Combining measurements and models to understand emissions, fate, exposure and pharmacokinetics of POPs

Matthew MacLeod

Stockholm University

Department of Applied Environmental Science

Stockholm, Sweden

University of Birmingham, UK – May 9 2014

Acknowledgments

- Global fate and transport modeling
  - Harald von Waldow, Lara Lamon, Henry Wöhrnschimmel
- Urban diffuse source characterization
  - Bojan Gasic, Claudia Moeckel, Zhanyun Wang, Christian Bogdal, Andreas Buser, Amelie Kierkegaard
- Population PK modeling
  - Roland Ritter, Fiona Wong, Qingwei Bu
- Concepts and collaboration
  - Martin Scheringer, Konrad Hungerbuhler, Tom McKone, Ian Cousins, Jochen Mueller, Kevin Jones

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1. Why model?

Why model?

- Because we cannot help it!
  - Everyone is an *implicit* modeler
- It is valuable to make models *explicit*
  - Assumptions are defined
  - Sensitivity and scenario analysis is possible
  - Others can replicate your results

Epstein, J. M. *Journal of Artificial Societies and Social Simulation*, 11(4), 12, **2008**.

Models of open systems can never be verified

- Models are limited conceptualizations of the real system
- Models are limited in the empirical accuracy of their governing equations
- Models are limited with respect to input parameterization

Oreskes, N. **2003**. "The role of quantitative models in science," in *Models in Ecosystem Science*, Princeton University Press, pp. 13-31.

The ground rules for model development…

- Epstein:
  - "You must make models"
- Oreskes:
  - "Your models will always be wrong"

- These two rules are unbreakable, and are not in conflict
- We should not fixate on modeling as a tool to make predictions

16 reasons other than prediction to build models

(Epstein, *Journal of Artificial Societies and Social Simulation* 11(4), 2008)

1. Explain (very distinct from predict)
2. Guide data collection
3. Illuminate core dynamics
4. Suggest dynamical analogies
5. Discover new questions
6. Promote a scientific habit of mind
7. Bound (bracket) outcomes to plausible ranges
8. Illuminate core uncertainties.
9. Offer crisis options in near-real time
10. Demonstrate tradeoffs / suggest efficiencies
11. Challenge the robustness of prevailing theory through perturbations
12. Expose prevailing wisdom as incompatible with available data
13. Train practitioners
14. Discipline the policy dialogue
15. Educate the general public
16. Reveal the apparently simple (complex) to be complex (simple)

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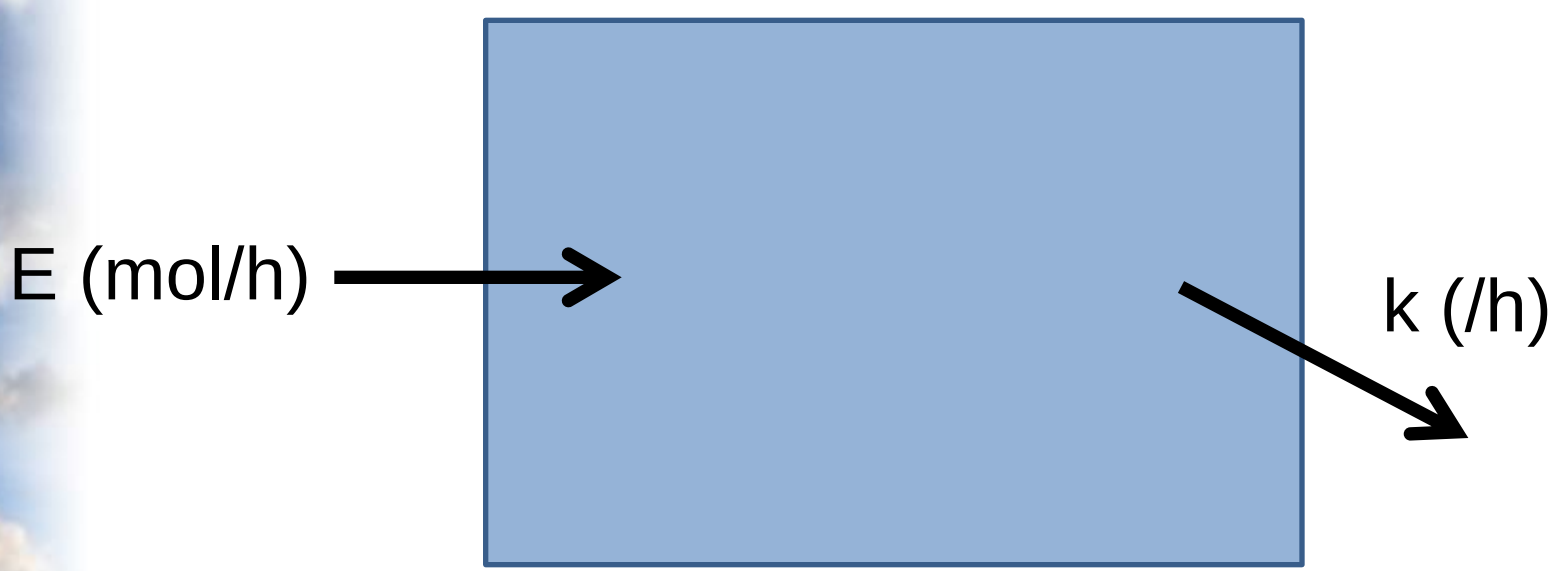
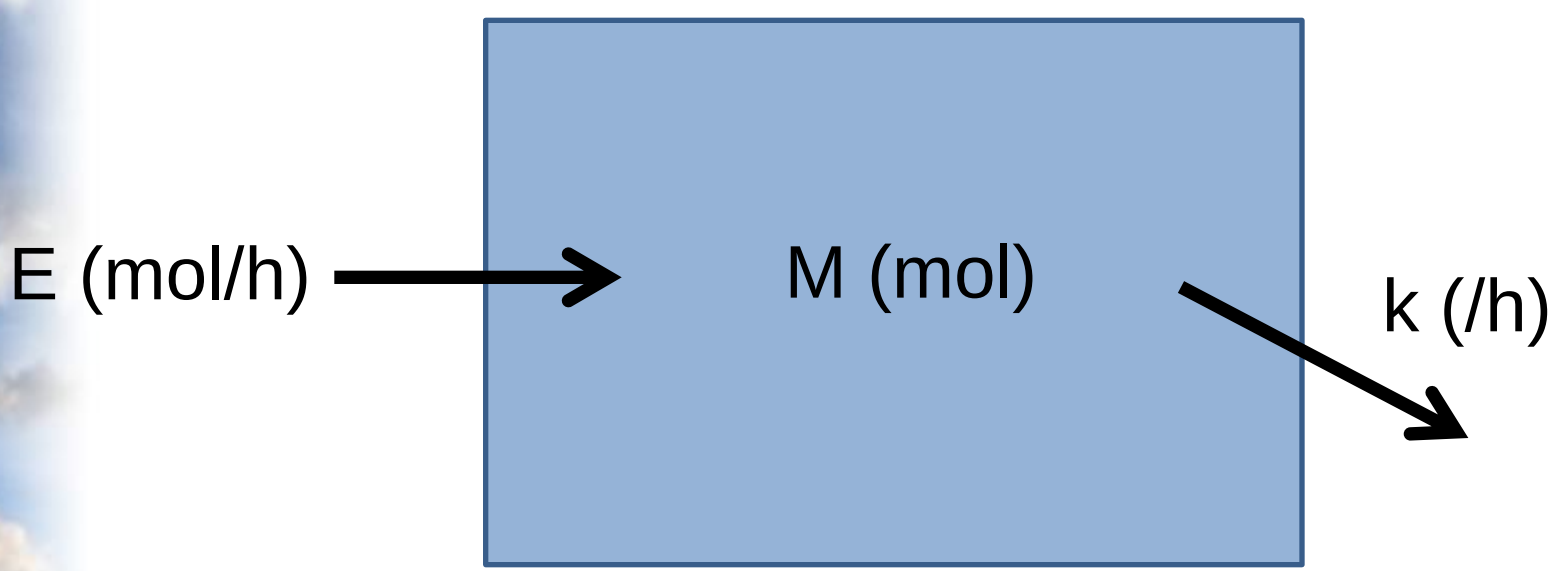
2. The global mass budget of POPs

A very simple model…

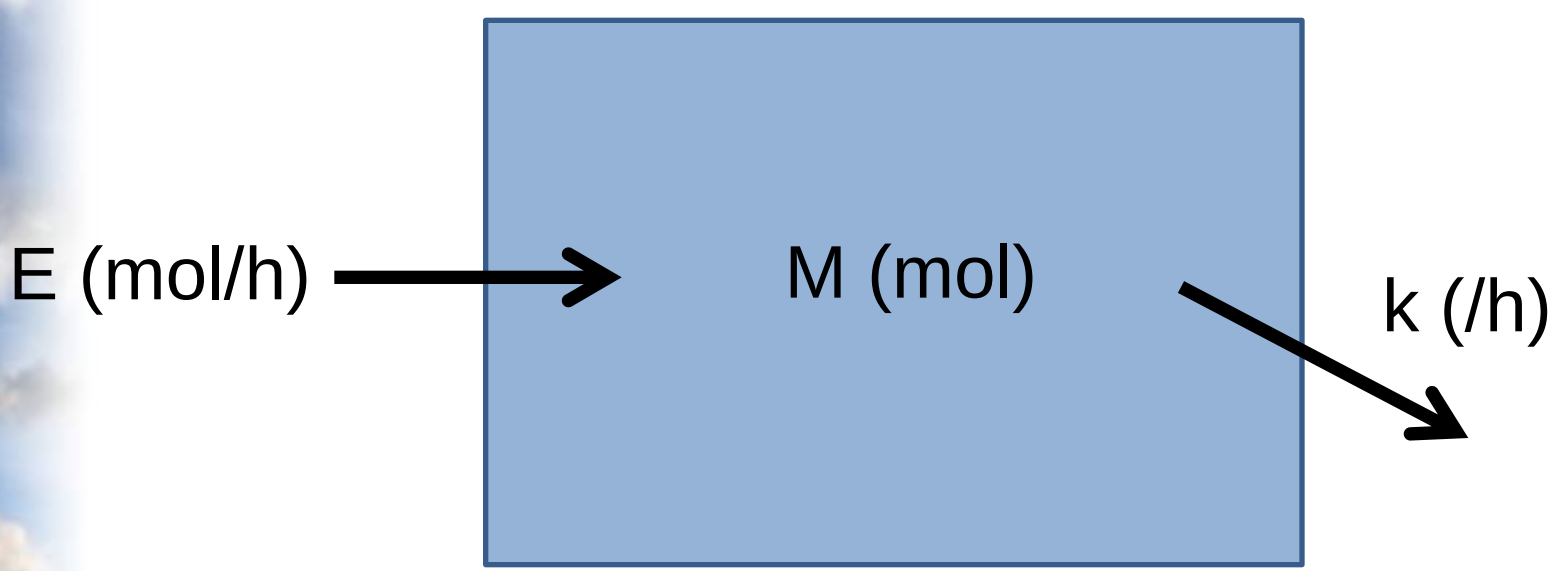


A very simple model…



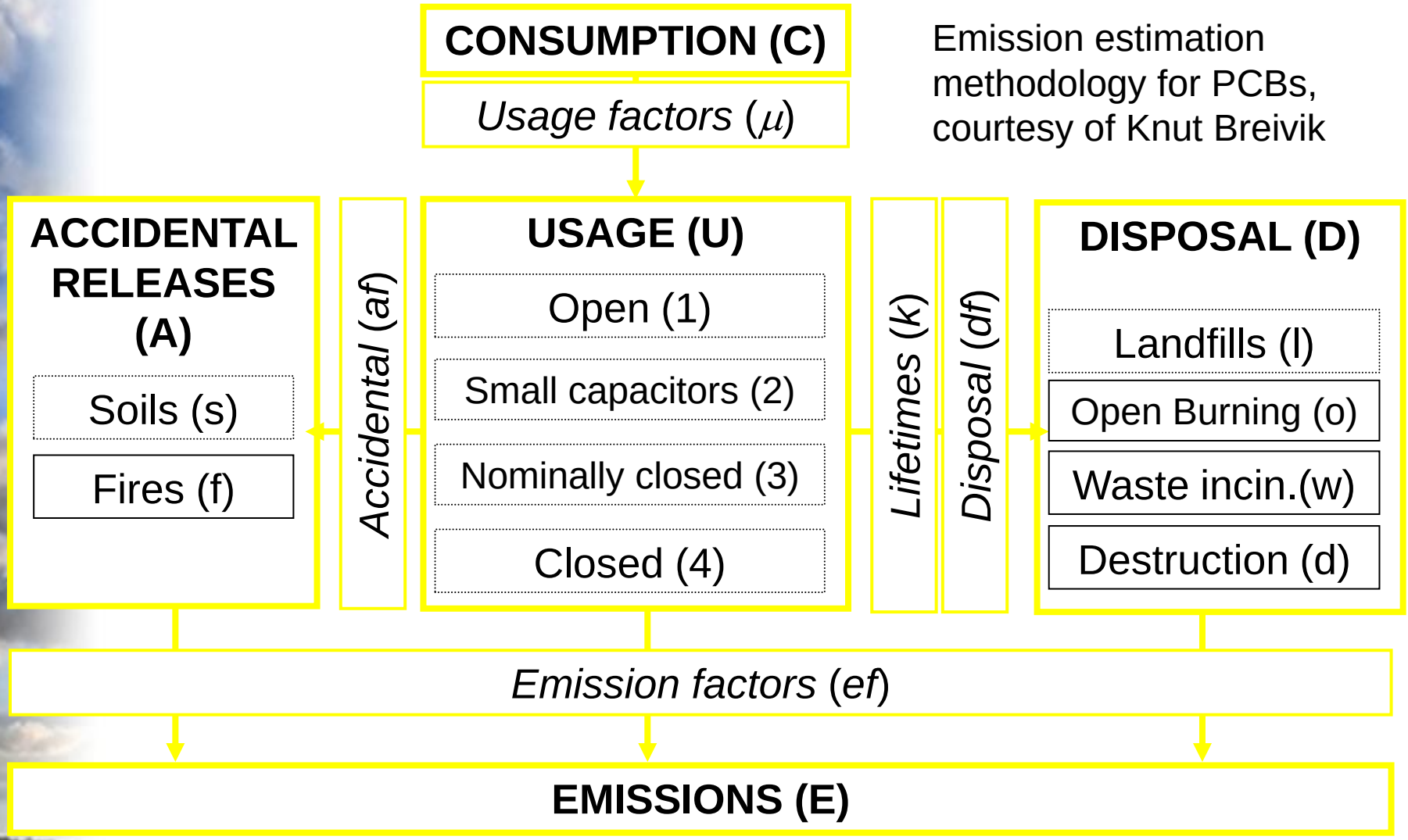
Sources: E

Sinks: M×k



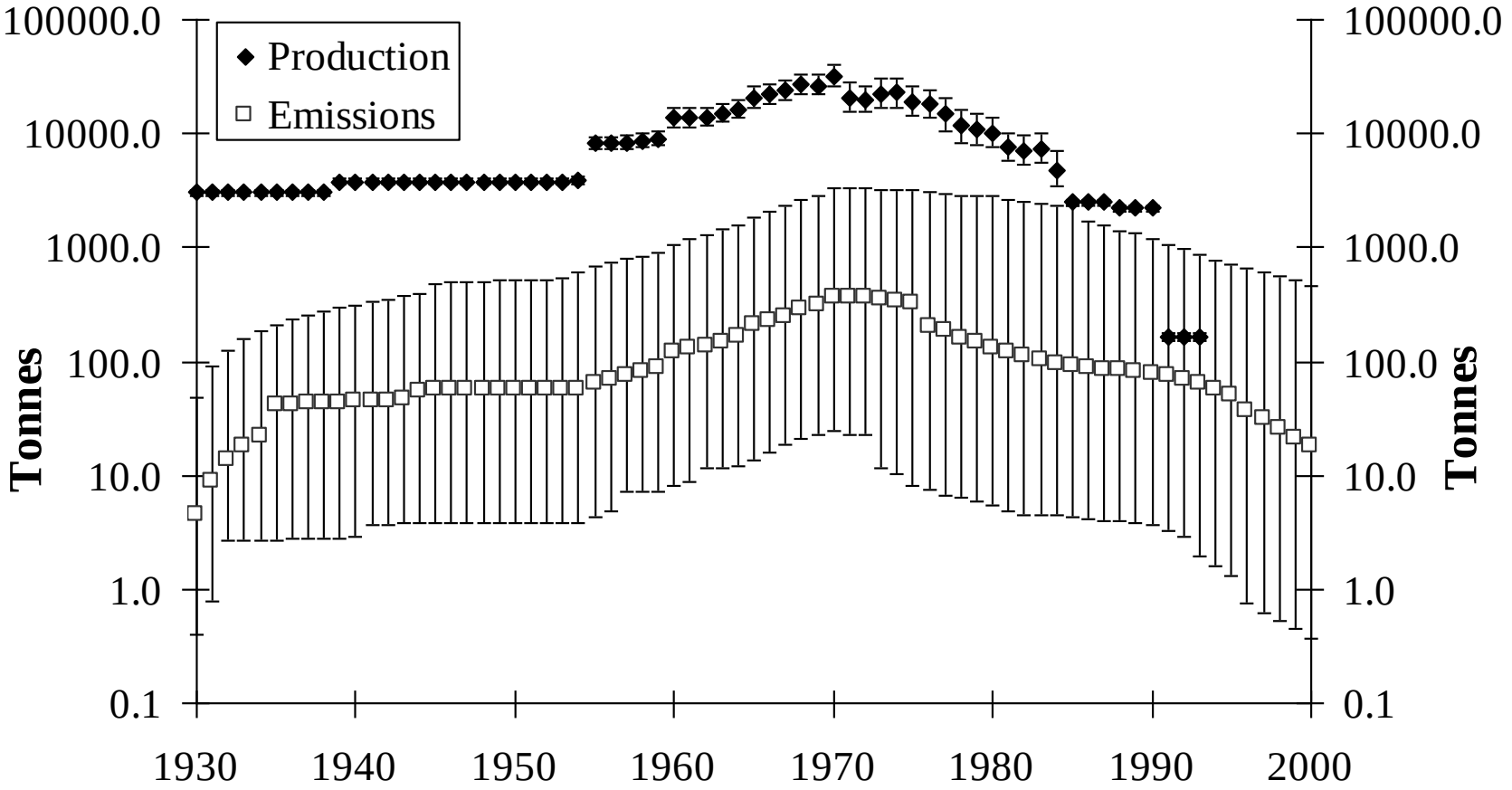
- The rate of emissions of chemicals to the environment often contributes most to uncertainty in exposure concentrations used in risk assessments (Arnot et al. 2006)

Emission estimates can be made with a “bottom-up” approach…



Emission estimation methodology for PCBs, courtesy of Knut Breivik

Breivik's "bottom-up" PCB emission estimates

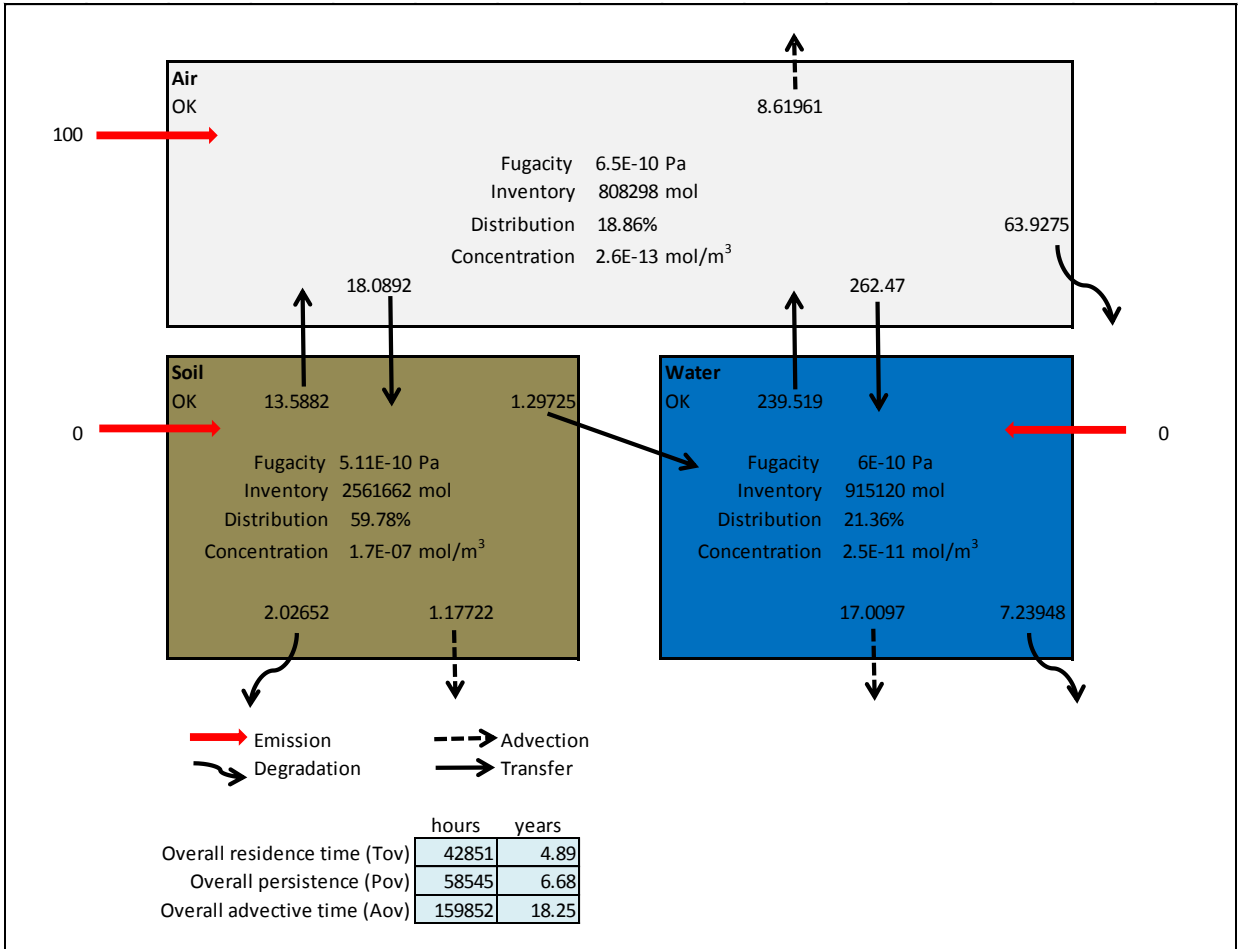


Ground-truthing Breivik's estimates…

Small World® - A global-scale fugacity model - Level I and Level III solutions

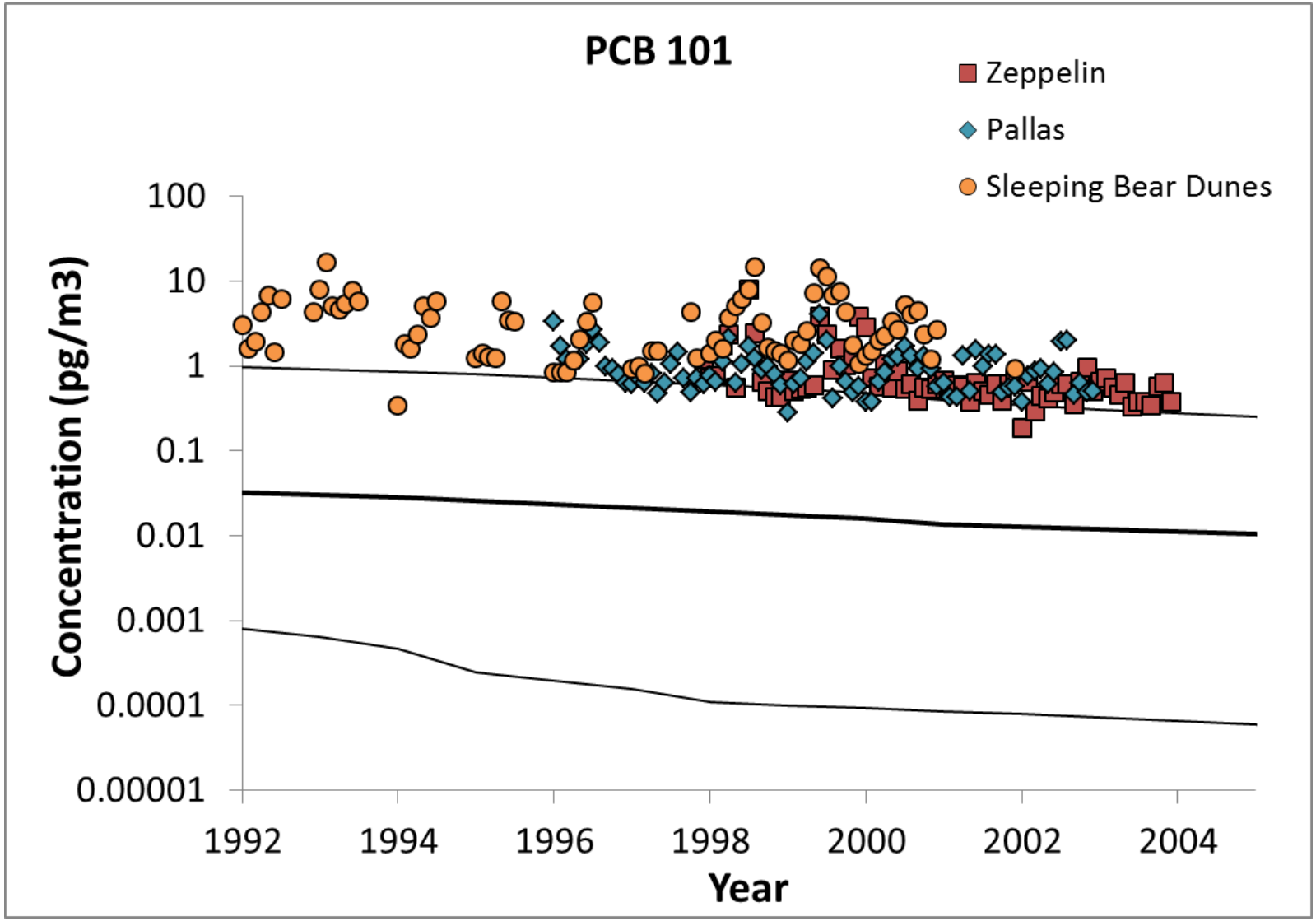
Developed at the Swiss Federal Institute of Technology, Zurich & Stockholm University, Sweden

Input Parameters
Calculated Values

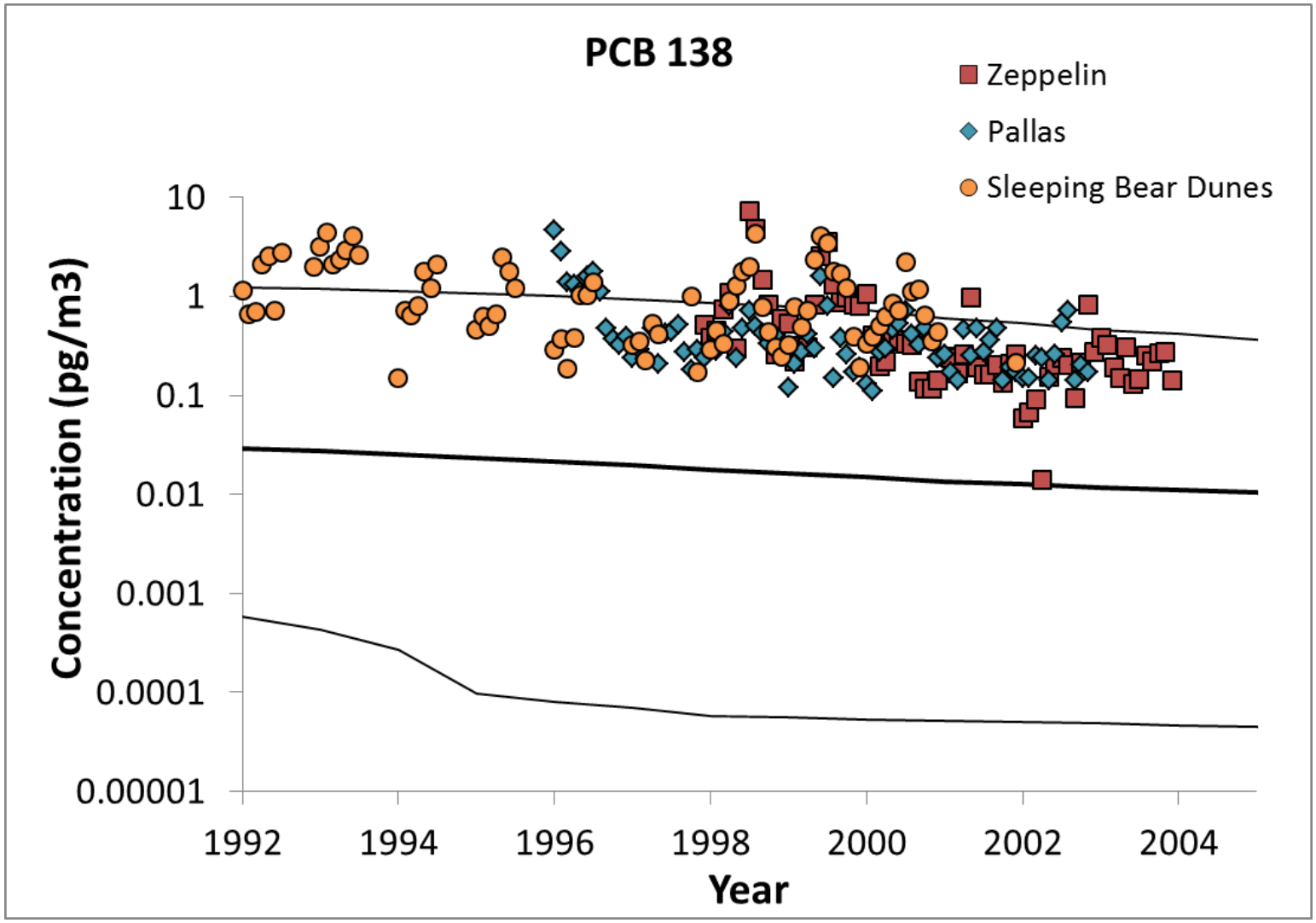


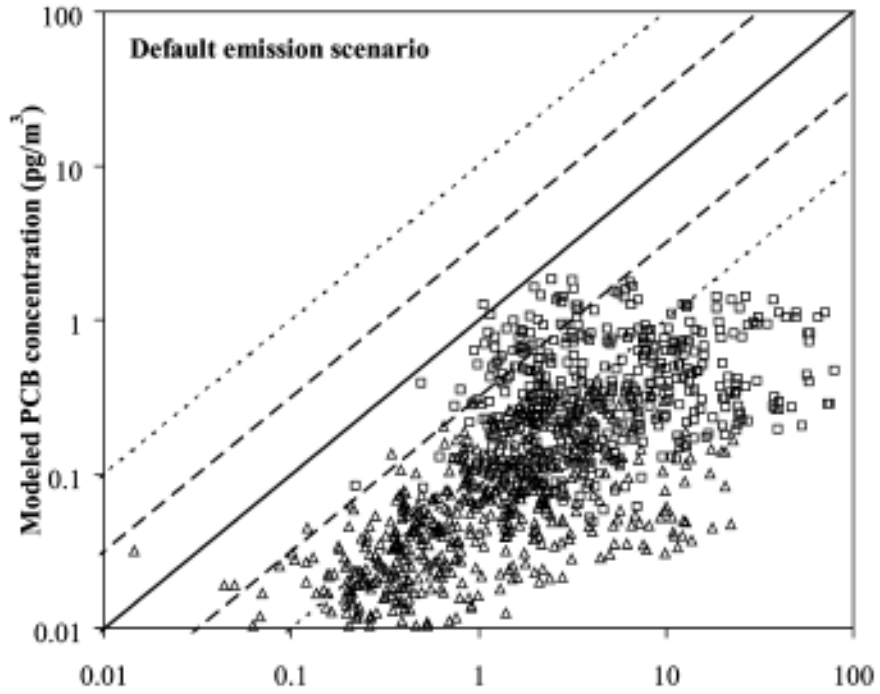
	hours	years
Overall residence time (Tov)	42851	4.89
Overall persistence (Pov)	58545	6.68
Overall advective time (Aov)	159852	18.25

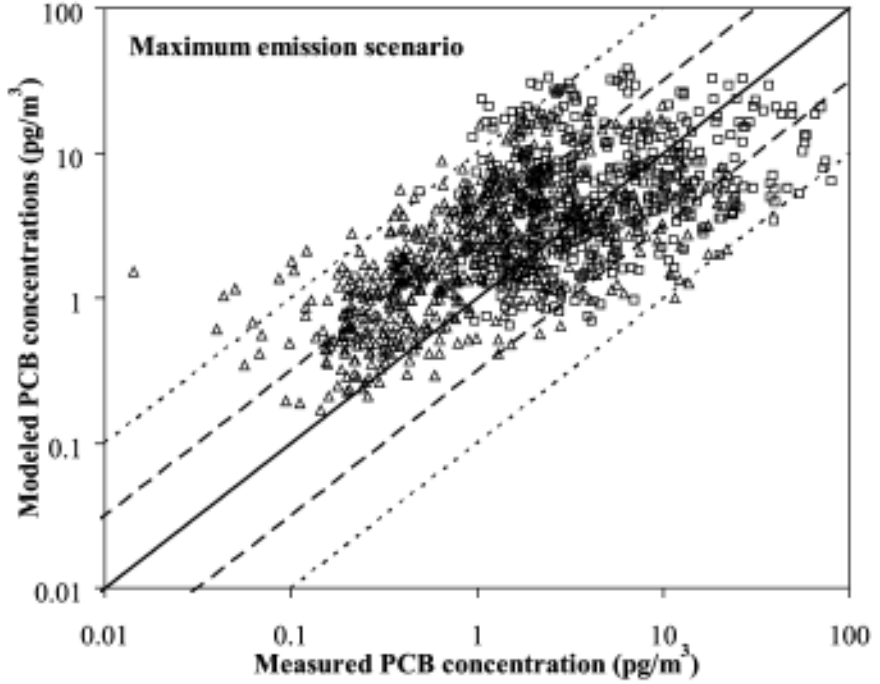
Ground-truthing with SmallWorld…



Ground-truthing with SmallWorld…







More detailed models agree…

Environ. Sci. Technol. **2009**, *43*, 5818–5824

Modeling the Global Levels and Distribution of Polychlorinated Biphenyls in Air under a Climate Change Scenario

LARA LAMON,[†,‡] HARALD VON WALDOW,[§] MATTHEW MACLEOD,[*,§] MARTIN SCHERINGER,[§] ANTONIO MARCOMINI,[†,‡] AND KONRAD HUNGERBÜHLER[§]

CMCC, Euro-Mediterranean Centre for Climate Change, Via Augusto Imperatore 16, 73100 Lecce, Italy, Department of Environmental Sciences, University Ca' Foscari of Venice, Calle Larga S. Marta 2137, 30123 Venice, Italy, and Safety and Environmental Technology Group, Swiss Federal Institute of Technology, Zürich, CH-8093, Switzerland

Received February 11, 2009. Revised manuscript received May 14, 2009. Accepted May 15, 2009.

We used the multimedia chemical fate model BETR Global to evaluate changes in the global distribution of two polychlorinated biphenyls, PCB 28 and PCB 153, under the influence of

So… Uncertainties in bottom-up emission estimates can bounded and reduced by evaluation them against observations with mass-balance models…

What about industrial chemicals where bottom-up estimates have not been made?

Short term (hourly) variability of concentrations in air could be used to estimate emission rates

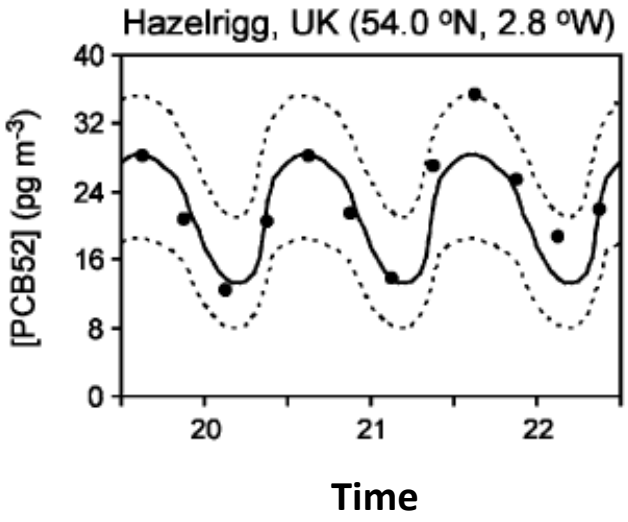
Environ. Sci. Technol. **2007**, *41*, 3249–3253

The Origin and Significance of Short-Term Variability of Semivolatile Contaminants in Air

MATTHEW MACLEOD,*,† MARTIN SCHERINGER,† HEIKE PODEY,† KEVIN C. JONES,‡ AND KONRAD HUNGERBÜHLER†

Institute for Chemical and Bioengineering, ETH Zurich, CH-8093, Zurich Switzerland, and Centre for Chemicals Management and Environmental Science Department, Lancaster Environment Centre, Lancaster University, LA1 4YQ, United Kingdom.

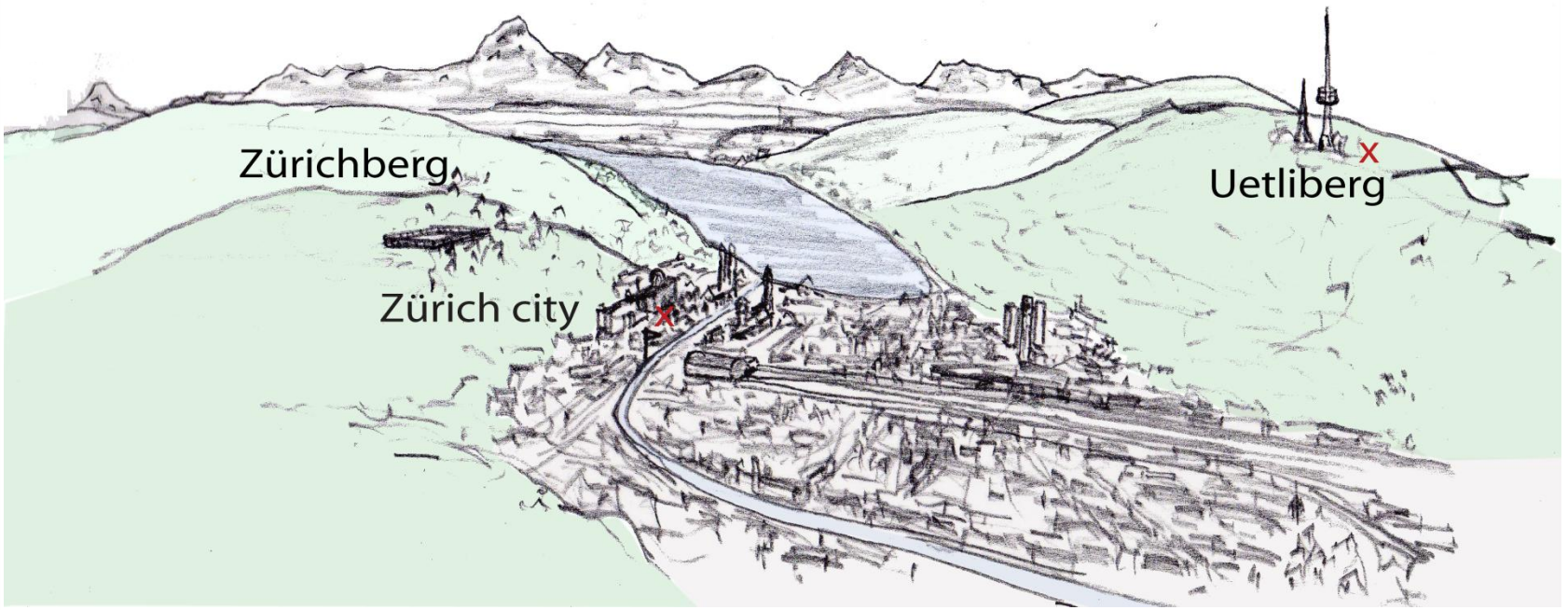
Persistent semivolatile contaminants such as polychlorinated biphenyls (PCBs) cycle between air and surface media



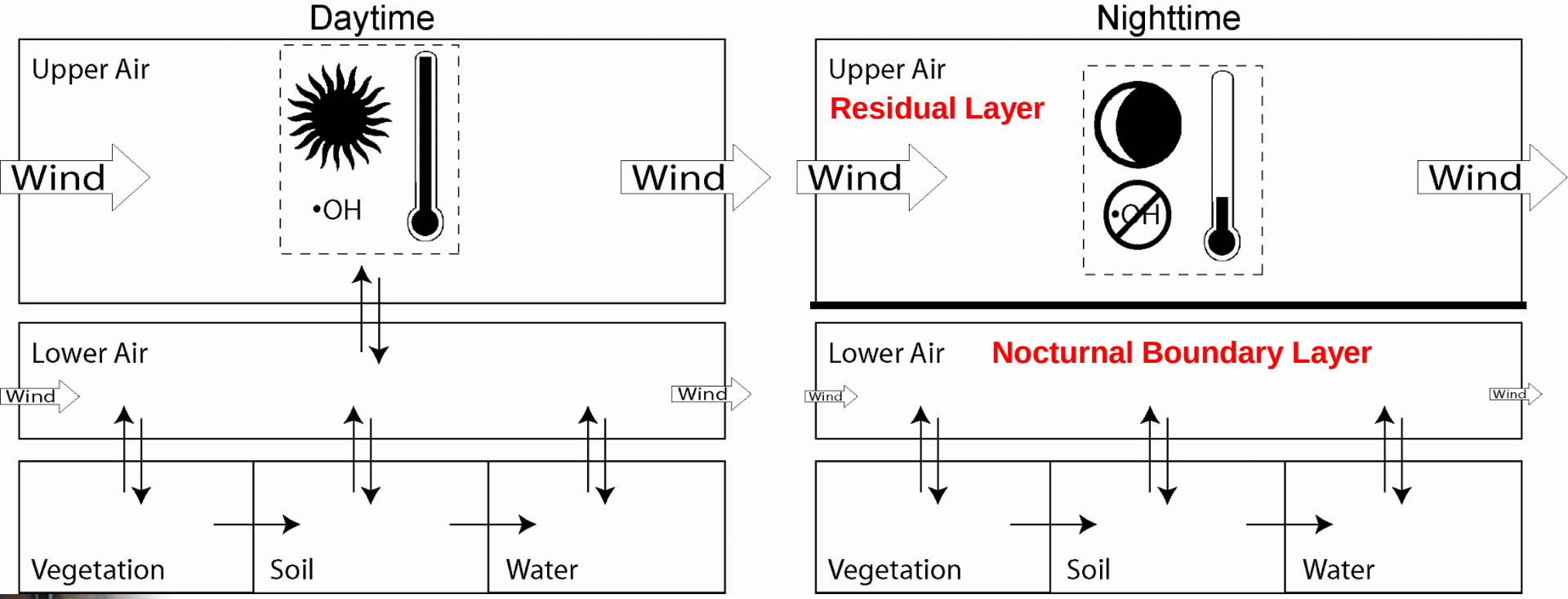
Diel (24-hour) cycles that may affect concentrations of SVOCs in air

- Temperature
- Hydroxyl radical concentration
- Boundary layer height and stability
- Wind speed

Zurich in summer time as a microcosm for Europe…



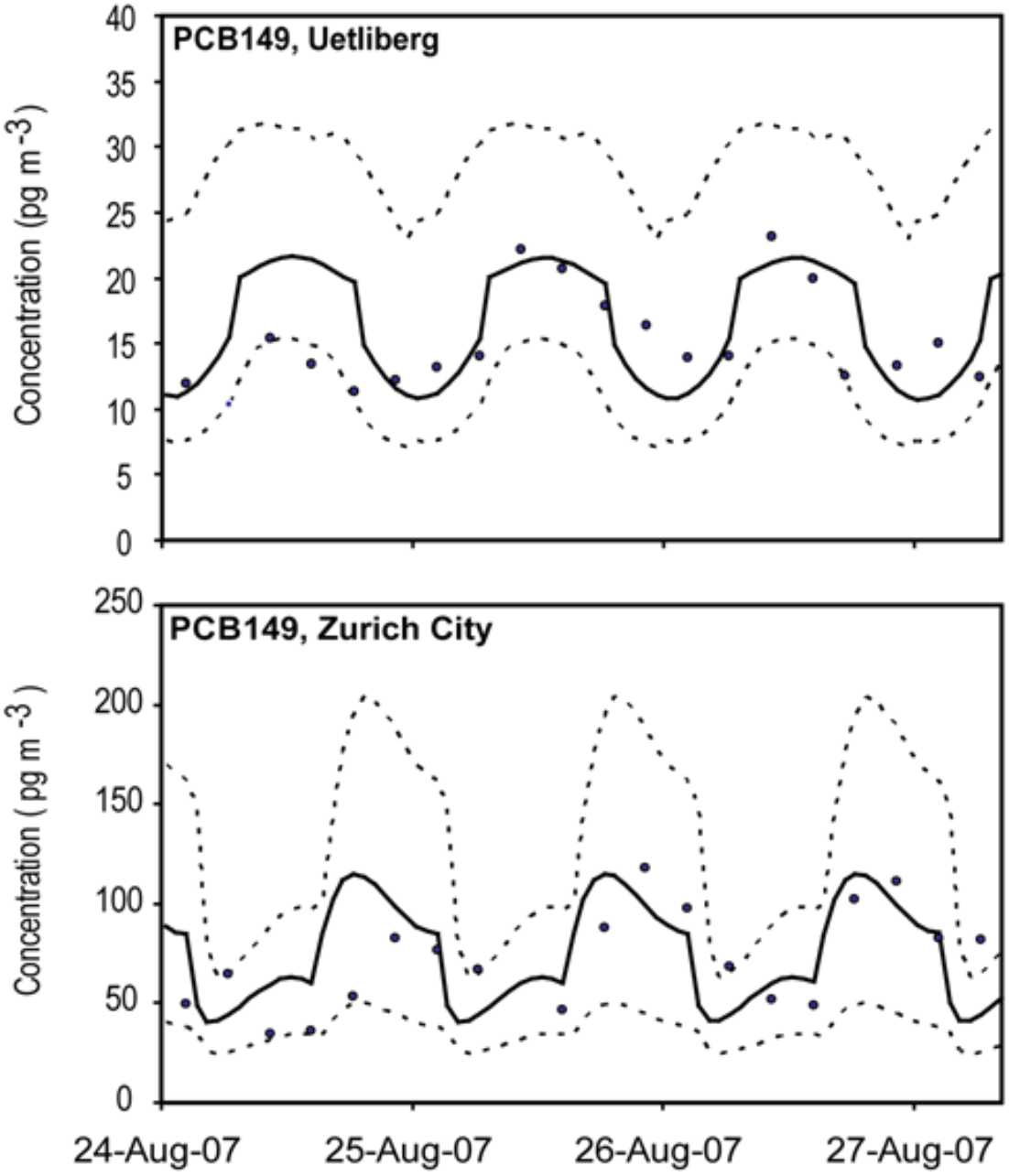
Model structure to investigate diel pollutant dynamics



MacLeod et al. *Environmental Science & Technology*, 41(9), 3249 - 3253, **2007**.

Zurich field campaigns 2007, 2009 & 2011

- Two sampling sites:
  - City site: Zurich ~450 m
  - Hill site, background: Uetliberg ~850m

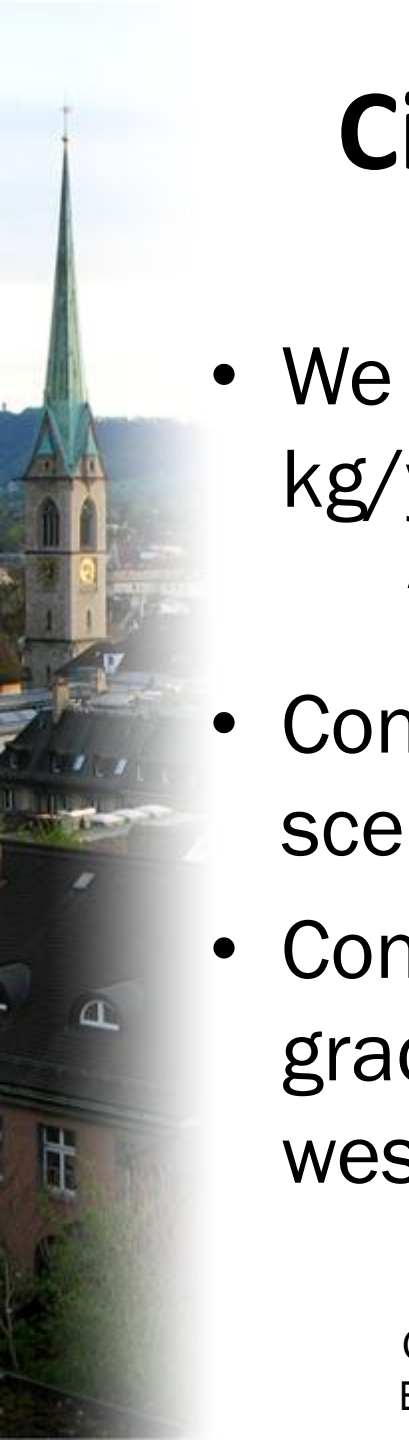


PCBs

Uetliberg

City site

Gasic et al. *Environmental Science & Technology*, 43(3), 769 - 776, **2009**.



Cities are sources of POPs

- We estimate that the city of Zurich emits 15 kg/y* of PCBs to the atmosphere.

  * ± factor 2
- Consistent with Breivik's 'max' emission scenario
- Consistent with urban-rural concentration gradients in cities in North America and western Europe

Gasic et al. *Environmental Science & Technology*, 43(3), 769 - 776, **2009**.
Bogdal et al. *Environmental Science & Technology*, 48(1), 482-490, **2014.**

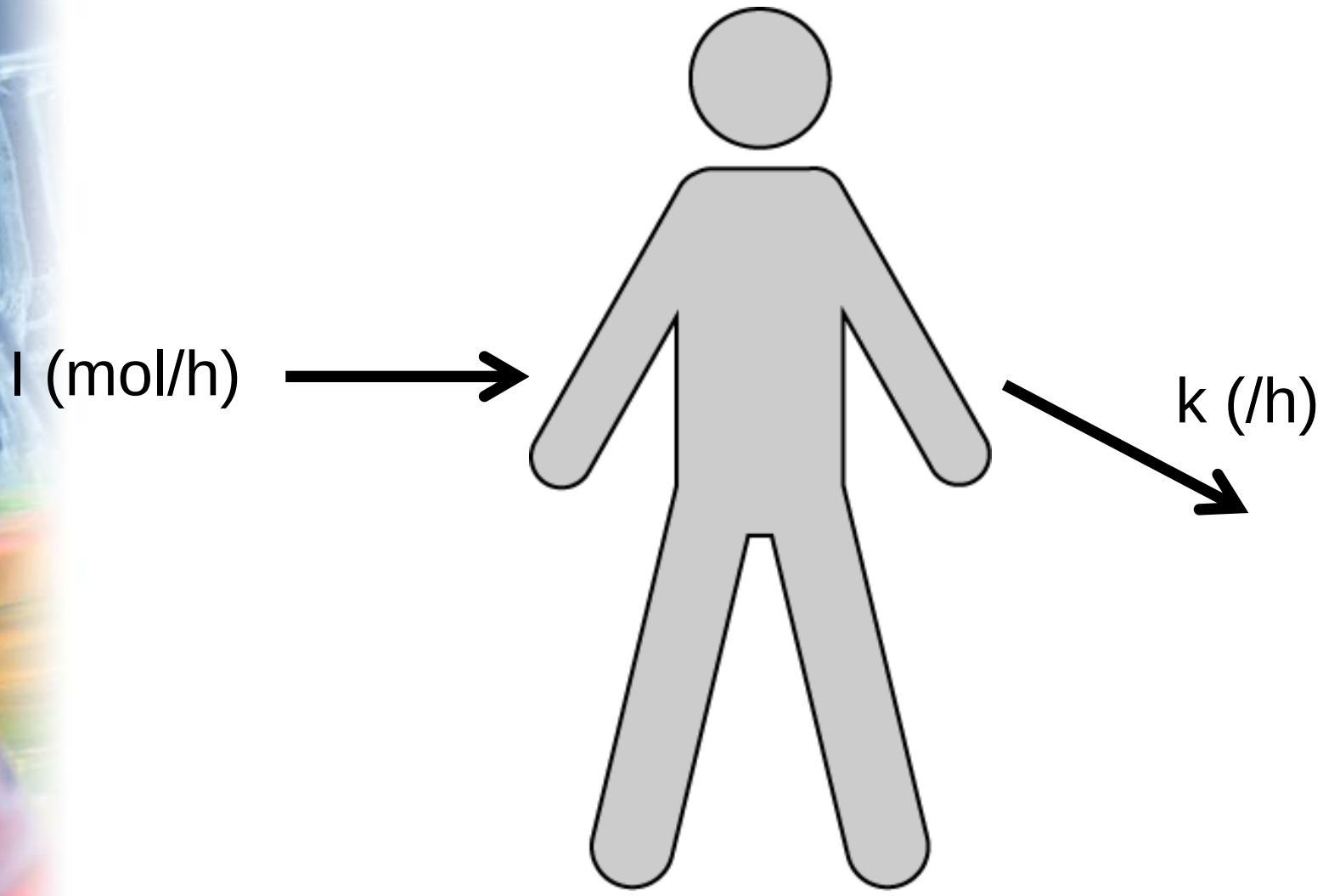
Cities are sources of POPs

- Brominated flame retardants (Moeckel et al. 2010)
  - Zurich emits ~10 kg/y of four congeners of PBDEs to the atmosphere
- Perfluorinated substances (Wang et al. 2011)
  - 8:2 FTOH (23 kg/y) 10:2 FTOH (7 kg/y)
  - MeFOSA (0.7 kg/y) EtFOSA (0.4 kg/y)
- Siloxanes (Buser et al. 2013)
  - Zurich emits 44 000 kg/y of D5 and 5 000 kg/y D6
- Other applications…

Combining measurements and models to understand emissions, fate, exposure and pharmacokinetics of POPs

3. Population-level exposure and pharamacokinetics

A very simple model…



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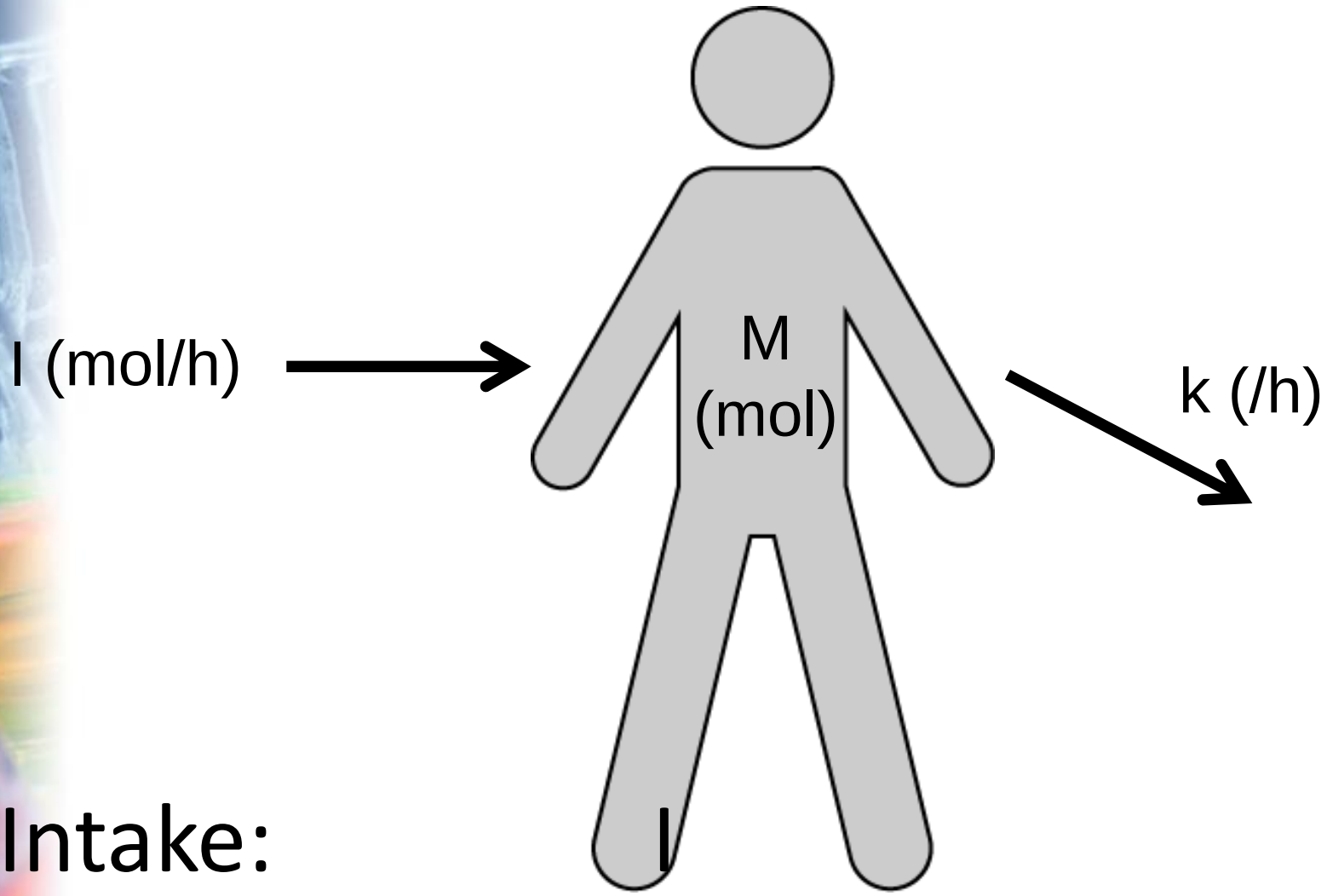
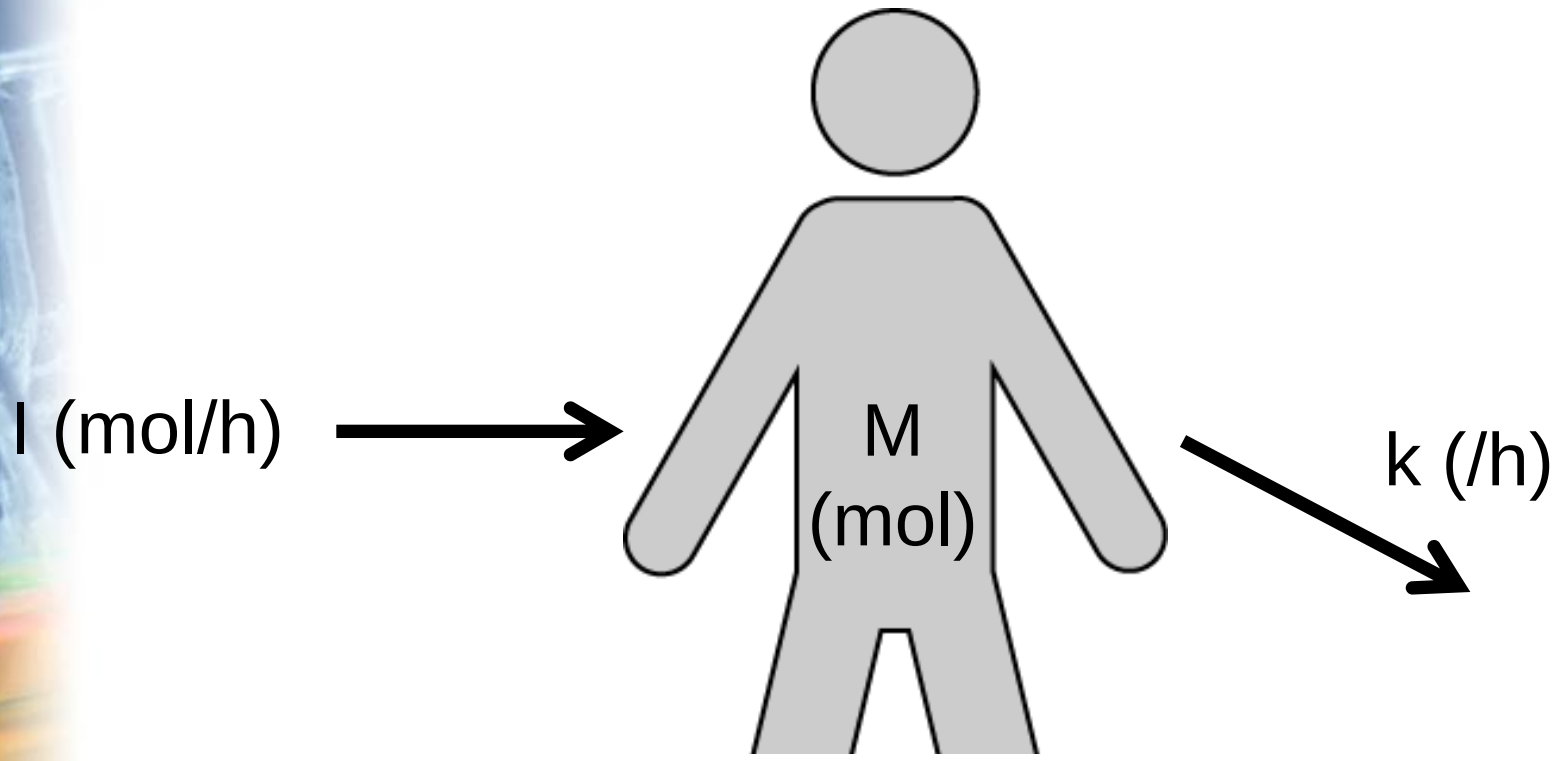


Intake: I

Clearance: M×k

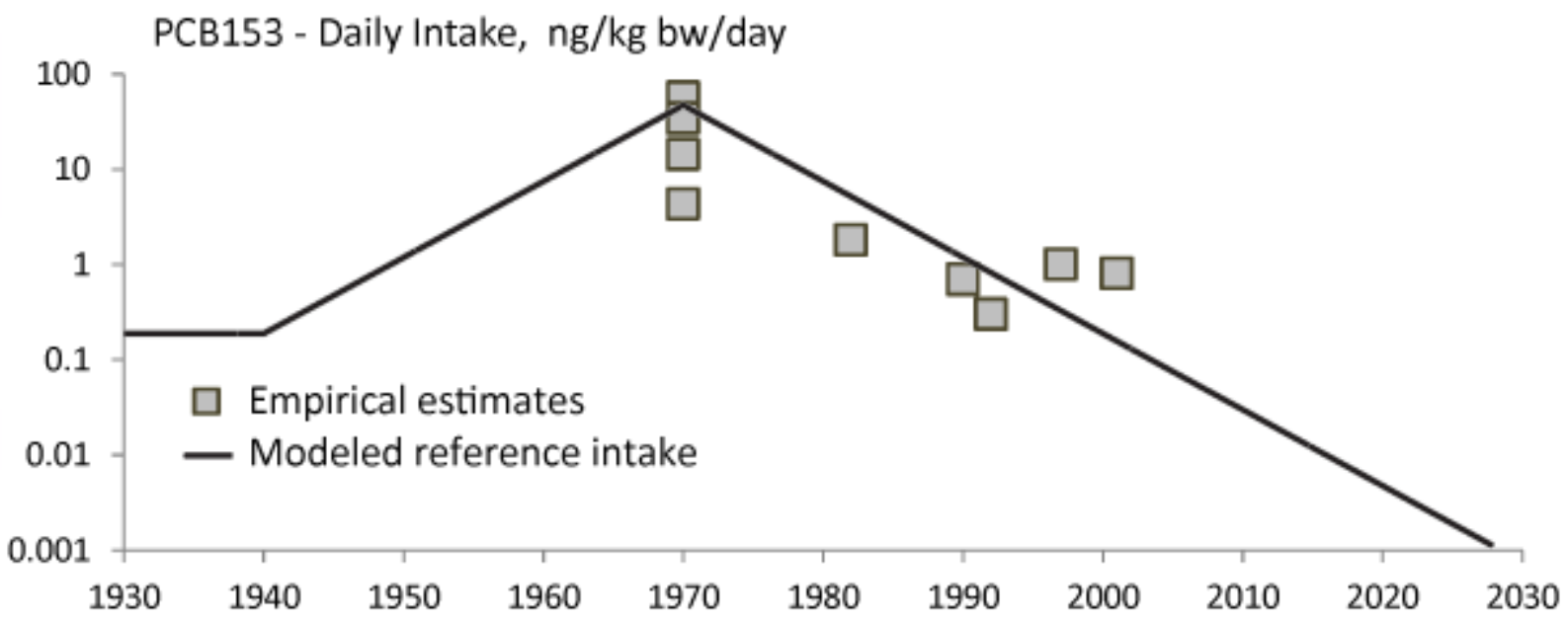


- Rates of intake (I) and whole-body clearance (k) are often highly uncertain, but in some cases we have good measurements of body burdens (M) from biomonitoring.

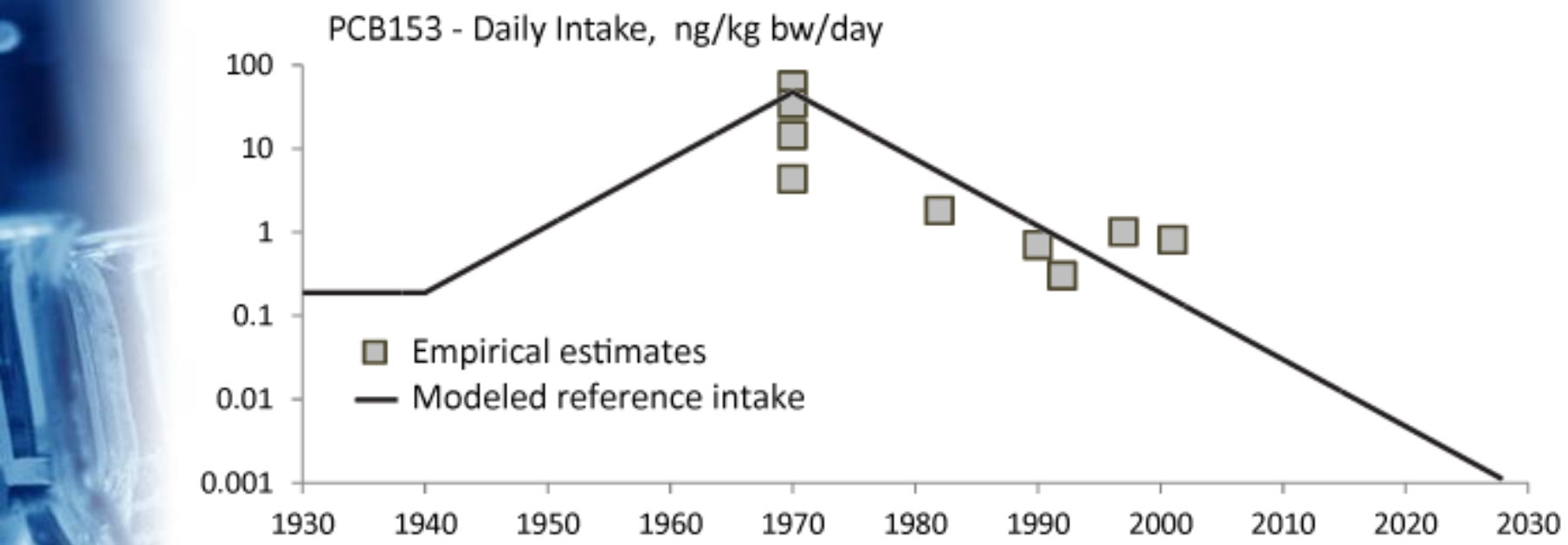
Case Study 1: PCBs in the UK population

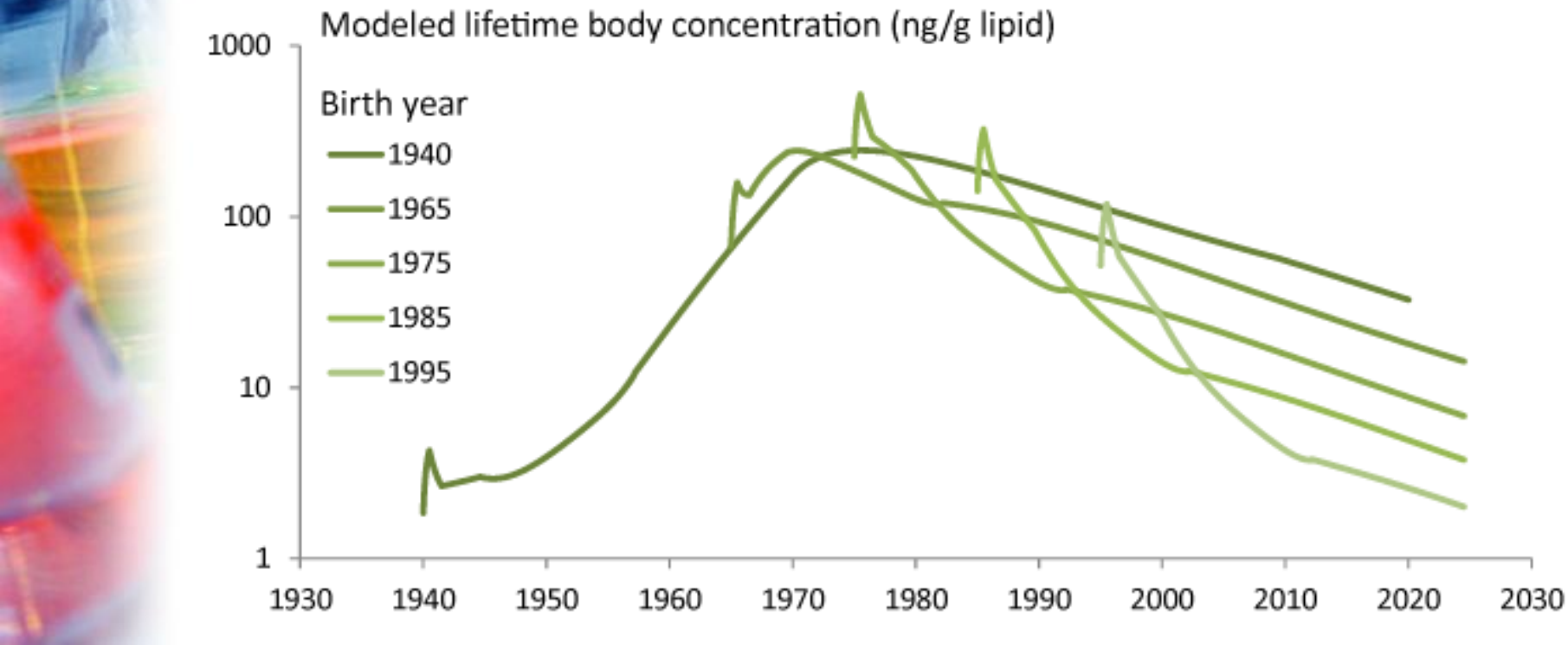
- Biomonitoring
  - Cross-sectional data from the entire population for 1990 & 2003
- Exposure
  - Results from 9 total diet studies between 1970 & 2002
- Elimination
  - Estimated elimination half-lives for different PCBs from weeks to years

Ritter et al. 2011. Environmental Health Perspectives 119 (2) 225.



PCB153 Exposure Studies


PCB153 - Daily Intake, ng/kg bw/day
100
10
1
0.1
0.01
0.001
Empirical estimates
Modeled reference intake
1930
1940
1950
1960
1970
1980
1990
2000
2010
2020
2030

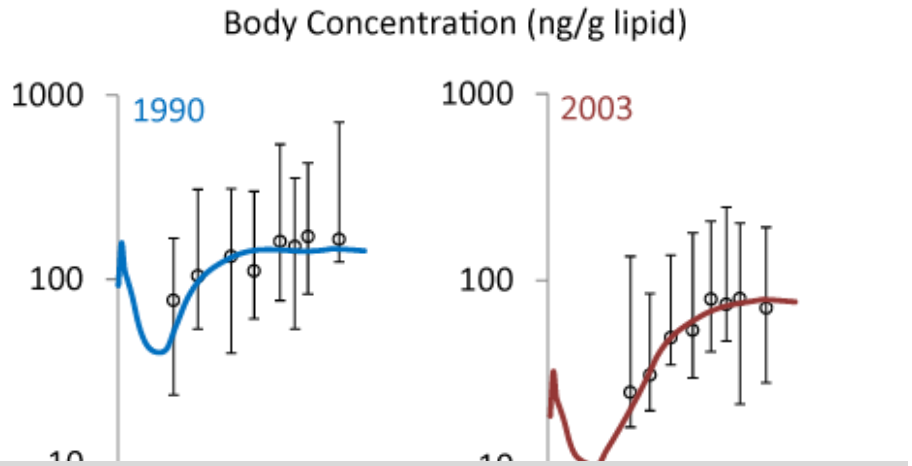

Modeled lifetime body concentration (ng/g lipid)
1000
100
10
1
Birth year
1940
1965
1975
1985
1995
1930
1940
1950
1960
1970
1980
1990
2000
2010
2020
2030

PCB153

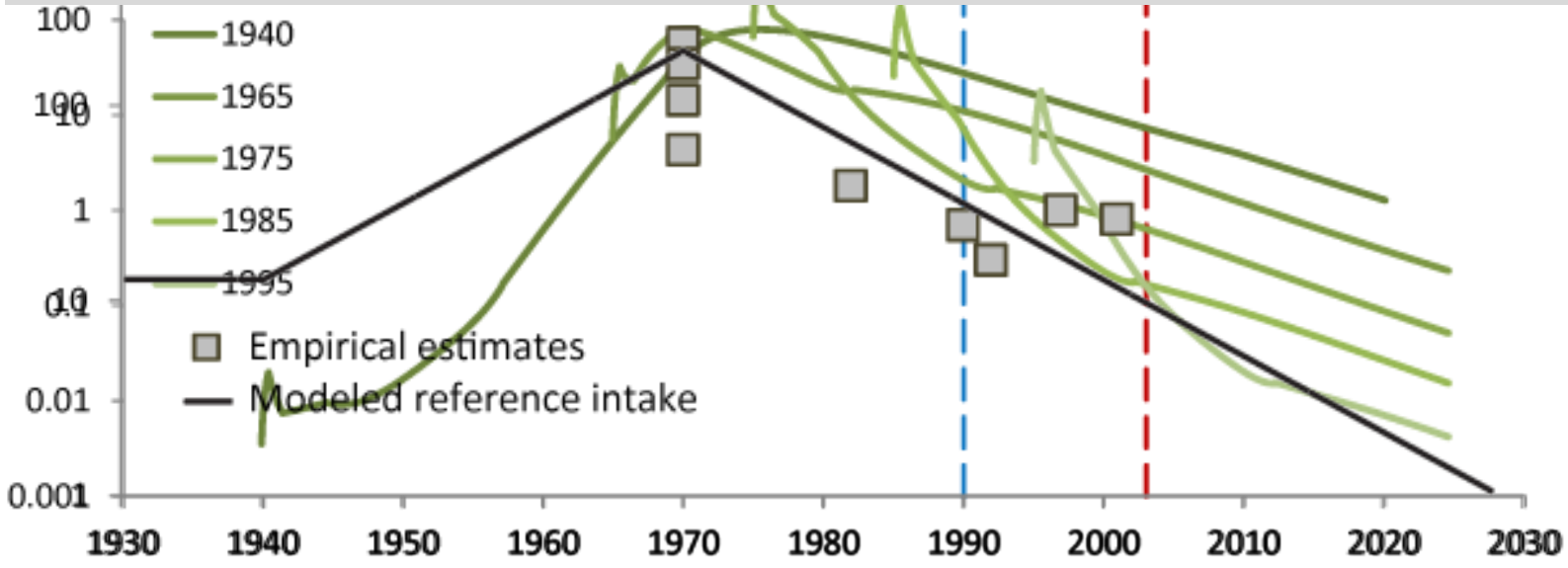
Biomonitoring and exposure data for PCB 153 can be fit simultaneously

Biomonitoring data

Human elimination half-life:



Similar story for 8 other PCB congeners



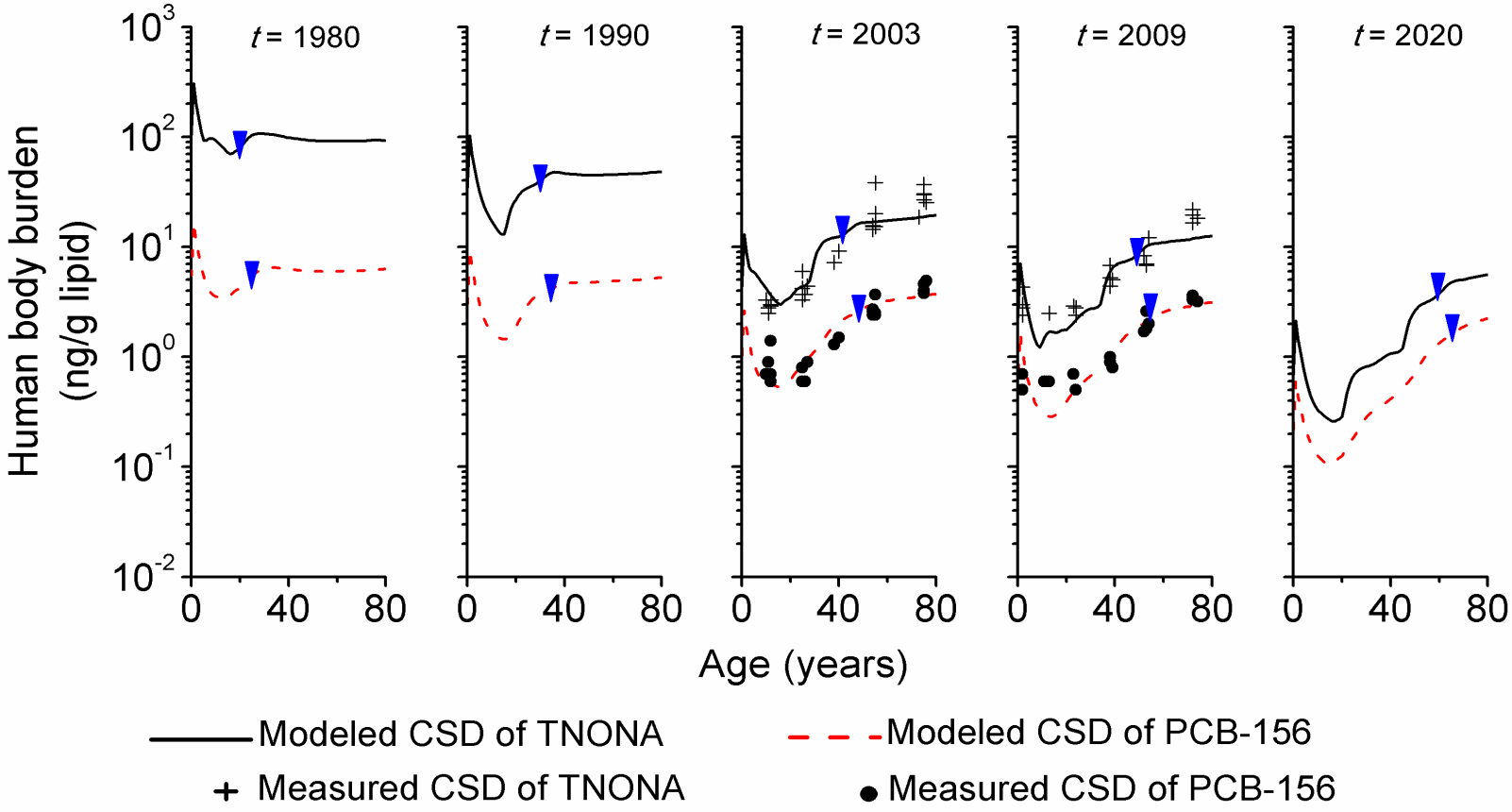
PCBs in the UK population

Is our empirical understanding of exposure, body concentration and elimination self-consistent?

- Yes!
  - Good model fits to intake estimates and biomonitoring data for 9 PCB congeners
  - Model-fitted human elimination half-lives between 3 and 16 years for different PCB congeners

Ritter et al. 2011. Environmental Health Perspectives 119 (2) 225.

PCBs in the Australian Population



Bu et al. *Environment International* (in revision).

PCBs in the Australian Population

- Human elimination half-lives for PCBs are similar in the UK and Australia, but perhaps a bit longer in Australians
- Peak intake of PCBs in Australia was 7-20 times lower than peak intake in the UK, and 60 times lower for PCB 180
- Intake follows a similar temporal trend in the UK and Australia

Bu et al. *Environment International* (in revision).

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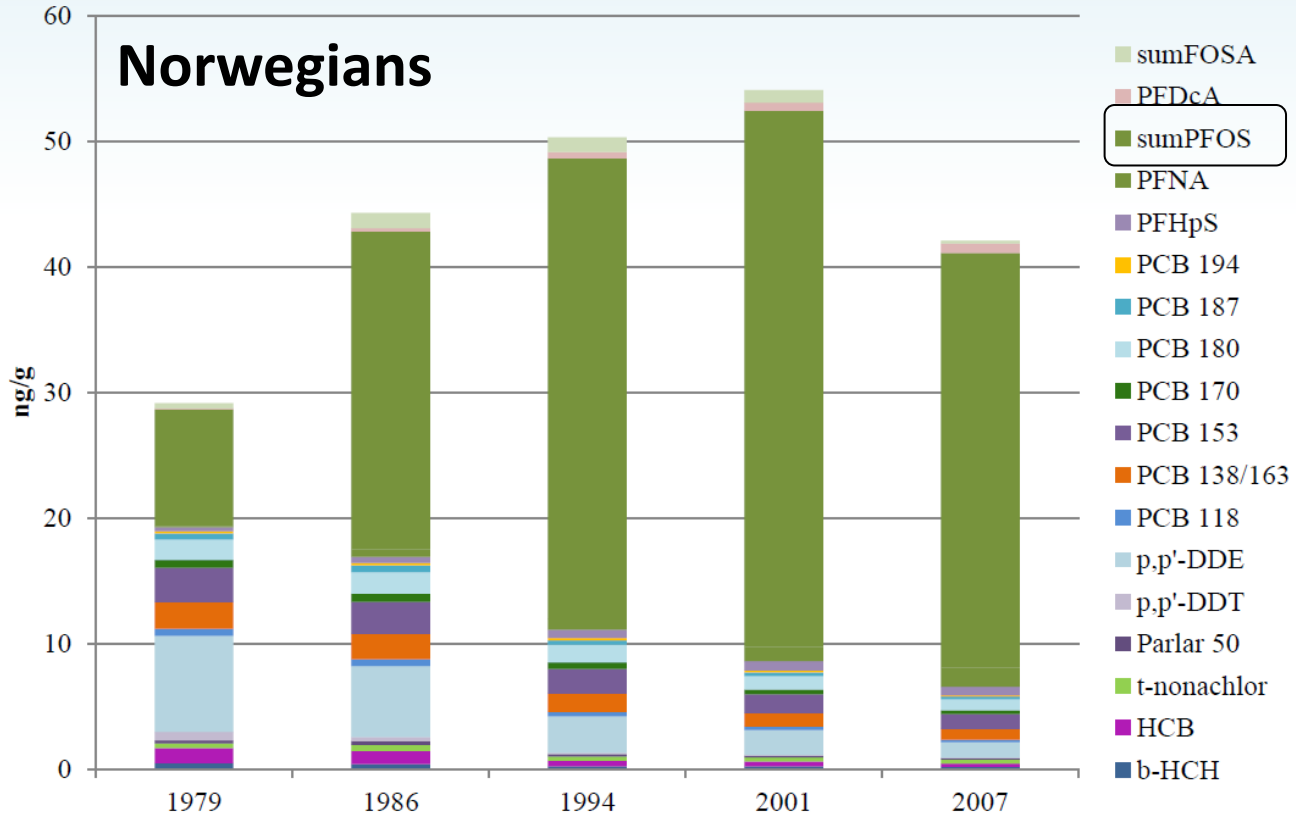
Trivia Challenge:

Which POP is most abundant in the bodies of Europeans?

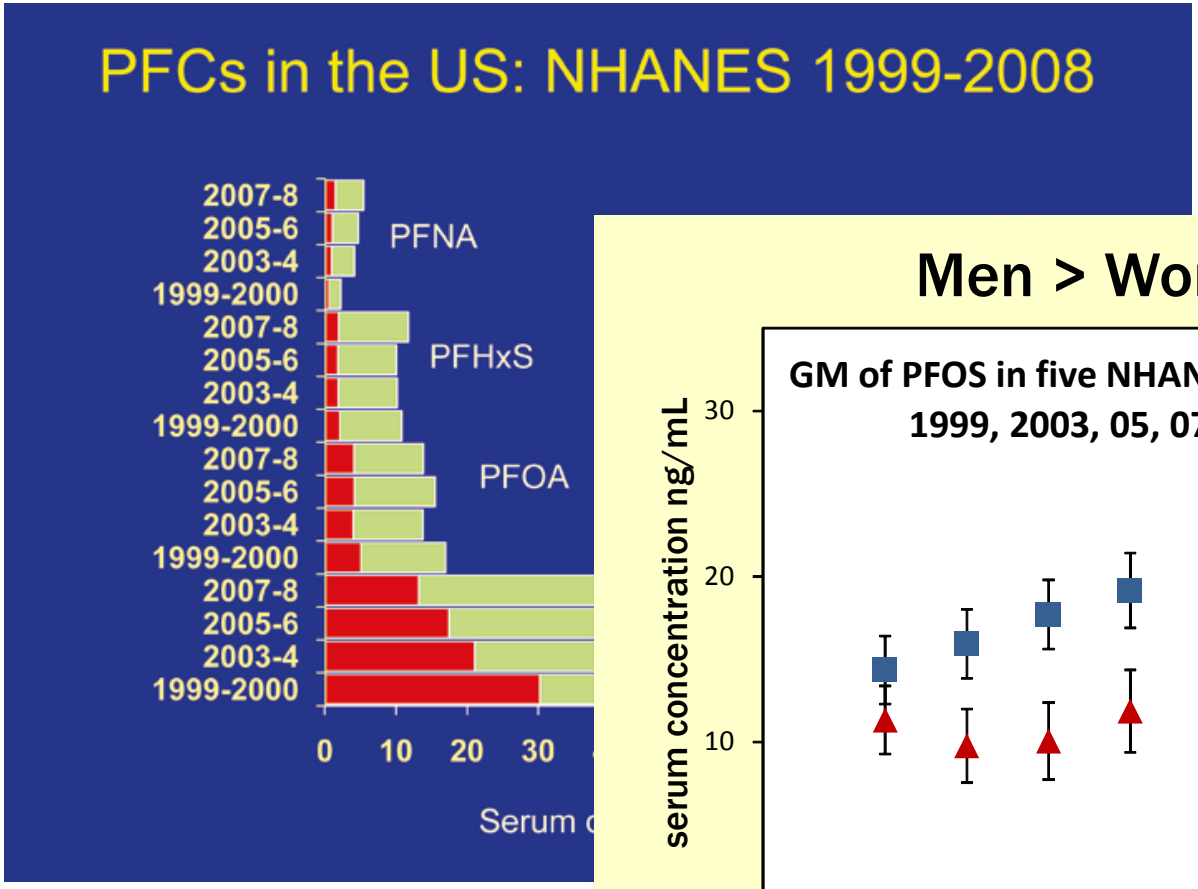
PFOS (Perfluorooctane sulfonate)

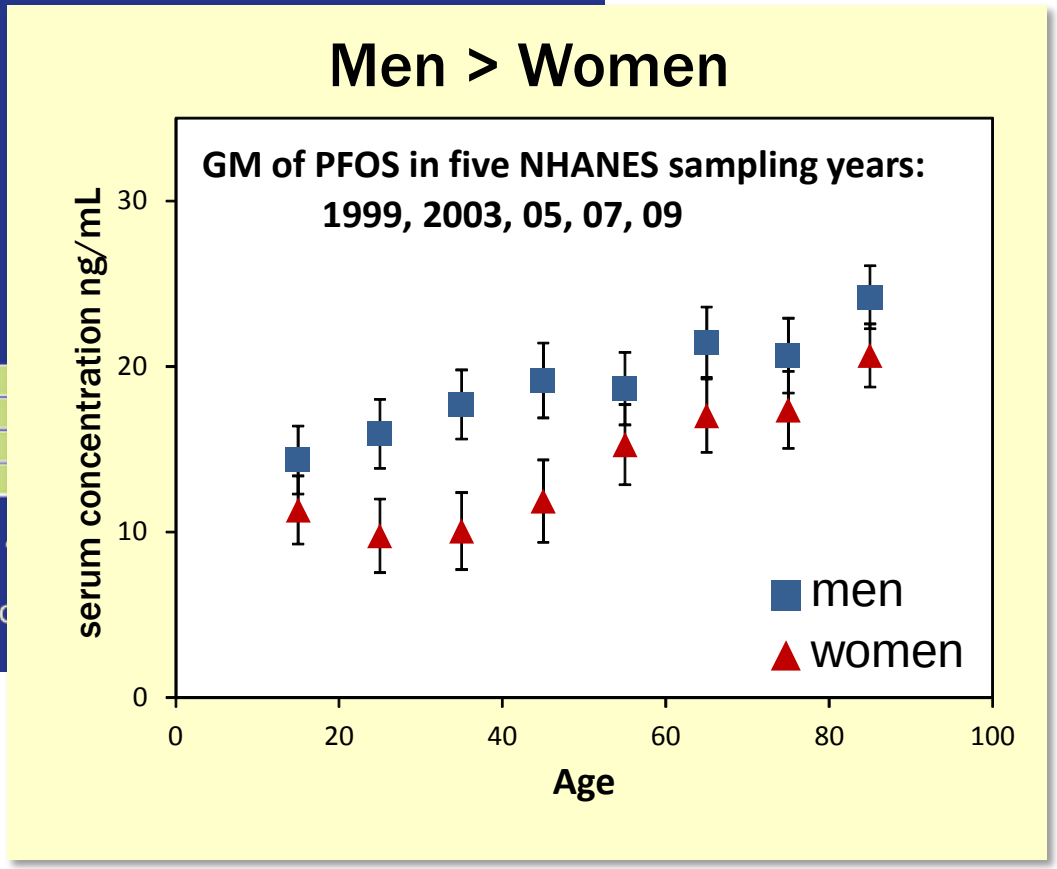


TH Nøst et al. / Environmental Health Perspectives (2013) 121:1292-1298 and unpublished results

Most abundant POPs measured in humans

Case Study 2: PFOS in US population





Research Question:

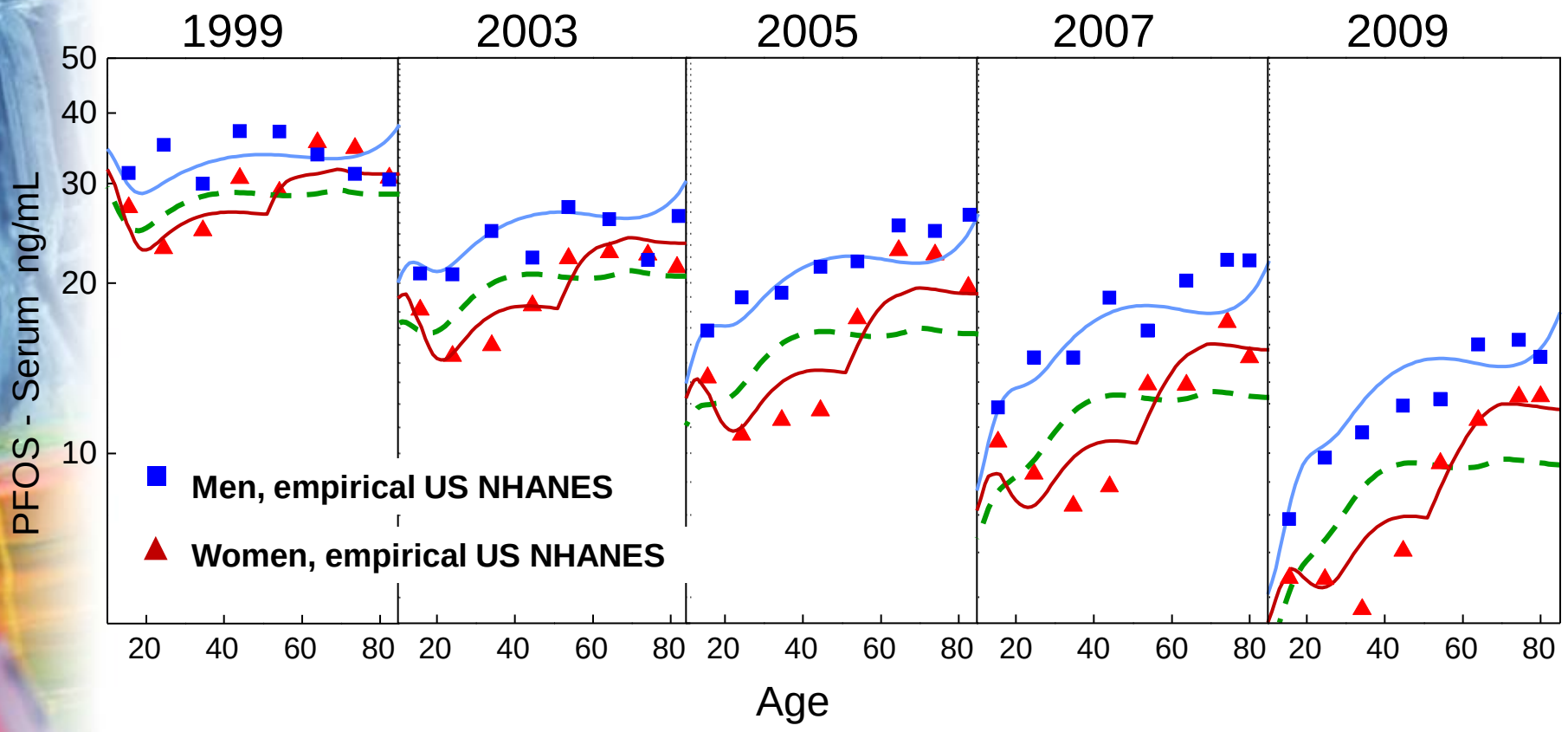
PFOS is known to bind to serum blood proteins…

Is there enhanced elimination of PFOS by menstruating women?

What is the elimination rate of PFOS for:

- Men
- Women (menstruating and non-menstruating)

Model Results

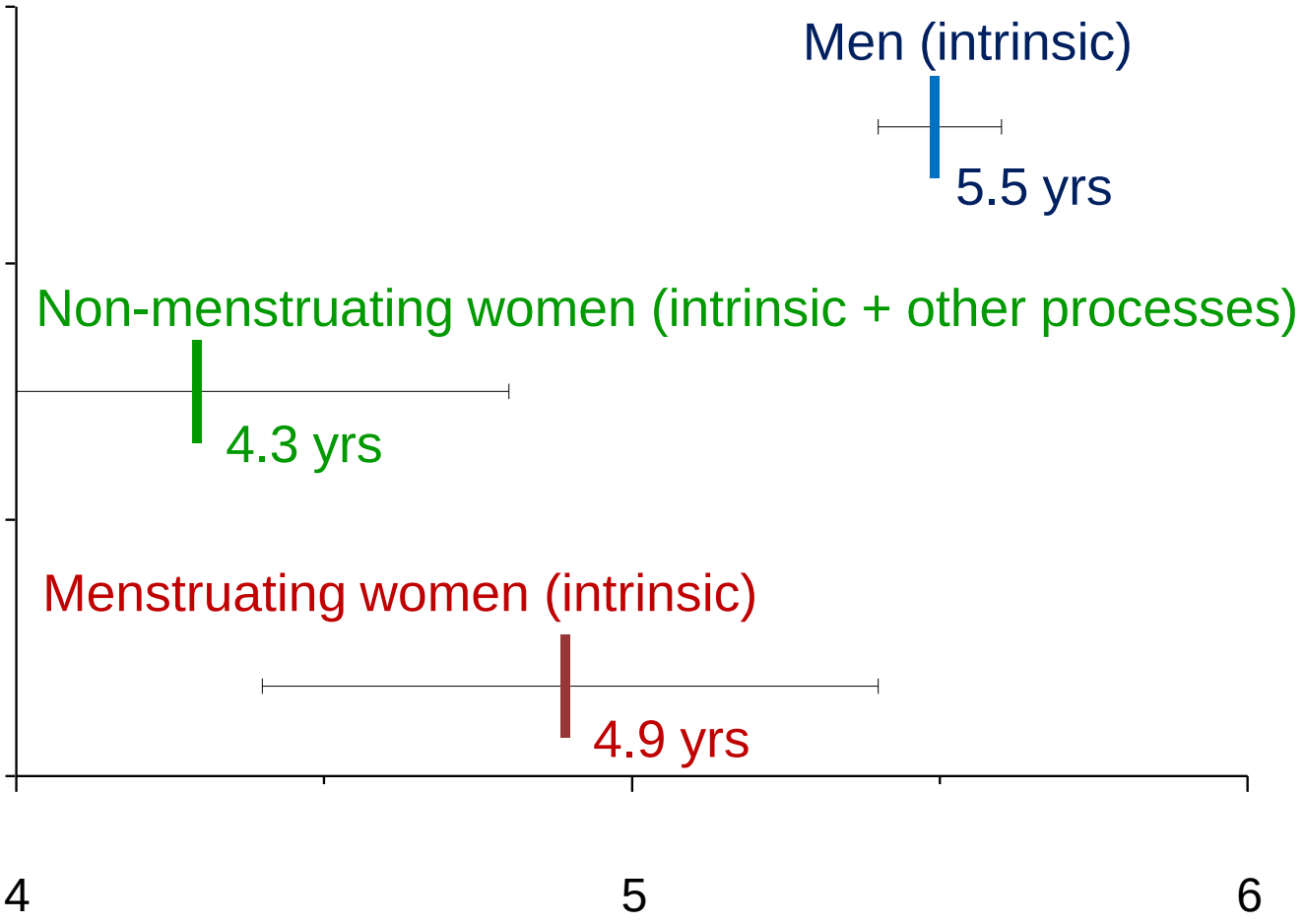


Men, modeled – HL 5.5 years

Women (*non-menstruating*), modeled – HL 4.3 years

Women (*menstruating*), modeled – HL 4.9 years

Model Results



PFOS Half-life in US population

Research Question:

Is there enhanced elimination of PFOS by menstruating women?

Elimination HL of PFOS in women is shorter than in men by 25%

Yes, but…

Menstruation only accounts for 12% of the 25% difference.

The remaining difference between men and women may be due to:

- Sex-specific elimination route (renal?)
- Model uncertainty

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Acknowledgments

- Swiss Federal Agency for the Environment (BAFU)

INFLAME

INTERFLAME

The State of Multimedia Mass-Balance Modeling in Environmental Science and Decision-Making

MATTHEW MACLEOD*
MARTIN SCHERINGER*
ETH Zurich, Switzerland

THOMAS E. MCKONE
Lawrence Berkeley National Laboratory, University of California Berkeley, Berkeley, California

KONRAD HUNGERBUHLER
ETH Zurich, Switzerland

Are multimedia models dinosaurs in the modern world?