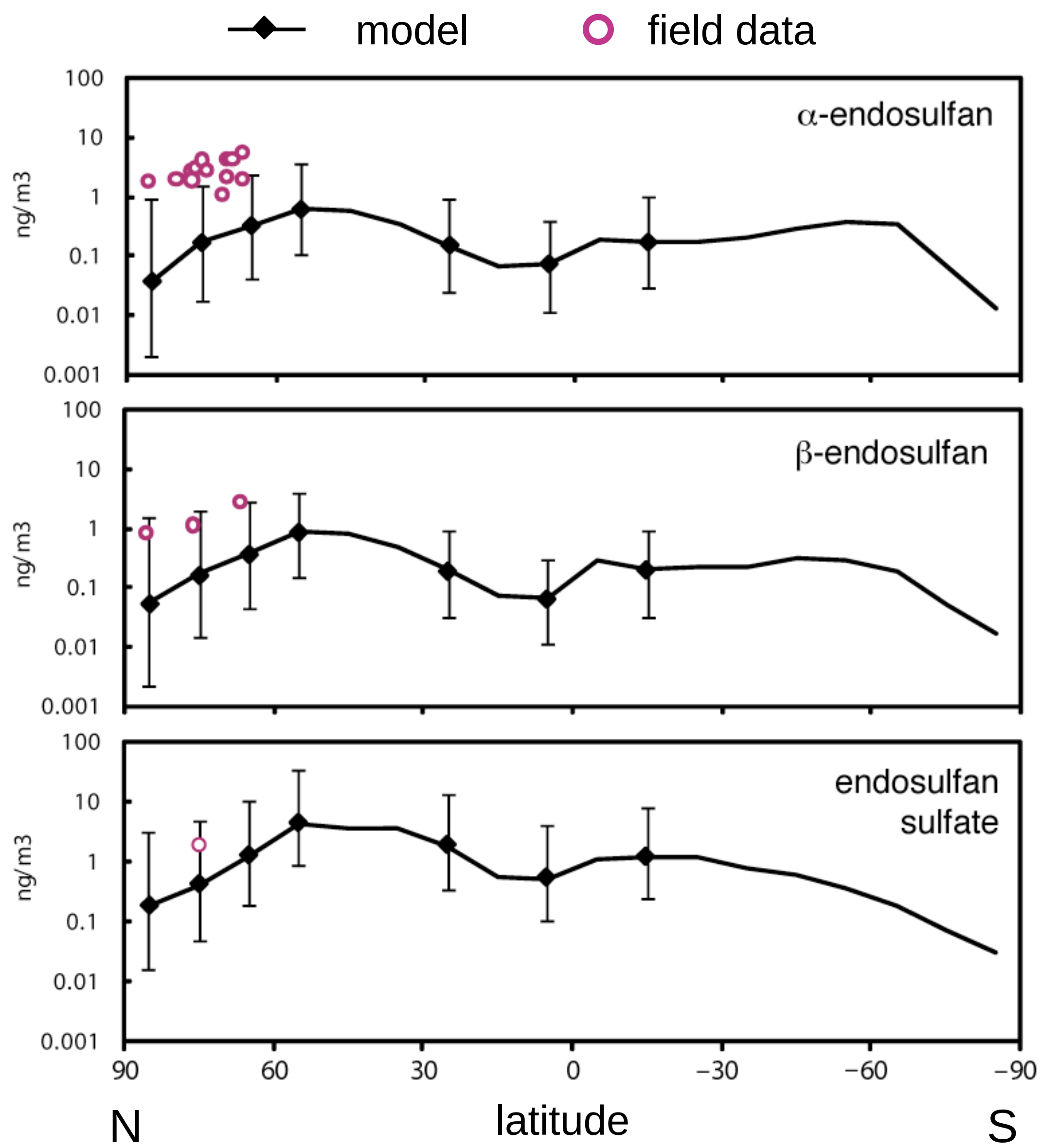
  for all three substances:
  - latitudinal trend: ok
  - α > β > sulfate: ok



ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Results: Concentrations in Ocean Water

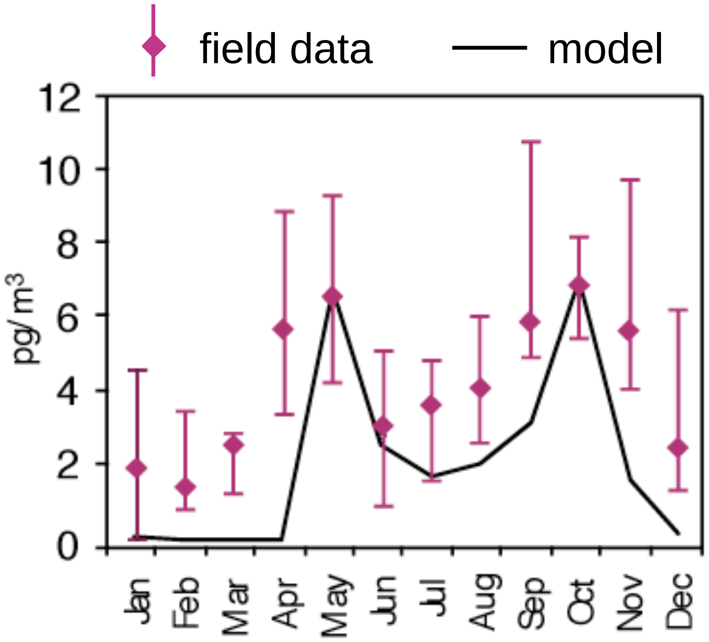
- Field data only north of 65° N
- sulfate > α ≈ β: ok
- all three substances: model by factor 10 too low
- Possible reasons:
  - activation energy of hydrolysis too low
  - half-life in water too low



Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Results: Time Trends in the Arctic

- concentrations of α-endosulfan in Arctic air
  - maximum in spring and fall
  - why?



L. Becker, M. Scheringer, U. Schenker, K. Hungerbühler, Environmental Pollution (2011), in press

Conclusions

- Global environmental fate of α-, β-endosulfan and sulfate can be reproduced with a multicompartment fate model.
- Model enables a consistency check of
  - emissions
  - chemical property data
  - field data
- Good agreement for levels in air.
- Discrepancy for levels in seawater –> higher half-lives (order of 4–5 years) at least in colder environments.
- Shorter half-lives are unlikely.
- All regions of the globe contribute to presence in Polar regions, but with different shares.

Hands-on Training with the “Small World Model”

Martin Scheringer

International Panel on Chemical Pollution

Armenia Workshop
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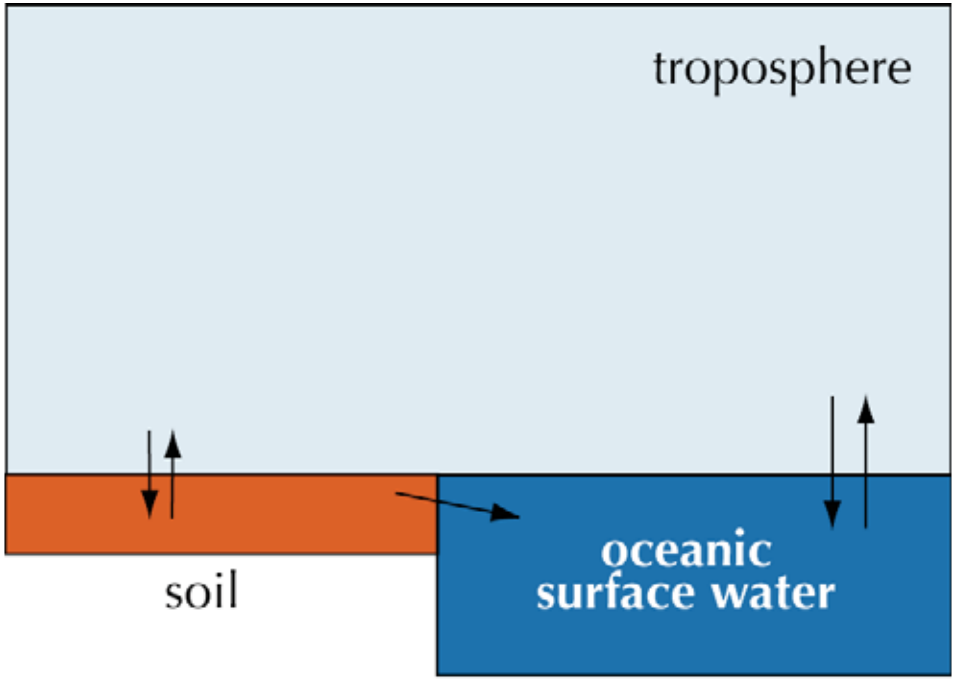
Goals

- The Small World Model is a simple multimedia box model, programmed by Matt MacLeod[1]
  - become familiar with the structure of such a model: input data needed, output obtained, advantages and limitations
  - parameterize the model for Armenia
  - estimate input data: chemical properties, emissions
  - run the model:
    - evaluative application
    - estimation of actual concentrations

1 2004-–2010 at ETH Zurich, now at Stockholm University; matthew.macleod@itm.su.se

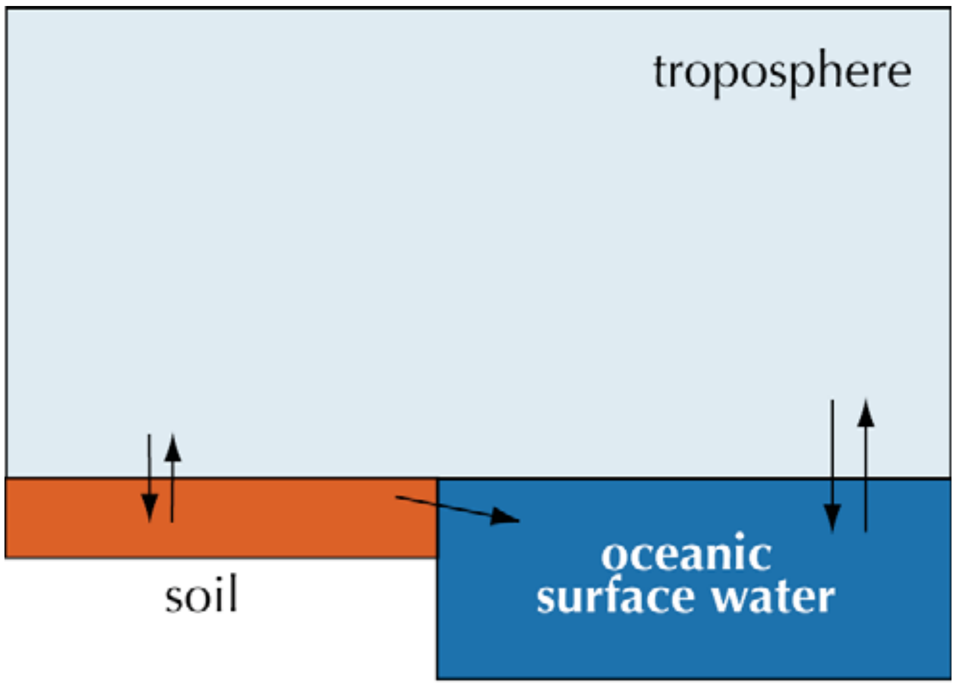
The „Small World Model“ (I)

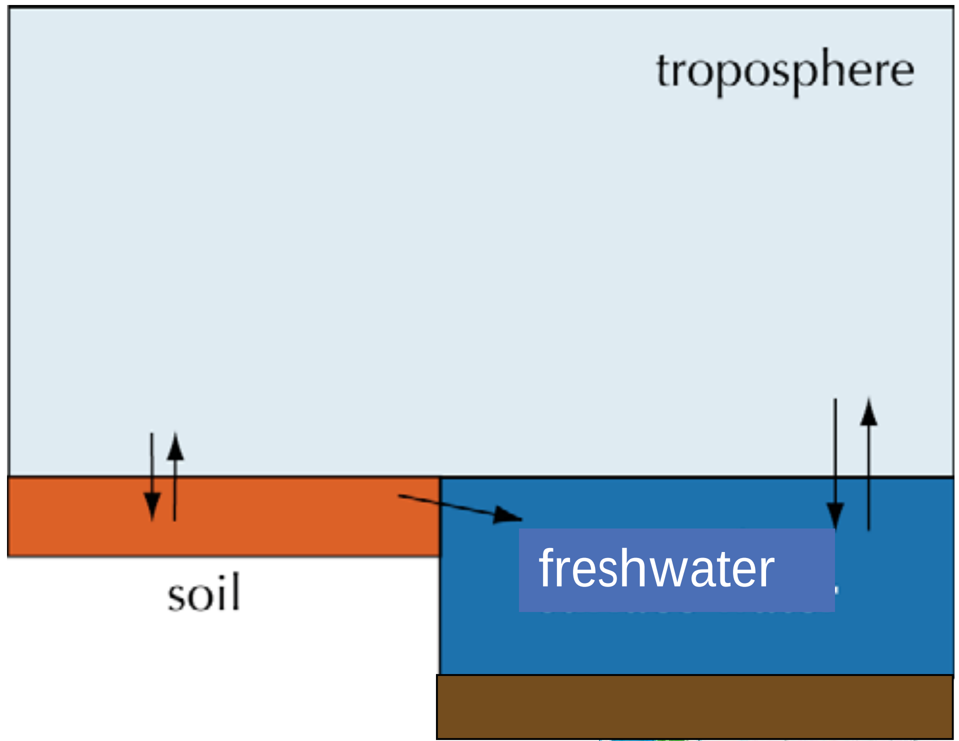
- A simple three-compartment model
- Structure of the model



The Small World Model (II)

- Three-box model, global
- Planned as extension: four-box model, regional





Using The Small World Model (I)

- Model inputs:
  - chemical specific: partition coefficients, degradation half-lives
  - environmental: dimensions of environmental media, temperature, rain rate, soil OC content, concentration of suspended matter in water, wind speed, ...

Small World® V002 - A Global-scale Level III Fugacity Model

Modeling Environmental Pollutants 2009

Model Coded by Matt MacLeod
March 17 2009

Input Parameters
Calculated Values

1. Chemical Properties

Chemical Name	Cname	Benzene
Log Kaw	LKAW	-0.64
Log Kow	LKOW	2.13
Degradation half-life in air (h)	ThA	48
Degradation half-life in water (h)	ThW	256
Degradation half-life in soil (h)	ThS	2560

2.1 Bulk Environmental Properties

Temperature (°C)	TC	25
Total Surface Area (m^2)	A	5.1E+14
Fraction of area covered by water	FAW	0.71
Fraction of area covered by soil	FAS	0.29
Height of the air compartment (m)	HA	6000
Depth of water compartment (m)	HW	100
Depth of soil compartment (m)	HS	0.1

2.2 Environmental Subcompartment Properties

Volume fraction of aerosols in air	VQA	2.00E-11
Volume fraction of particles in water	VPW	5.00E-07
Volume fraction of air in soil	VAS	0.2
Volume fraction of water in soil	VWS	0.3
Density of water (kg/m^3)	rhoW	1000
Density of aerosols (kg/m^3)	rhoQ	2400
Density of soil solids (kg/m^3)	rhoS	2400
Density of particles in water (kg/m^3)	rhoP	2400
Fraction of OC in particles in water	FOCP	0.1
Fraction of OC in soil solids	FOCS	0.02

3.1 Thermodynamic Controls - Dimensionless Partition Coefficients

Log Koa	LKOA	2.77
Kaw	Kaw	0.229086765
Kow	Kow	134.8962883
Koa	Koa	588.8436554
K(particles:water)	Kpw	11.33128821
K(soil solids:water)	Ksw	2.266257643
K(aerosol:air)	Kqa	76.5496752

3.2 Sub-Compartment Fugacity Capacities (mol/Pa m^3)

Z pure air	Zpa	0.000403418
Z pure water	Zpw	0.001760983
Z pure aerosol	Zpq	0.030881509
Z pure soil solids	Zps	0.003990841
Z pure particles	Zpp	0.019954206

3.3 Bulk Compartment Fugacity Capacities (mol/Pa m^3)

Z bulk air	ZA	0.000403418
Z bulk water	ZW	0.001760992
Z bulk soil	ZS	0.002604399

3.4 Equilibrium (Level 1) Distribution

Equlibrium Fraction in Air	EFA	95.09%
Equilibrium Fraction in Water	EFW	4.91%
Equilibrium Fraction in Soil	EFS	0.00%

3.4 Equilibrium (Level 1) Distribution

2.3 Intermedia Mass Transfer Coefficients (m/h)

Air side air-water MTC	MTCawa	30
Water side air-water MTC	MTCaww	0.03
Rainfall rate	MTCrain	9.70E-05
Aerosol deposition velocity	MTCQd	10.8
Soil side air phase diffusion MTC	MTCas	0.04
Soil side water phase diffusion MTC	MTCsw	1.00E-05
Soil side solid phase diffusion MTC	MTCss	4.54E-07
Air side air-soil MTC	MTCasa	1
Soil to water runoff rate	MTCwrun	3.90E-05
Soil solids runoff rate	MTCsrun	2.30E-08

2.4 Advective Removal Process Mass Transfer Coefficients (m/h)

Air transfer to stratosphere	MTCstrat	0.064
Water particle sinking velocity	MTCsink	2.17E-08
Water mixing velocity to deep oceans	MTCmix	1.14E-04
Soil solids deep migration	MTCburial	2.28E-08
Soil water leaching	MTCleach	3.00E-06

2.5 Other Environmental Parameters

Rain scavenging ratio	Scav	200000
Temperature (K)	TK	298.15

Using The Small World Model (II)

- Chemical-specific parameters:
  - Use estimation tools in EpiSuite (US EPA) to estimate model input data (K_{ow}, K_{aw}, $t_{1/2,air}$, $t_{1/2,water}$, $t_{1/2,soil}$)
  - Specific description of how EpiSuite is used are provided
- Structure of the model and environmental parameters
  - some are easy to adjust: volumes of compartments, rain rates, soil OC, wind speed
  - **What else is needed here (link to ecosystem properties, services, vulnerability)?**

Using The Small World Model (III)

- Understanding of model output
  - level I and level III according to D. Mackay
  - pie charts and flow diagram
  - concentrations and mass fluxes (sinks)

Activities (I)

- Open the model in MS Excel
- When opened, the model contains data for benzene: degradation half-lives and partition coefficients
  - modify these data and investigate the behavior of the model
- Partition coefficients and half-lives of 2,3,7,8-TCDD
  - measured data?
  - estimation tools: Epi Suite (US EPA)

Activities (II)

- Adjust environmental conditions for Armenia
  - surface area, depth/height of environmental media
- Investigate the environmental fate of TCDD in Armenia using the model
- Put together information about releases of TCDD in Armenia (estimates in kg/year)
- Estimate levels of TCDD in air, water, soil in Armenia