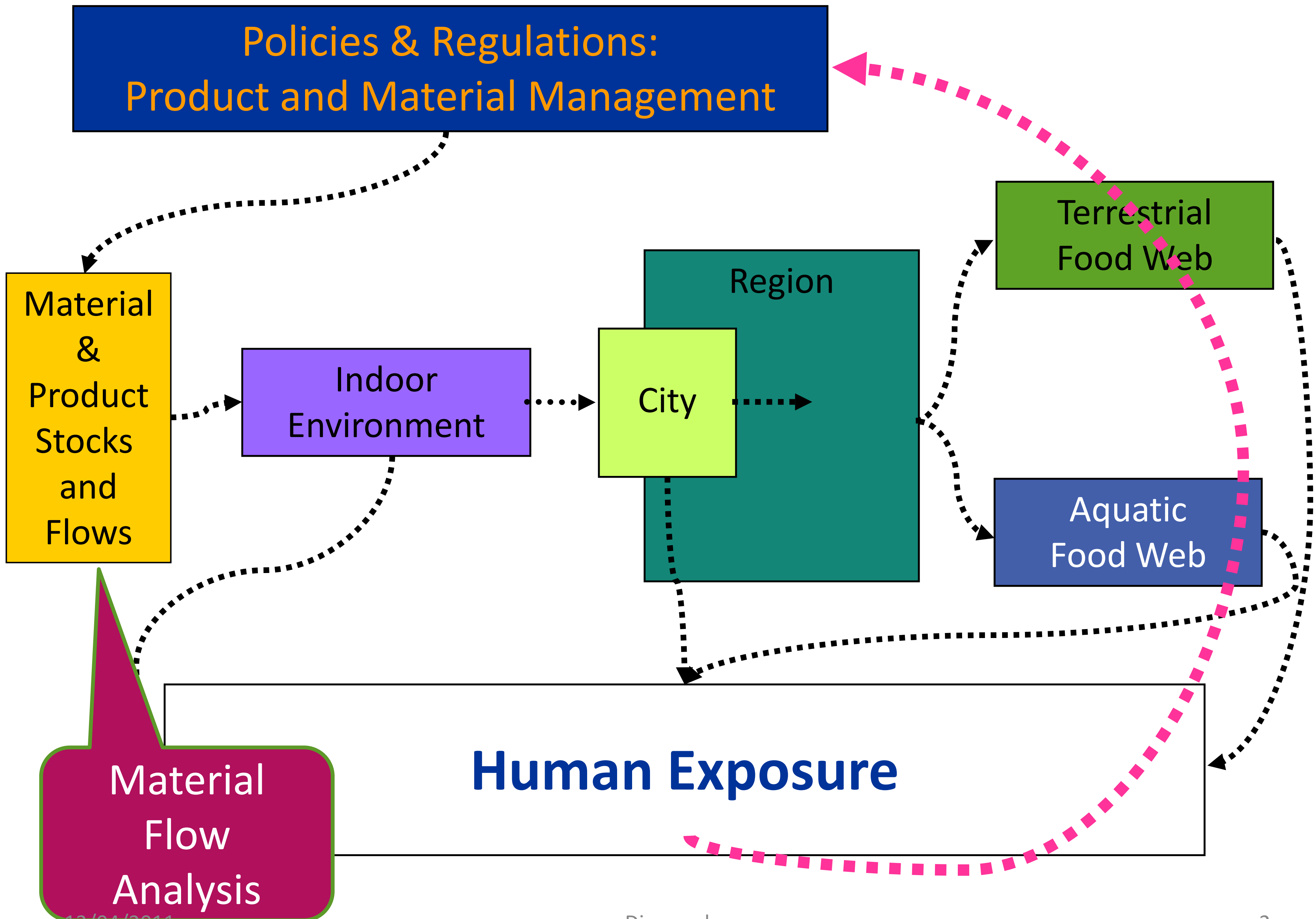
DAY 2: Source ⇨ Emission ⇨ Fate ⇨ Exposure ⇨ Toxicity⇨ Policy

1. Phthalates
   - Exposure
   - Toxicity
2. <u>Polybrominated diphenyl ethers (PBDEs) & Polychlorinated biphenyls</u>
   - Material Flow Analysis (MFA)
   - Indoor Environment
   - Urban Environment
3. PBDEs & Bisphenol A
   - Food web transfer
   - Modelling Made Easy


Policies & Regulations:
Product and Material Management
Material & Product Stocks and Flows
Indoor Environment
Region
City
Terrestrial Food Web
Aquatic Food Web
Human Exposure
Material Flow Analysis

Polybrominated Diphenyl Ethers

~~Penta~~	• Textiles, PUF, paint, household plastic product[illegible] automotive parts • BDE-99, 47, 1[illegible]
~~Octa~~	• ABS plastic fo[illegible] circuit boards, [illegible] • BDE-153, 154
Deca	• Electrical & e[illegible] equipment casings for TVs[illegible] backings (e.g., [illegible] • BDE-209

2004
•EU banned production & use in consumer goods
•US agreement to stop production

2008
•EU banned use in electrical & electronic goods
2011
• Canada to ban use in electrical & electronic goods

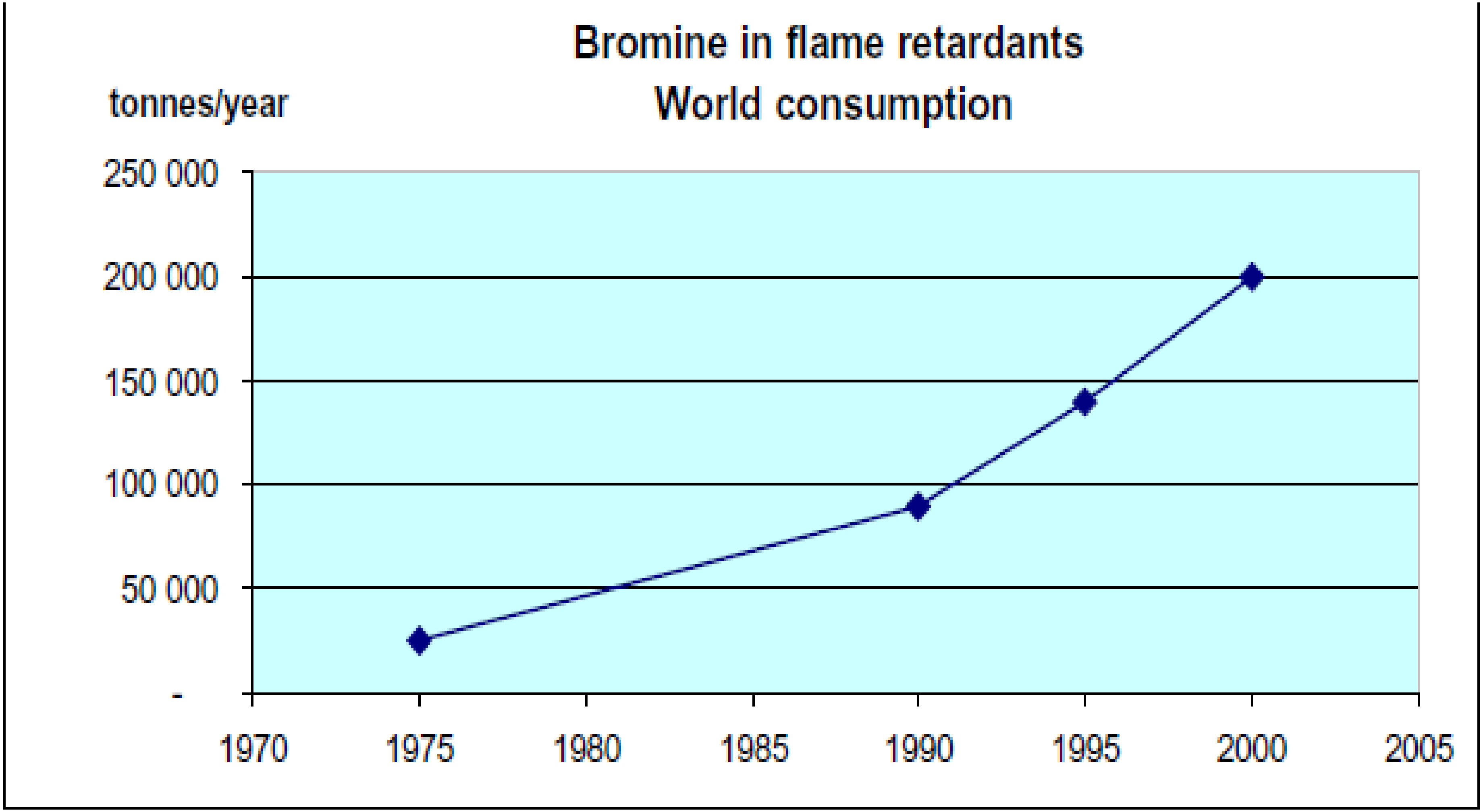
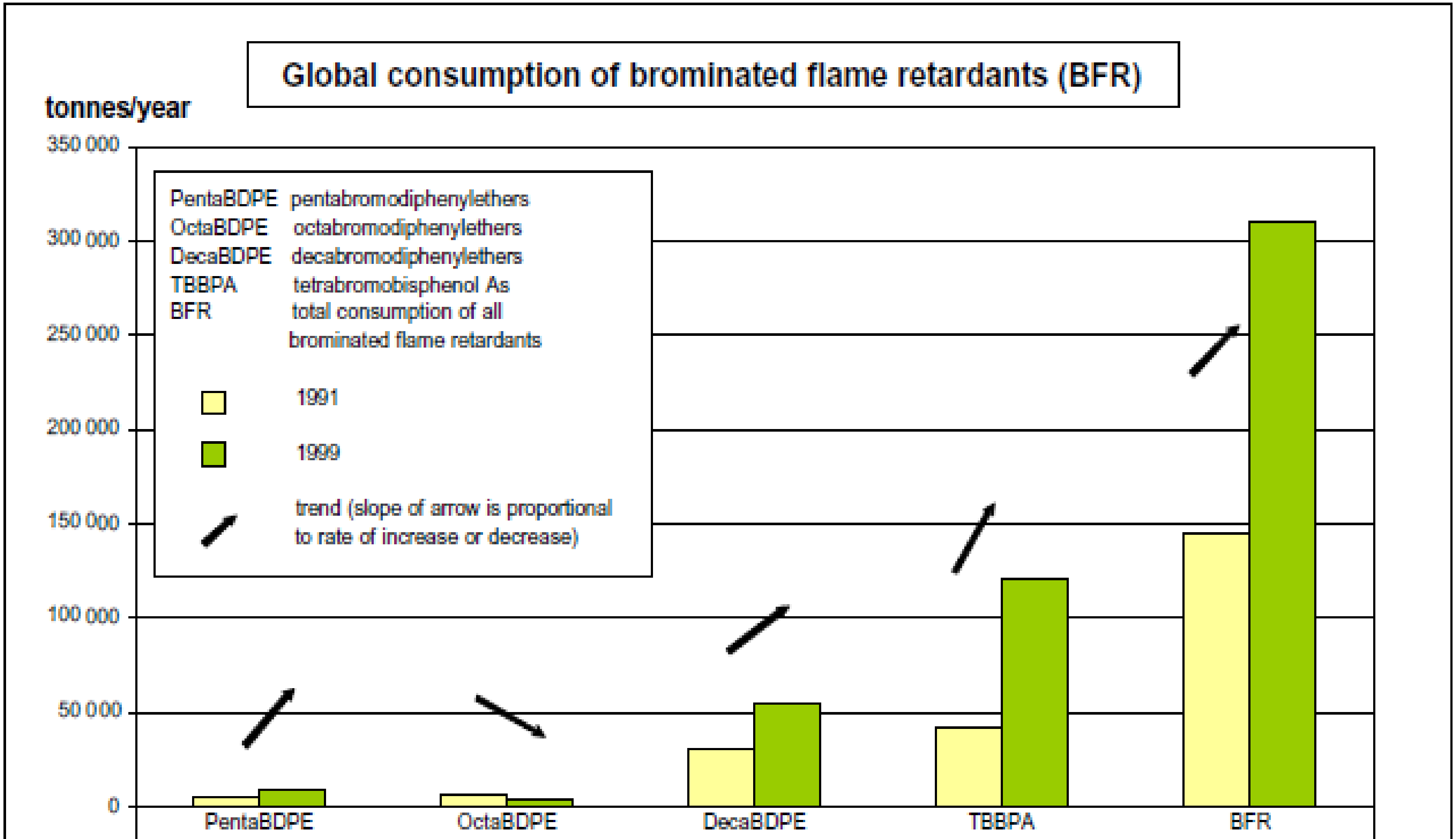


Fig. 3-1: Annual consumption of bromine in the production of flame retardants [Arias, 2001]

Annual growth rate of ~4% per year

Morf et al. 2003



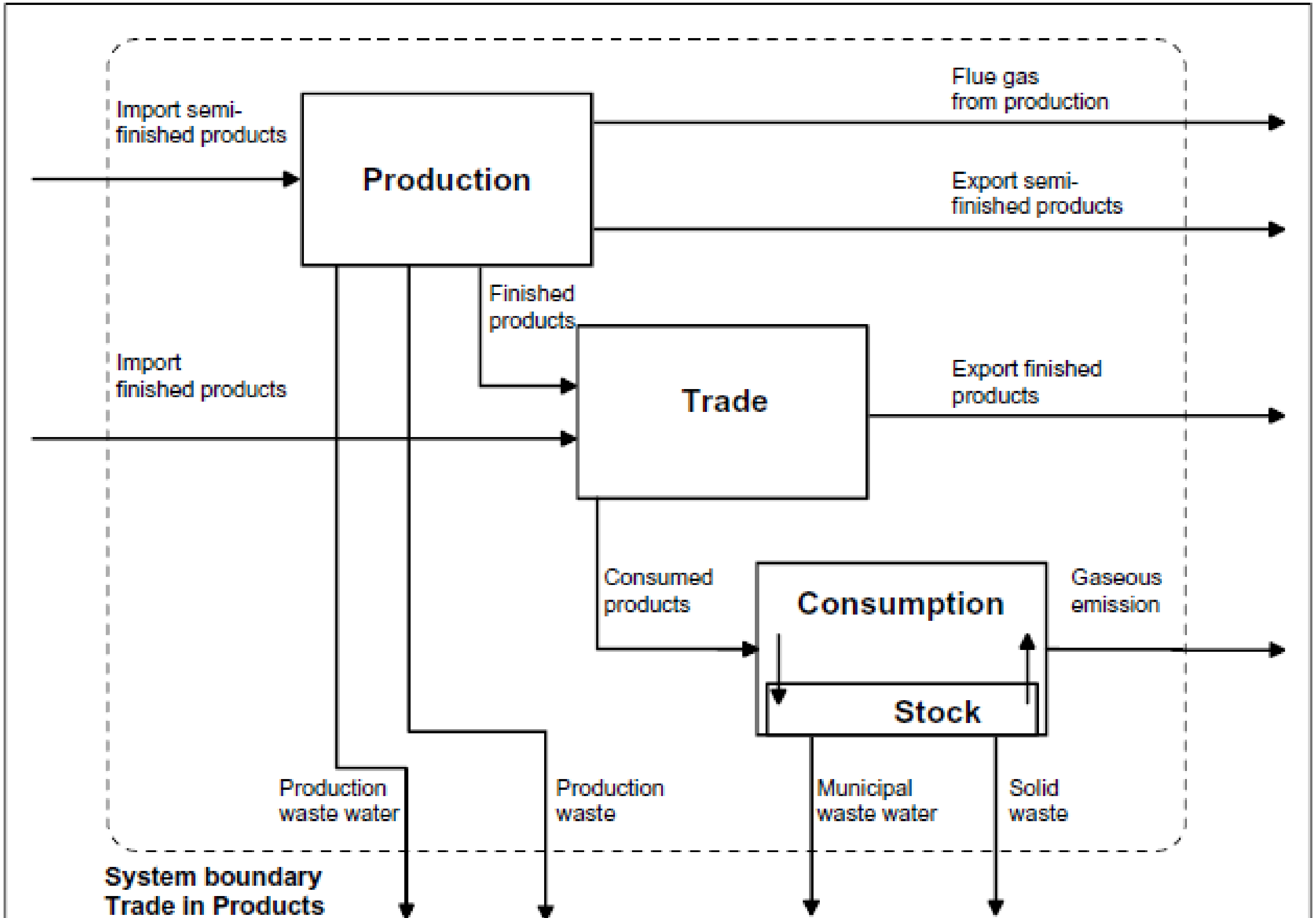
	PentaBDPE	OctaBDPE	DecaBDPE	TBBPA	BFR
1991	4 000	6 000	30 000	41 000	145 000
1999	8 500	3 825	54 800	121 300	310 000

Figure 1: Comparison of world consumption for selected BFR (sources: TBBPA 1991 [OECD, 1994], PBDEs 1991 [IPCS 1994b], TBBPA + PBDEs 1999 [Leisewitz & Schwarz, 2000], total BFR: values for 1990 and 2000 [Arias, 2001]).

Morf et al. 2003

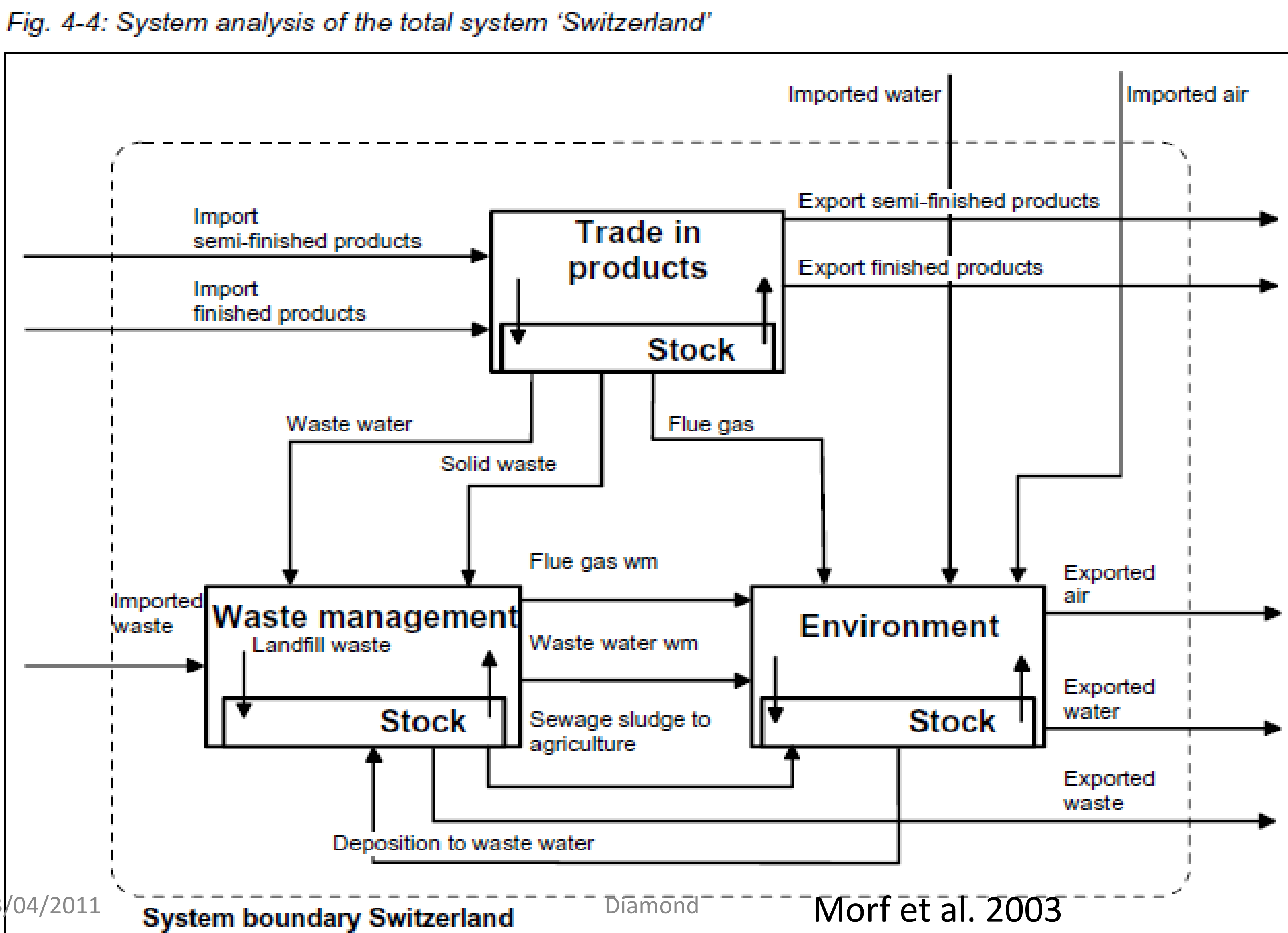
Material Flow Analysis of a Product

Fig. 4-1: System analysis of the subsystem 'trade in products'



Morf et al. 2003

Material Flow Analysis for a Country



Morf et al. 2003

Material Flow Analysis of Penta BDE

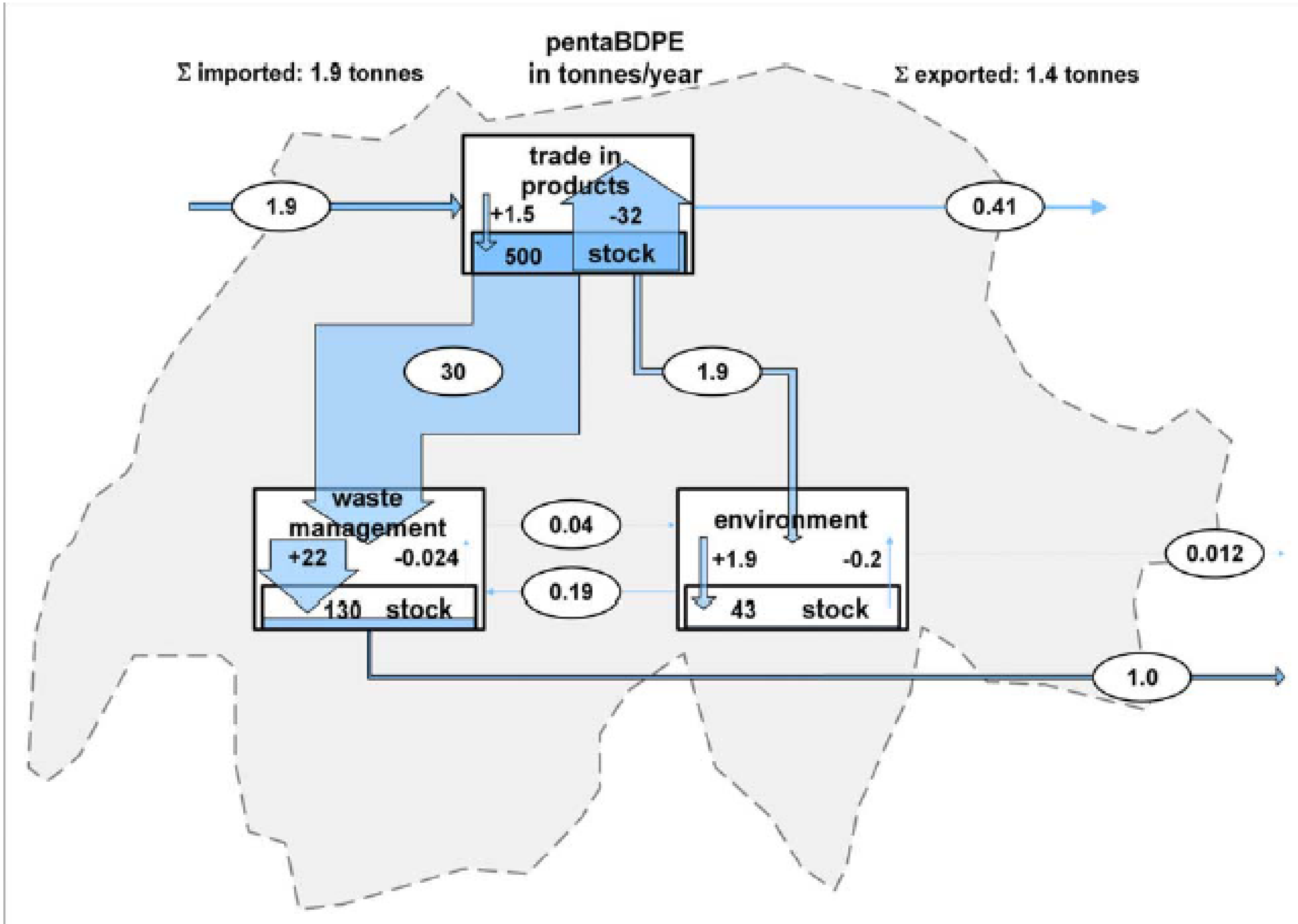


Figure 2: Flows of PentaBDPE in Switzerland in the late 1990s

Morf et al. 2003

Material Flow Analysis of Deca-BDE

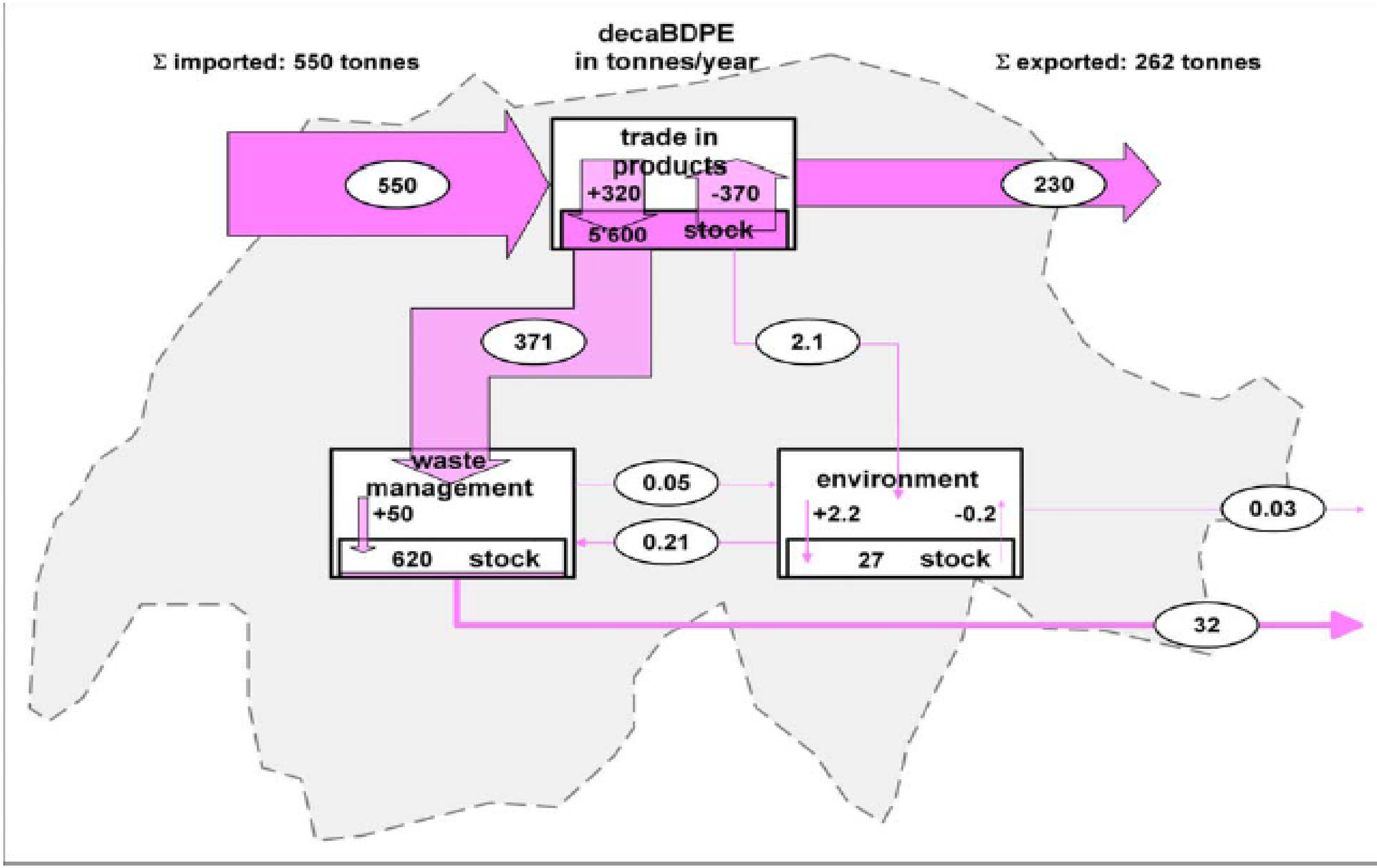
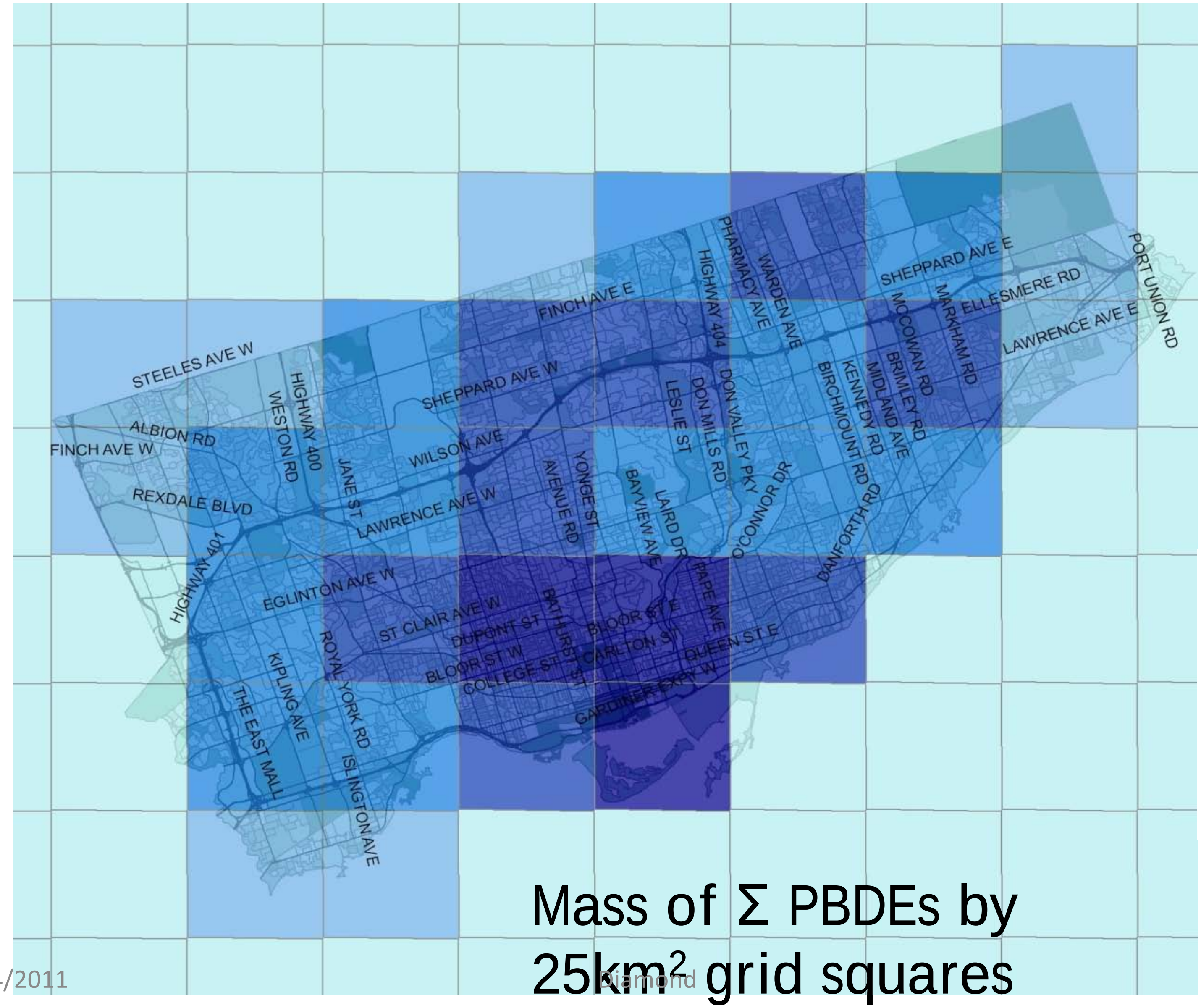


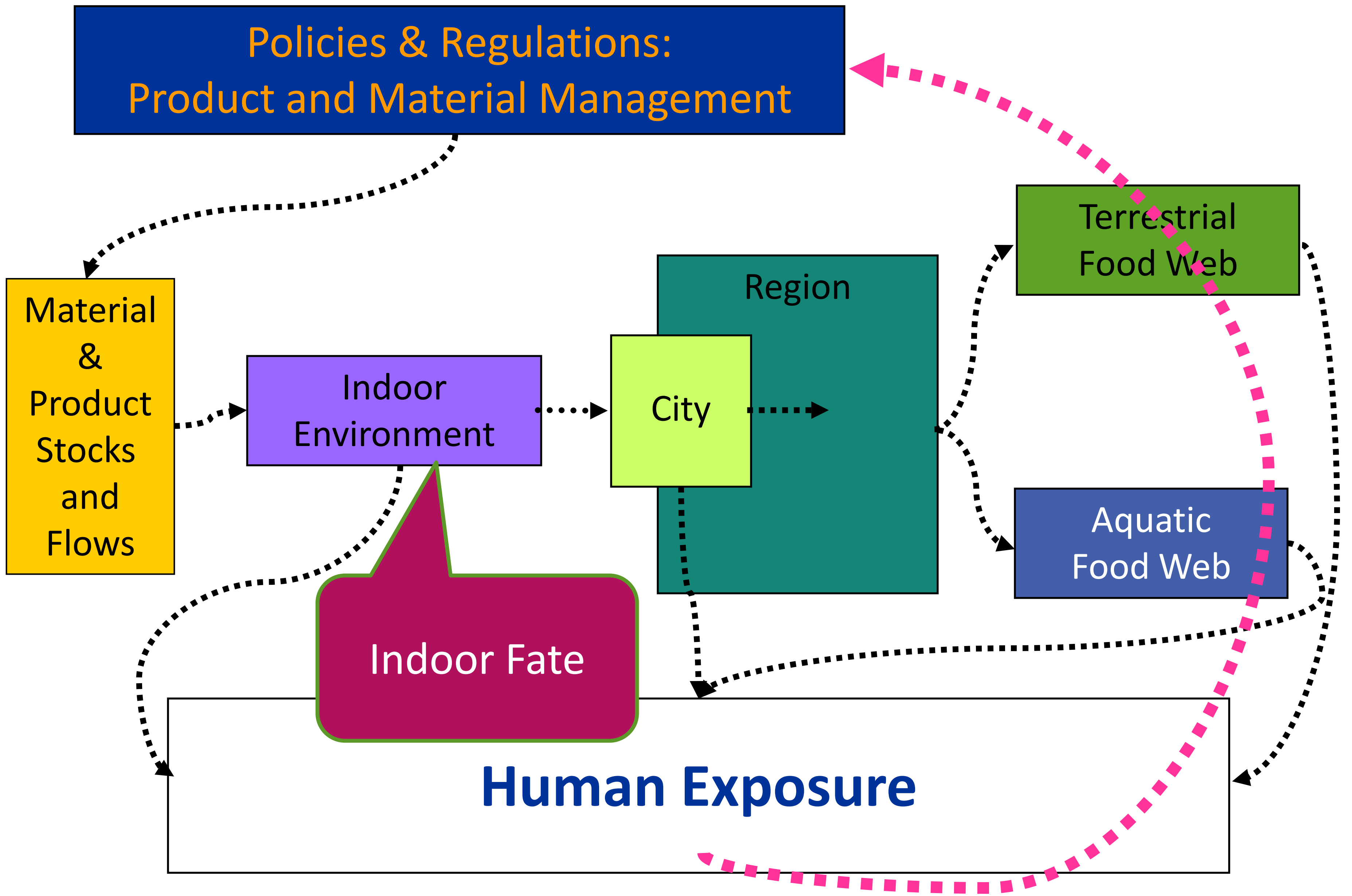
Figure 4: Flows of DecaBDPE in Switzerland, late 1990s

Morf et al. 2003

Mass of PBDEs in Computers in Toronto



Mass of Σ PBDEs by 25km² grid squares


Policies & Regulations:
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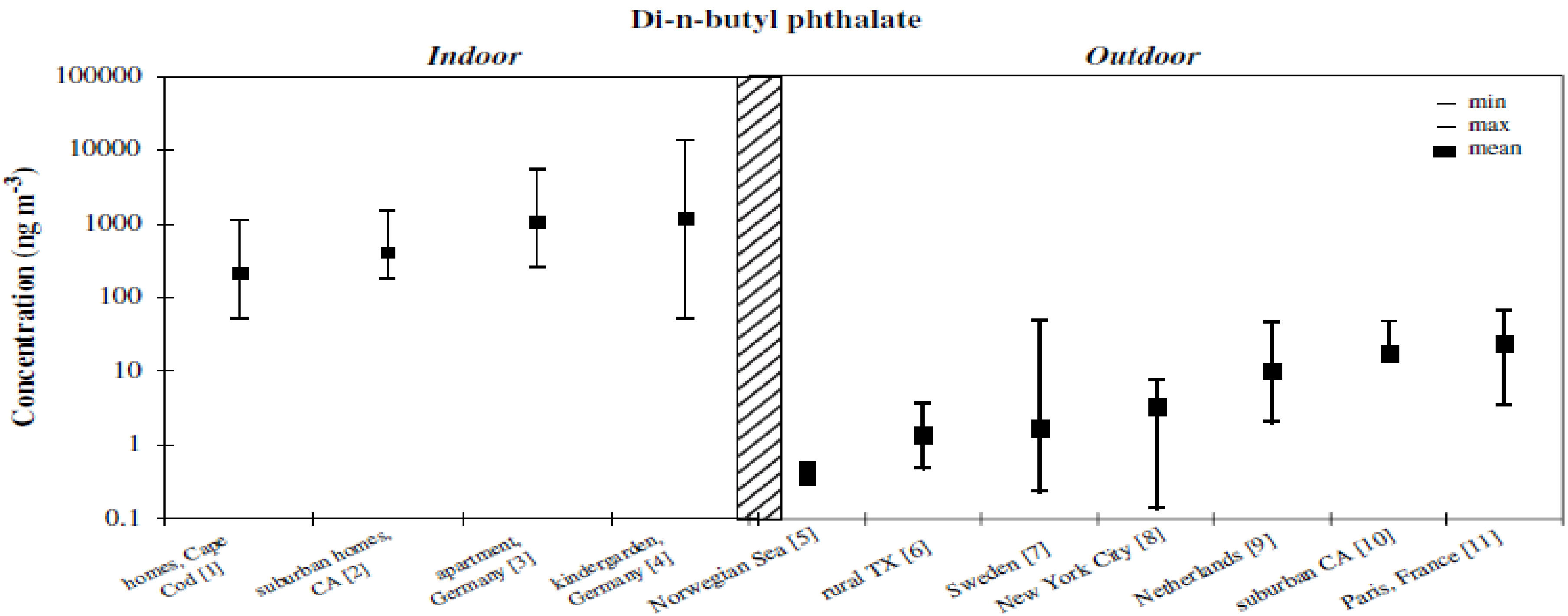
Material & Product Stocks and Flows
Indoor Environment
City
Region
Terrestrial Food Web
Aquatic Food Web
Indoor Fate
Human Exposure

Why Indoors?

- concentrations higher
- we spend 22/24 hours/d indoors

R.A. Rudel, L.J. Perovich / Atmospheric Environment 43 (2009) 170–181

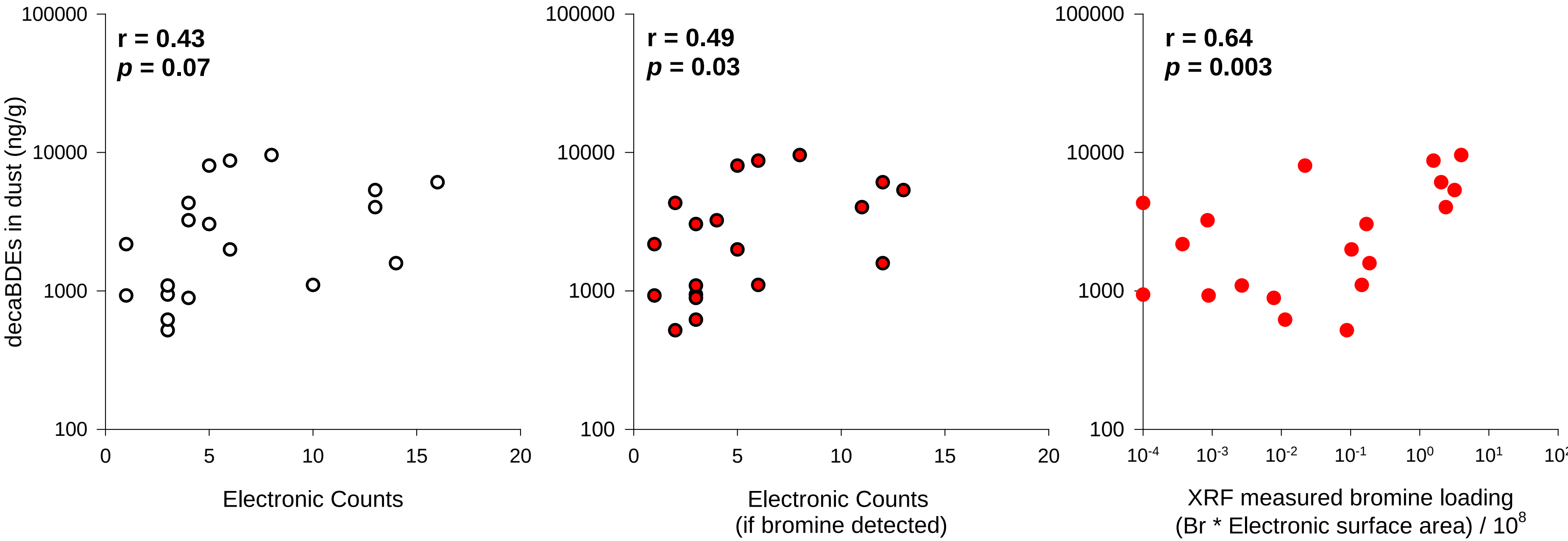


[1] (Rudel et al., 2003), n = 120, median (not mean) plotted
[2] (Sheldon et al., 1992), n = 104, range shown is 10th to 90th percentile , median (not mean) plotted
[3] (Fromme et al., 2004), n = 59 , median (not mean) plotted
[4] (Fromme et al., 2004), n = 74 , median (not mean) plotted
[5] (Xieet al., 2007), n = 6
[6] (Atlas and Giam, 1988), n =13

[7] (Thuren and Larsson, 1990), n = 51 , median (not mean) plotted
[8] (Bove et al., 1978), n = 138, particulate phase only, min and max from monthly averages , median (not mean) plotted
[9] (Peijnenburg and Struijs, 2006), n = 32, range shown is MQL to 95th percentile, gas phase only , median (not mean) plotted
[10] (Sheldon et al., 1992), n = 36, range shown is MQL to 90th percentile , median (not mean) plotted
[11] (Teil et al., 2006), n = 20

Fig. 5. Di-n-butyl phthalate air concentrations (sum of vapor and particulate phases unless otherwise noted) in selected studies.

Prediction of PBDE indoor dust concentrations

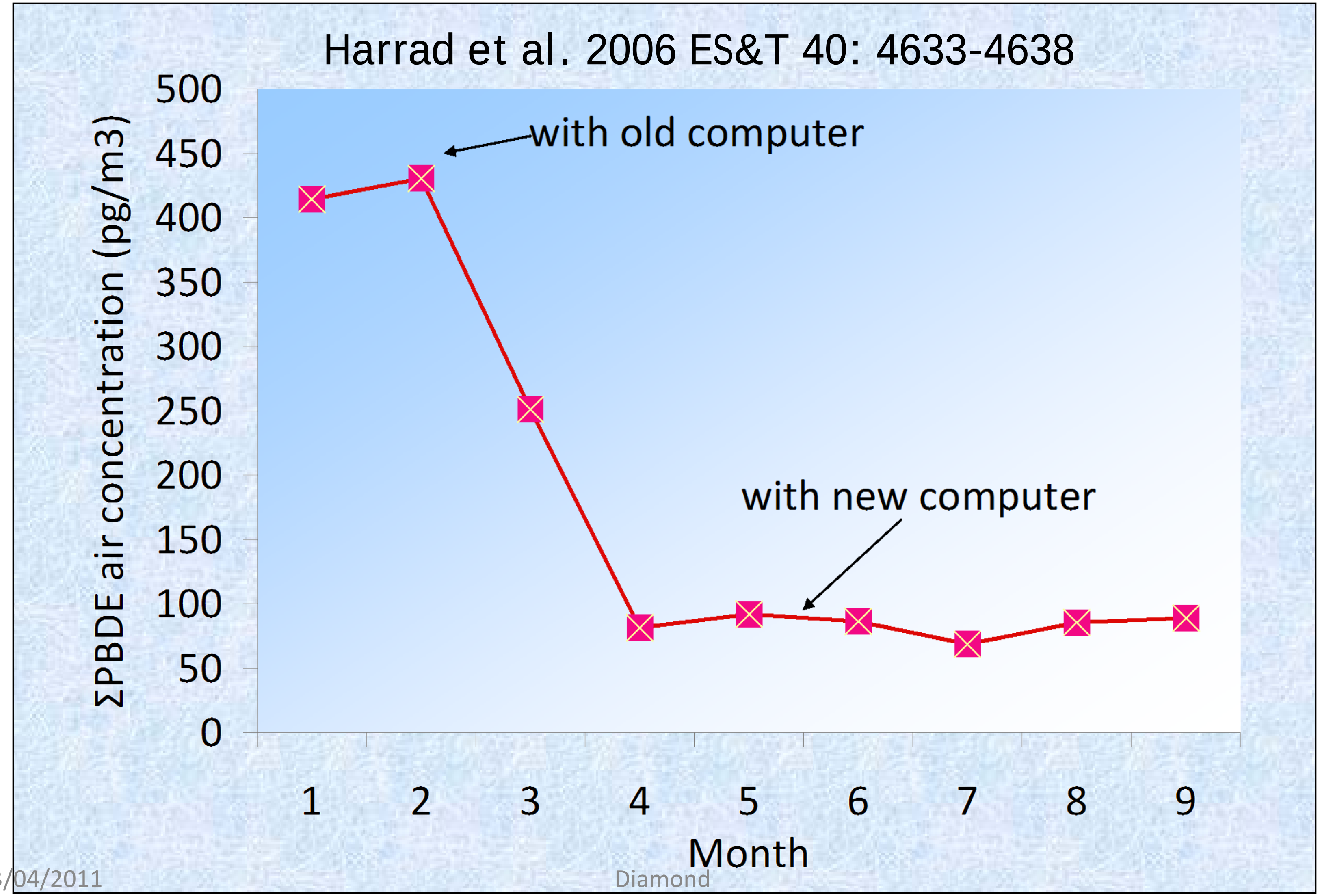


Linking PBDEs in House Dust to Consumer Products using X-ray Fluorescence

Joseph G. Allen,*‡† Michael D. McClean,‡ Heather M. Stapleton,§ and Thomas F. Webster‡

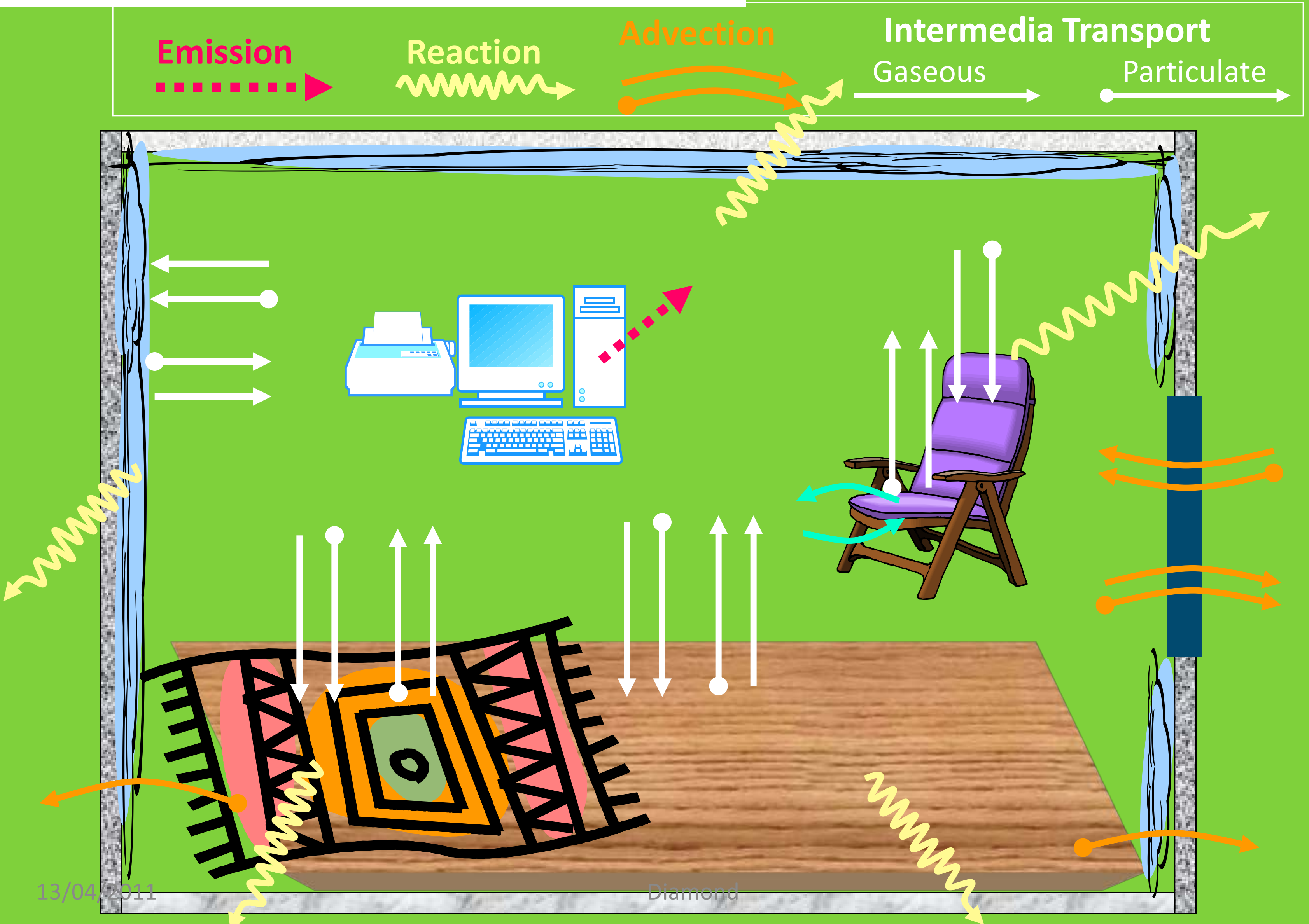
Environ. Sci. Technol., 42 (11), 4222-4228, 2008. 10.1021/es702964a

PBDE Air Concentrations in Stuart's Office



Model Structure

Zhang et al. 2009 *Environ Sci Technol* 43: 2845-50



Modelling PUF Furniture

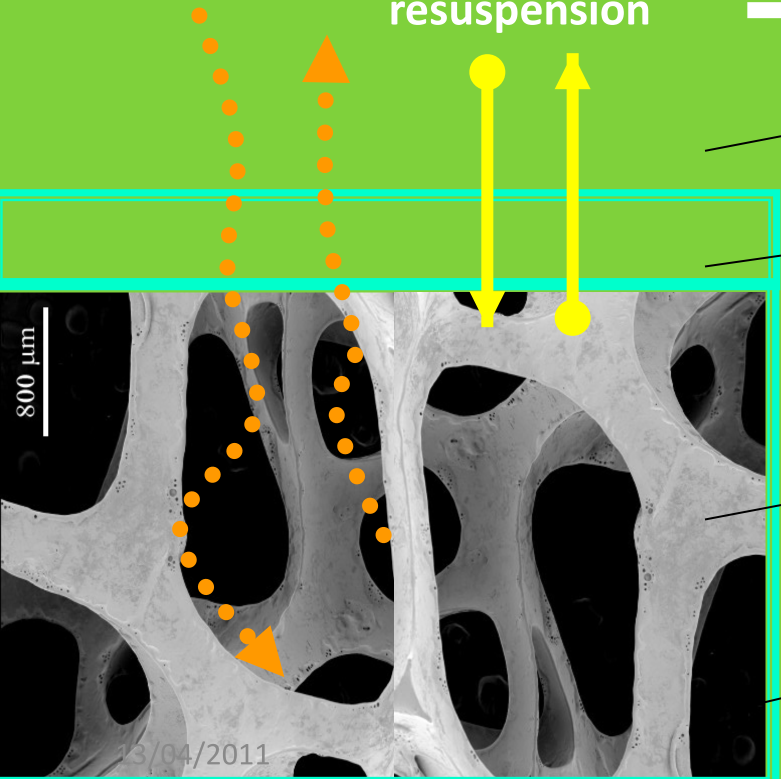
$$D_{diff} = 1/(\frac{\delta_{bl}}{B_a A_{ap} Z_a} + \frac{h_p \ln 2^*}{B_a v_a^{4/3} A_{ap} Z_a})$$

*Daly and Wania, 2004 ES&T. 2004,38,4176-4186

Gas diffusion

Particle deposition/ resuspension

$$D_{dep} = U_Q A_{sp} v f_Q Z_Q$$



Air

Boundary layer

PUF material

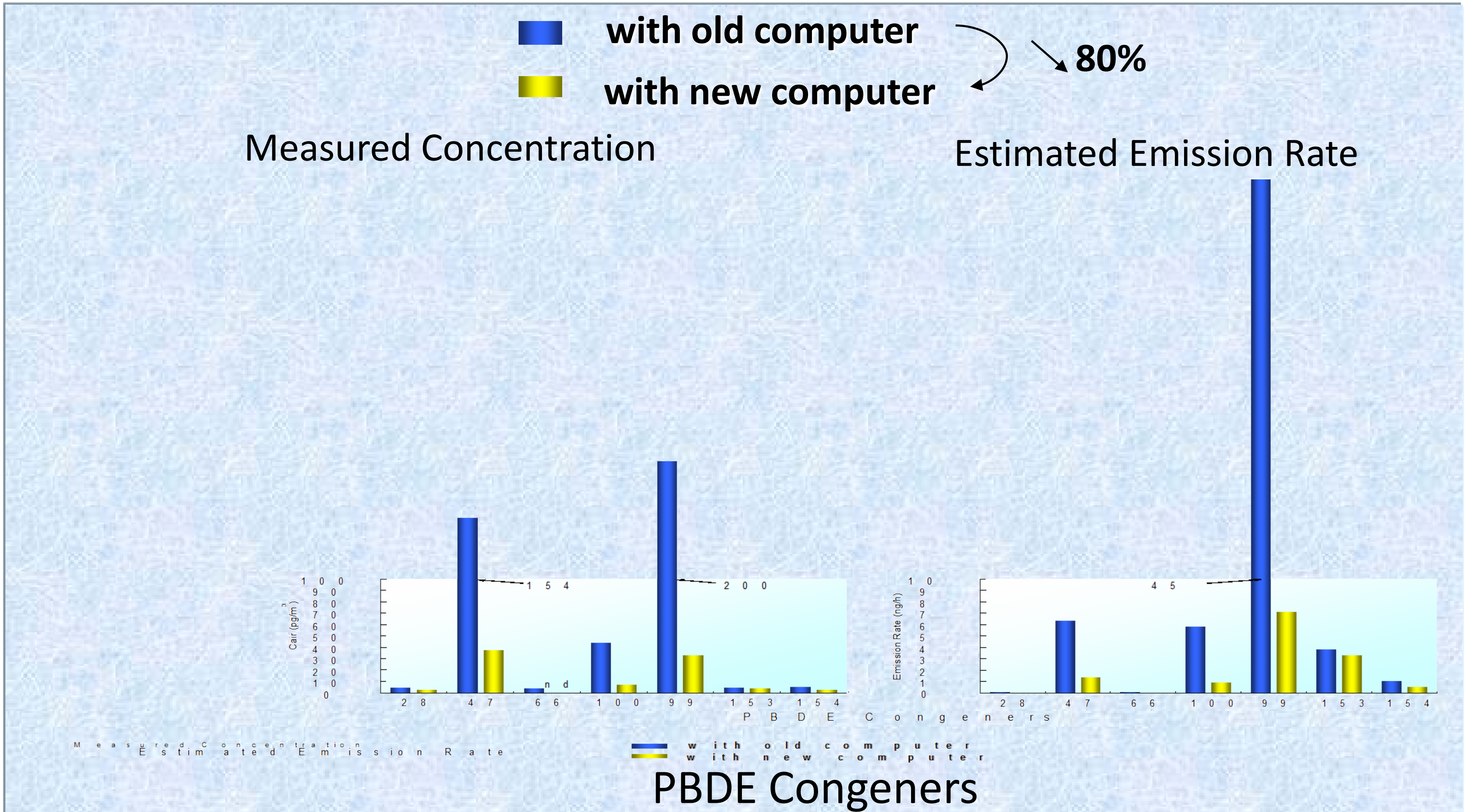
Air filled pore space

$$Zp = \frac{Kpa}{RT}, \; f = C/Z$$

Kpa

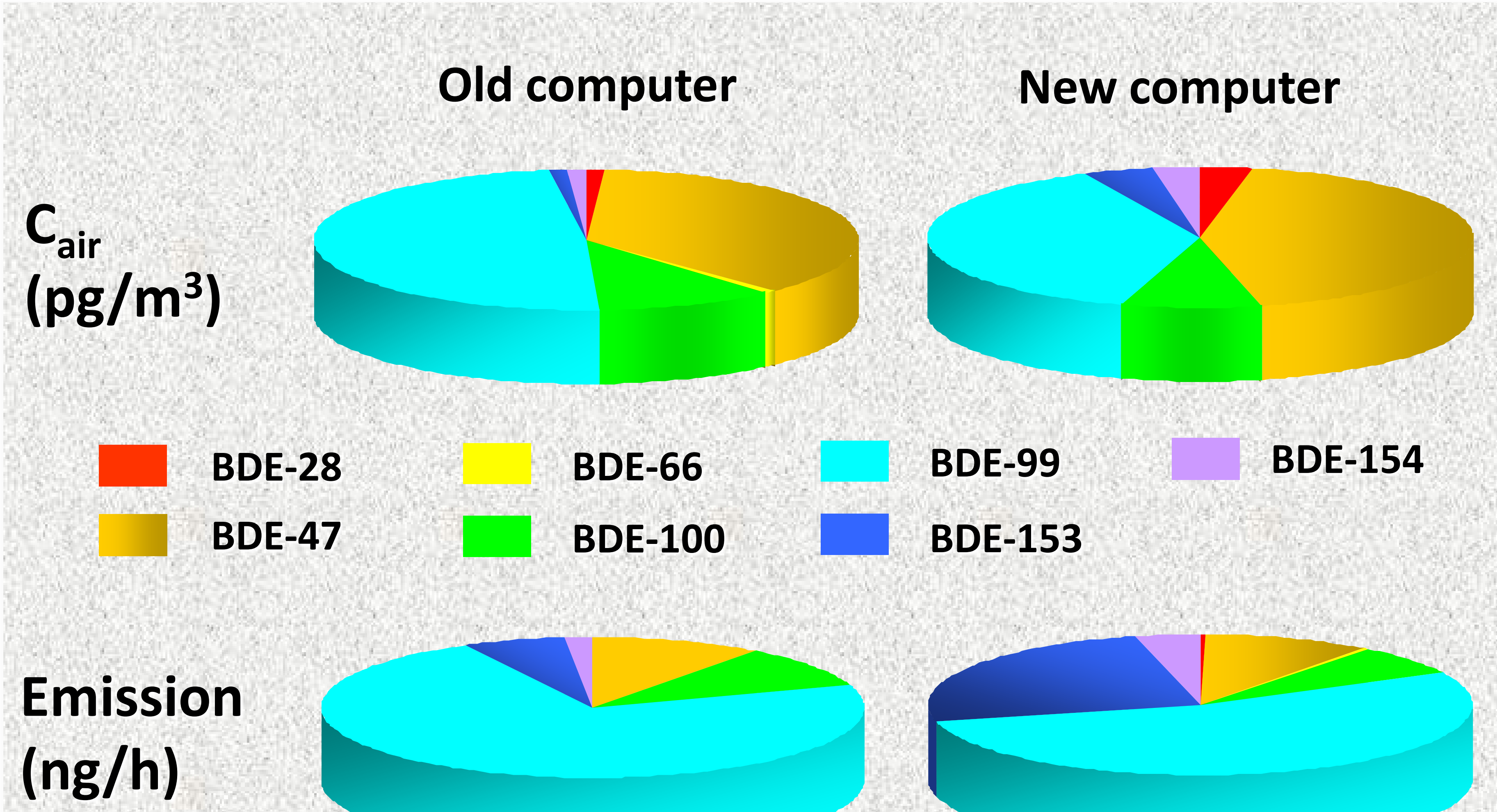
PUF

Estimated Emission Rate from Measured Air Concentration

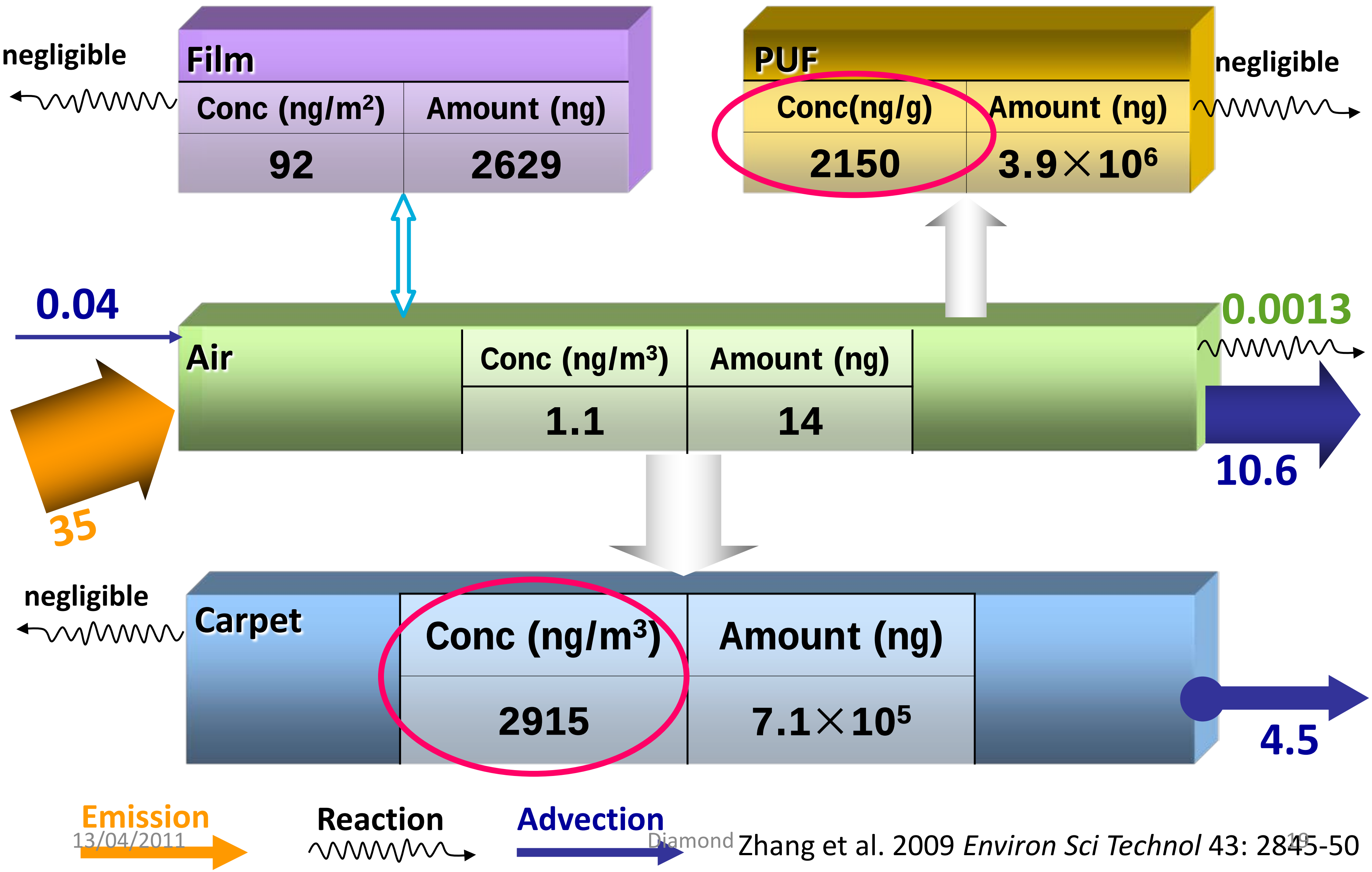


ΣC_{old} = 420 pg/m³, ΣC_{new} = 90 pg/m³ ΣE_{old} = 35 ng/h, ΣE_{new} = 5.4 ng/h

PBDE Congener Profile before & after Computer Replacement



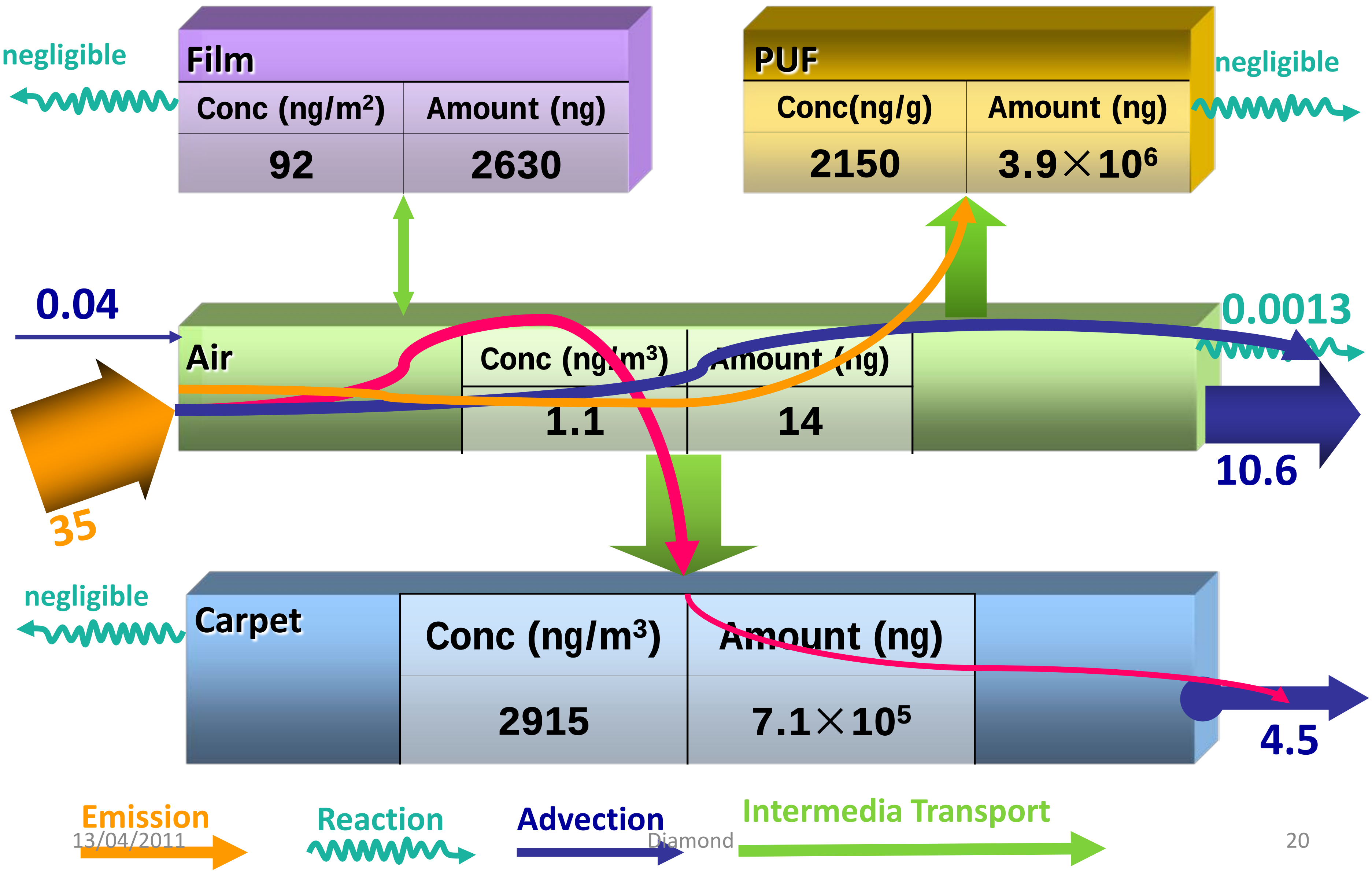
Indoor Fate of P_7BDEs – old computer



Zhang et al. 2009 *Environ Sci Technol* 43: 2845-50

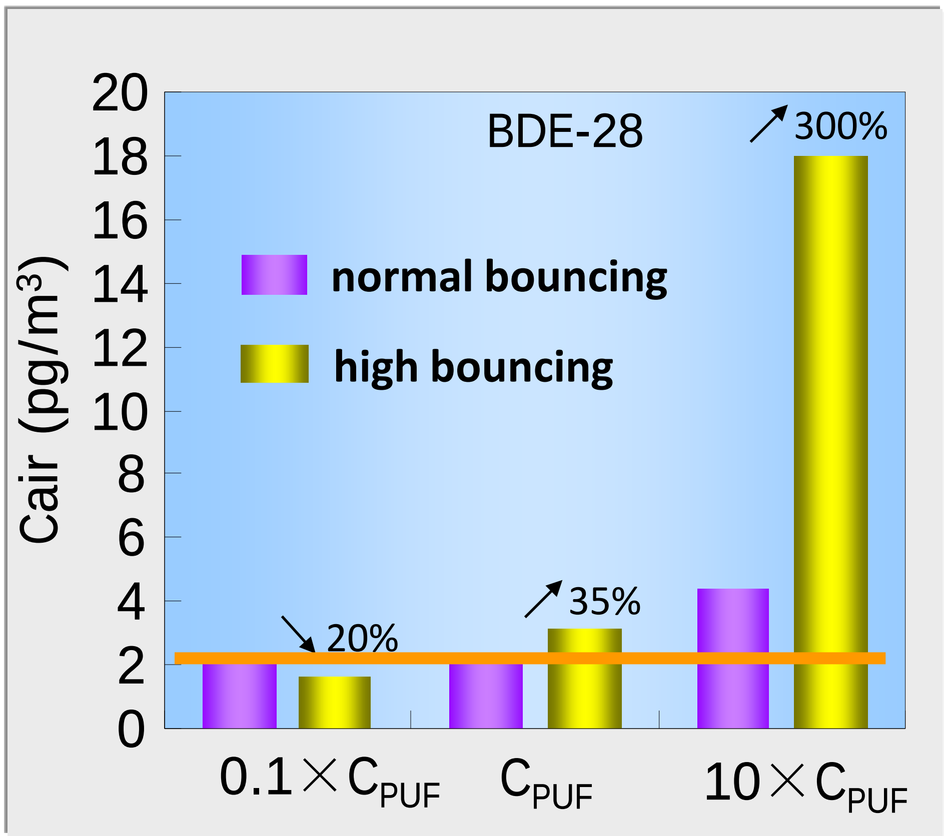
Indoor Fate of P_7BDEs – old computer

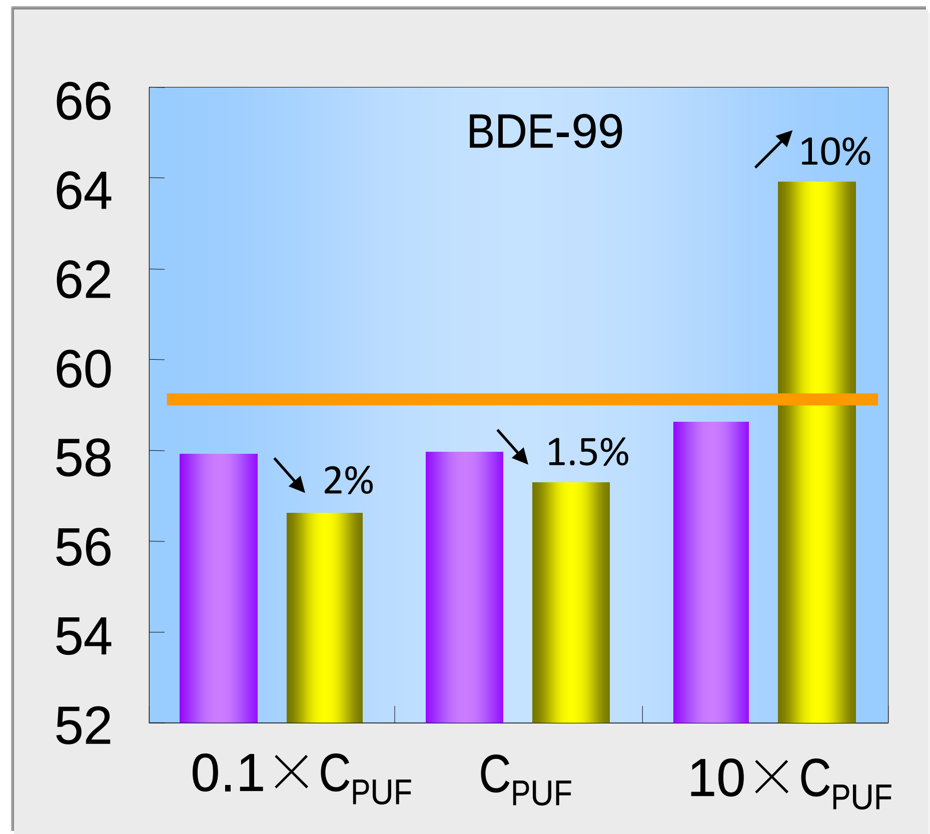
Zhang et al. 2009 *Environ Sci Technol* 43: 2845-50



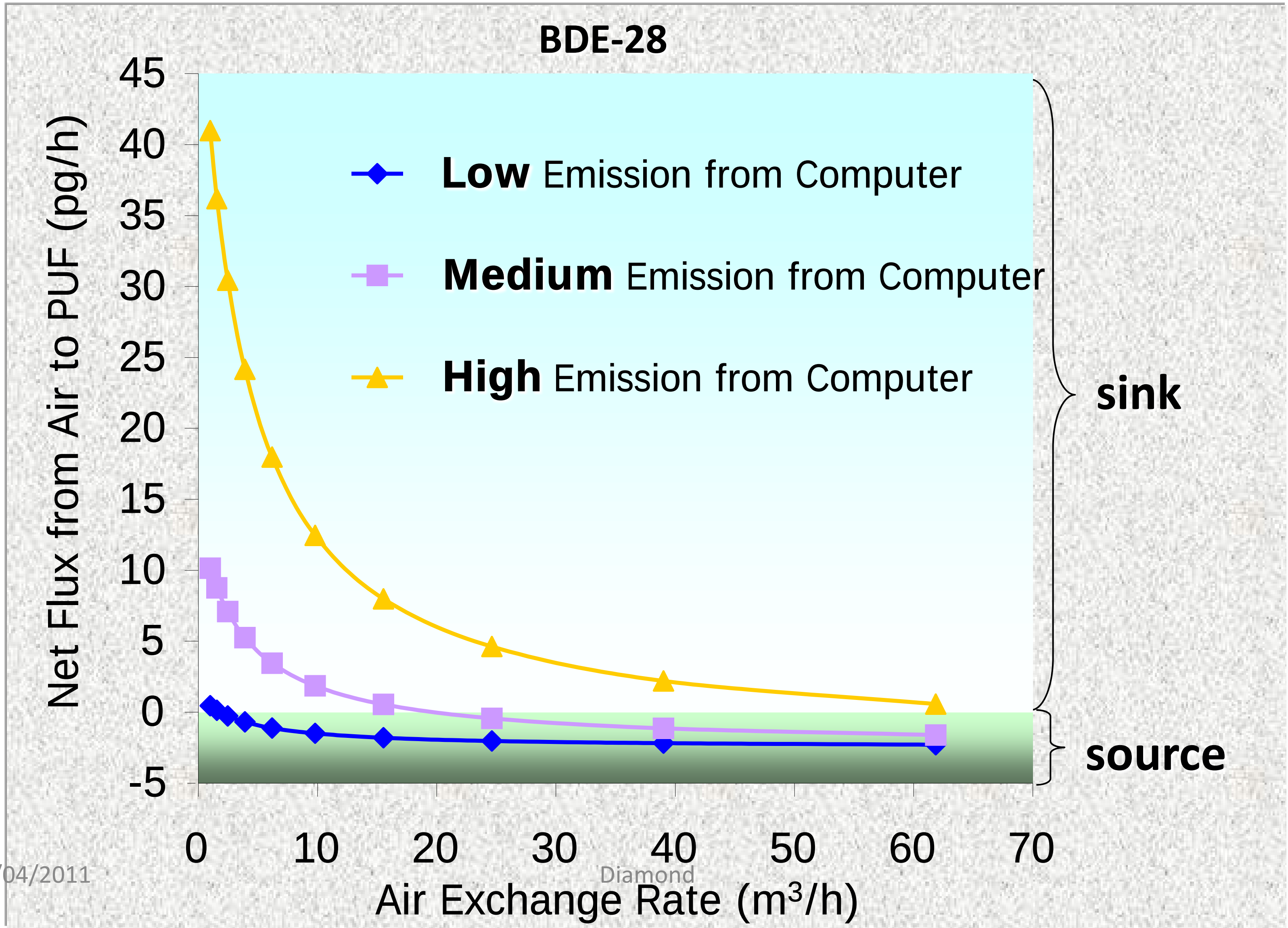
Influence of Bouncing on the Furniture

Zhang et al. 2009 *Environ Sci Technol* 43: 2845-50

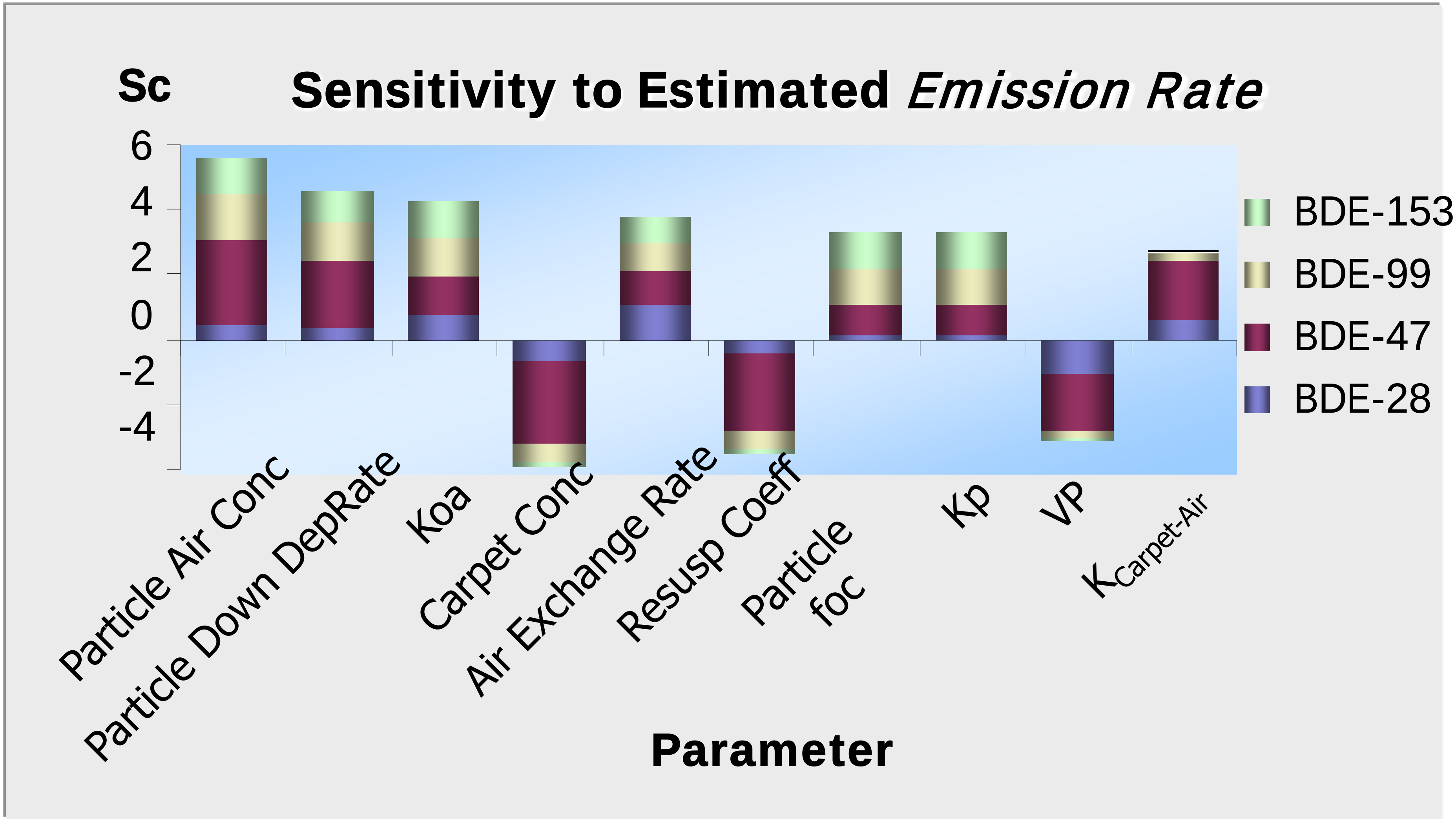


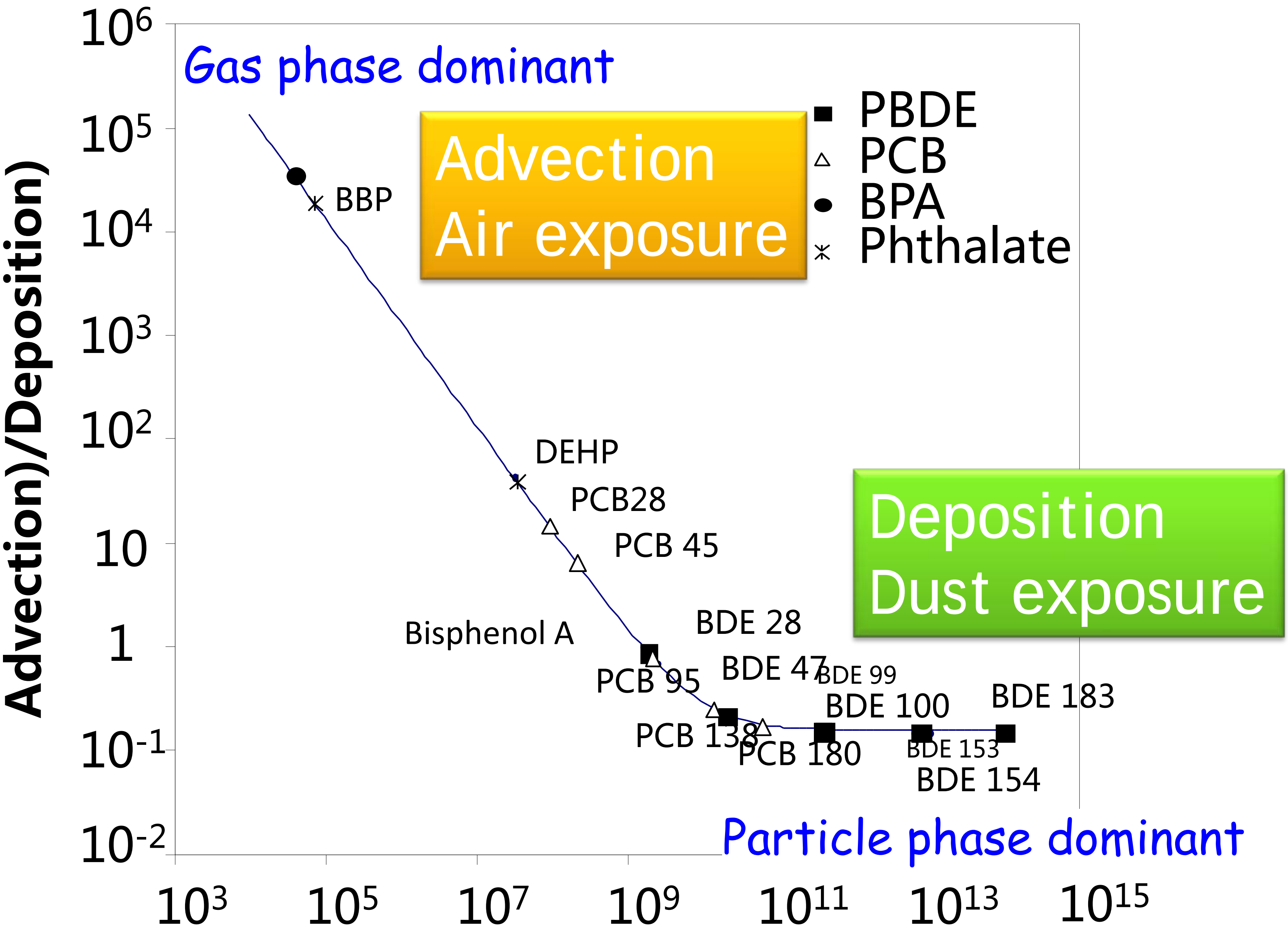


AER & Computer Emission Rate
PUF as Source/Sink



Sensitivity Analysis Result 2

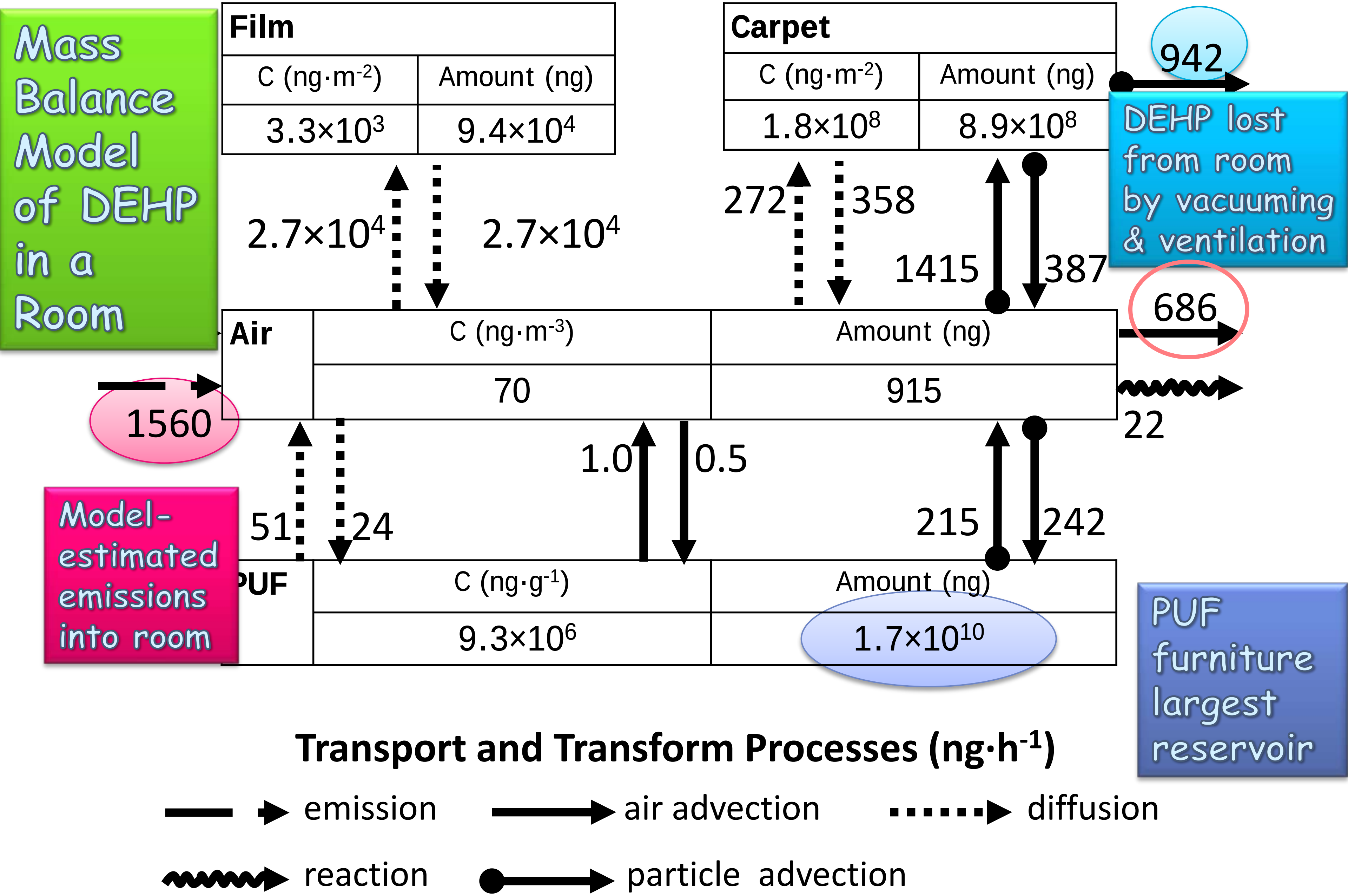




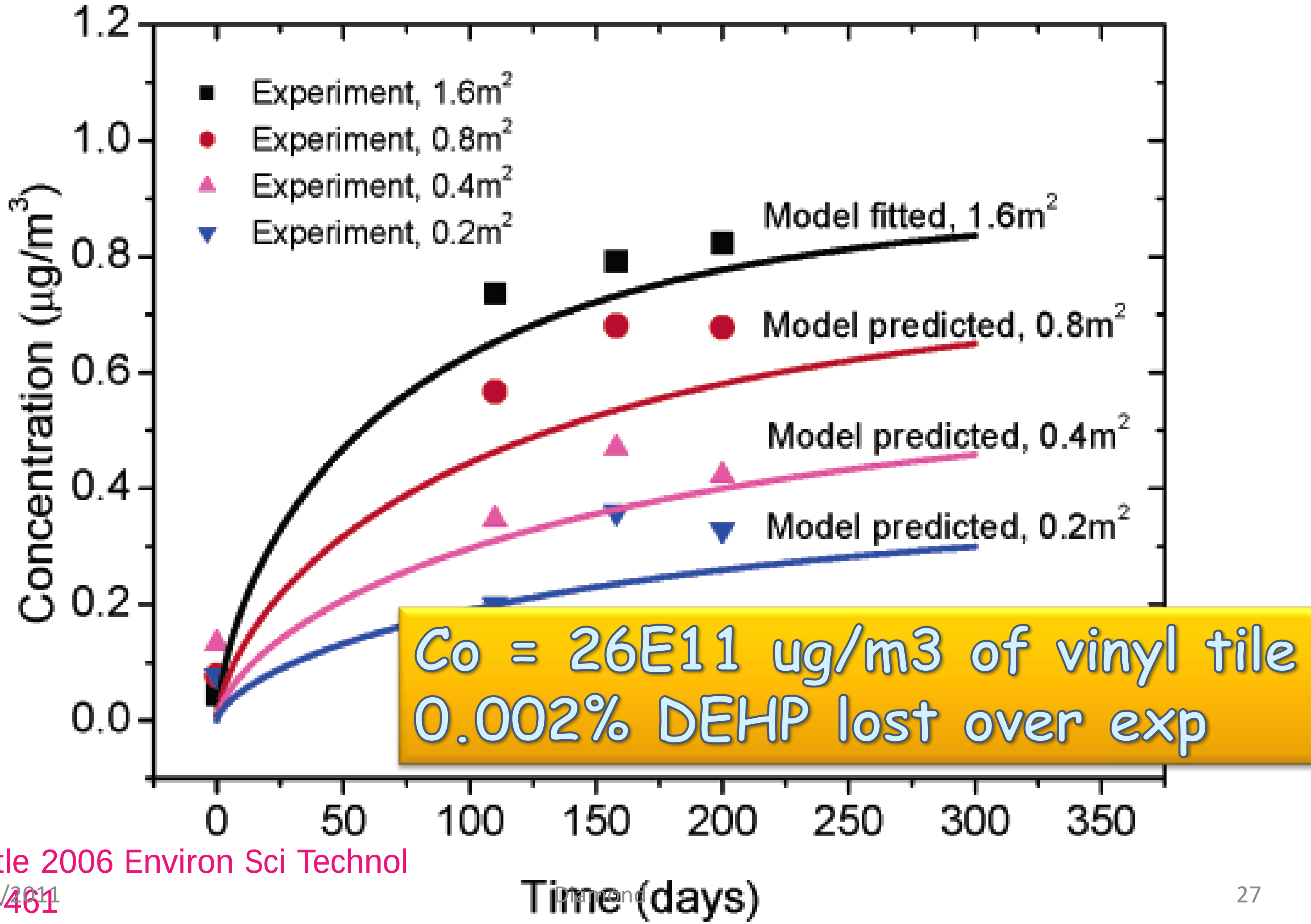
Gas phase dominant
Advection
Air exposure
Deposition
Dust exposure
Particle phase dominant
PBDE
PCB
BPA
Phthalate
BBP
DEHP
PCB28
PCB 45
Bisphenol A
BDE 28
PCB 95
BDE 47
BDE 99
BDE 100
BDE 183
PCB 138
PCB 180
BDE 153
BDE 154
10^6
10^5
10^4
10^3
10^2
10
1
10^{-1}
10^{-2}
10^3
10^5
10^7
10^9
10^{11}
10^{13}
10^{15}
Advection)/Deposition)
KOA

Indoor Phthalates

http://www.cleanandhealthyme.org/Portals/0/bodyburden/images/toys.jpg

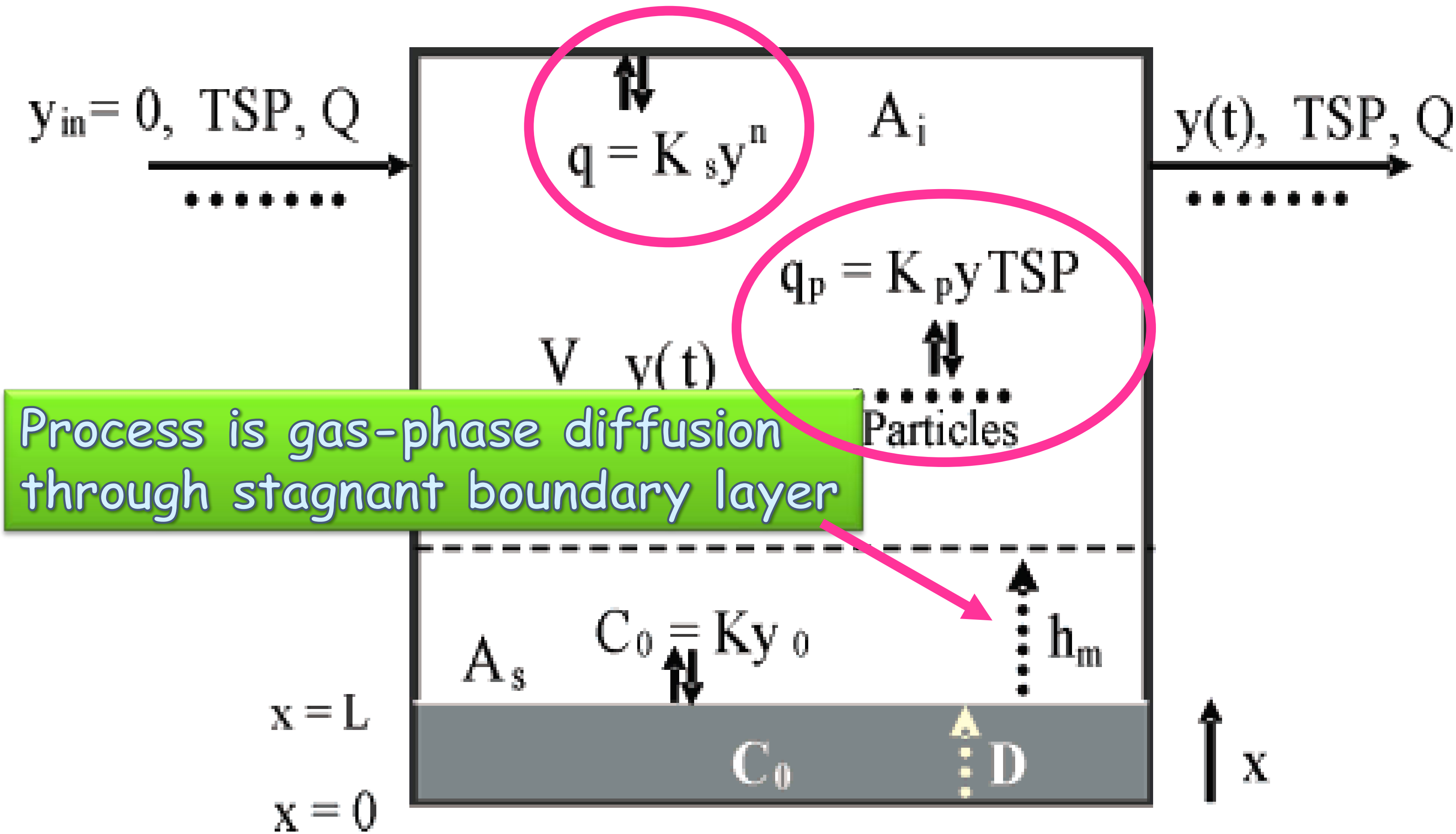

Mass Balance Model of DEHP in a Room
Film
C (ng·m-2) | Amount (ng)
3.3×10³ | 9.4×10⁴
Carpet
C (ng·m-2) | Amount (ng)
1.8×10⁸ | 8.9×10⁸
942
DEHP lost from room by vacuuming & ventilation
2.7×10⁴
2.7×10⁴
272
358
1415
387
686
Air
C (ng·m-3) | Amount (ng)
70 | 915
1560
22
1.0
0.5
51
24
215
242
Model-estimated emissions into room
PUF
C (ng·g-1) | Amount (ng)
9.3×10⁶ | 1.7×10¹⁰
PUF furniture largest reservoir
Transport and Transform Processes (ng·h-1)
emission
air advection
diffusion
reaction
particle advection

Gas-phase DEHP Release from Vinyl Tiles



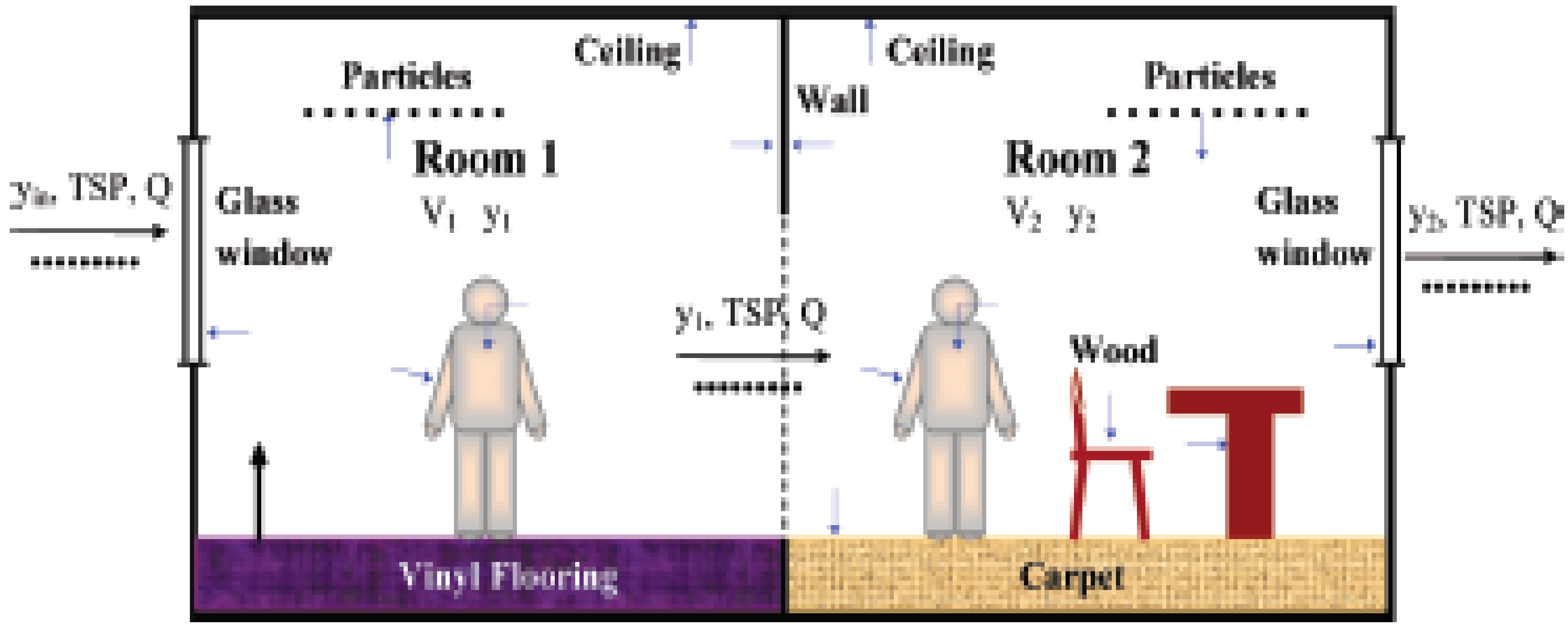
Xu & Little 2006 Environ Sci Technol 40: 456-461

Model of DEHP Release into Room



Xu & Little 2006 Environ Sci Technol 40: 456-461

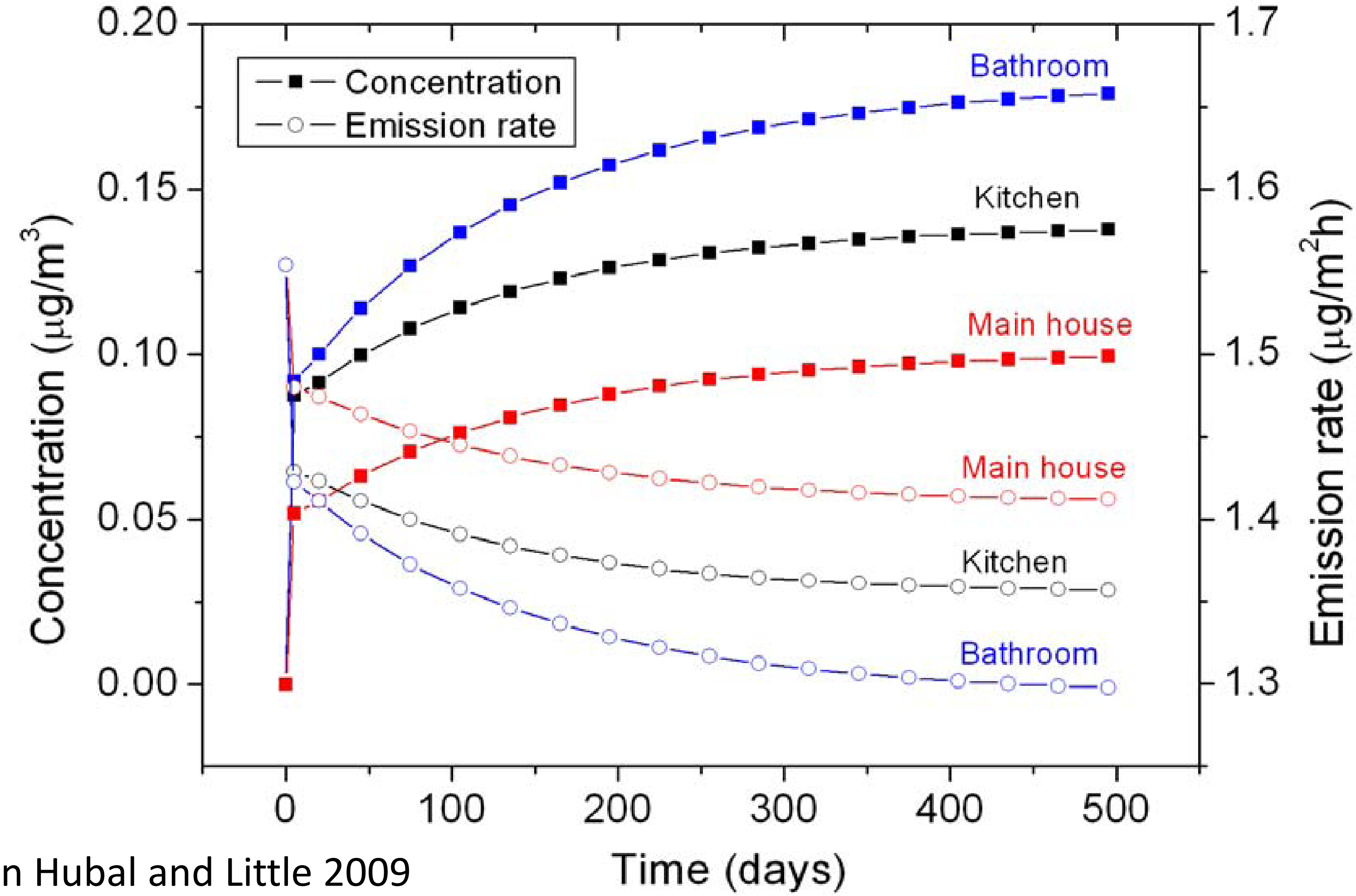
Xu, Cohen Hubal, Clausen & Little 2009 Environ Sci Technol 43:2374-2380



c representation of the two-room model.

- Data from CTEPP Study
- Mechanistic fate model

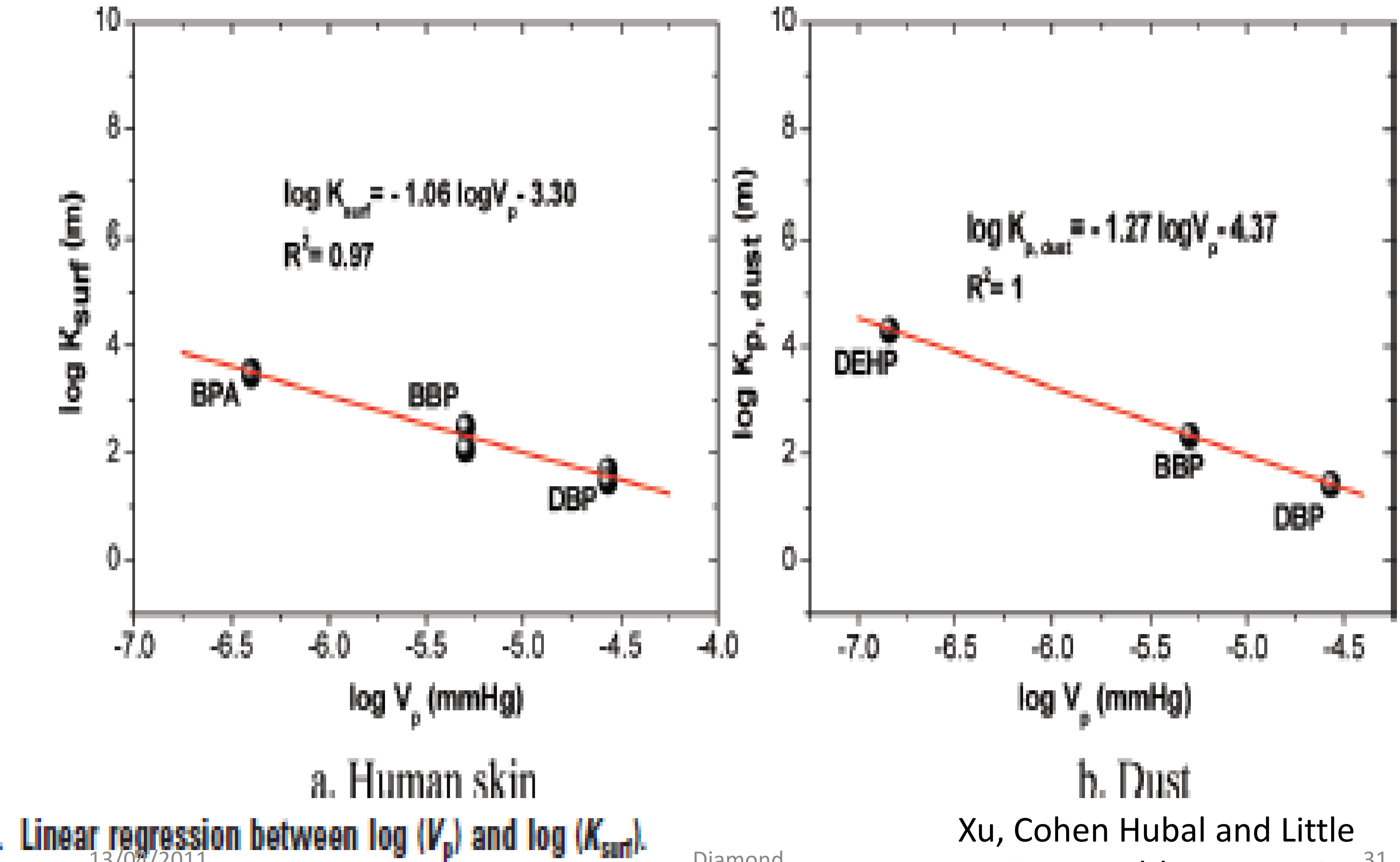
DEHP Emissions & Conc



Xu, Cohen Hubal and Little 2009
Environ Health Perspectives

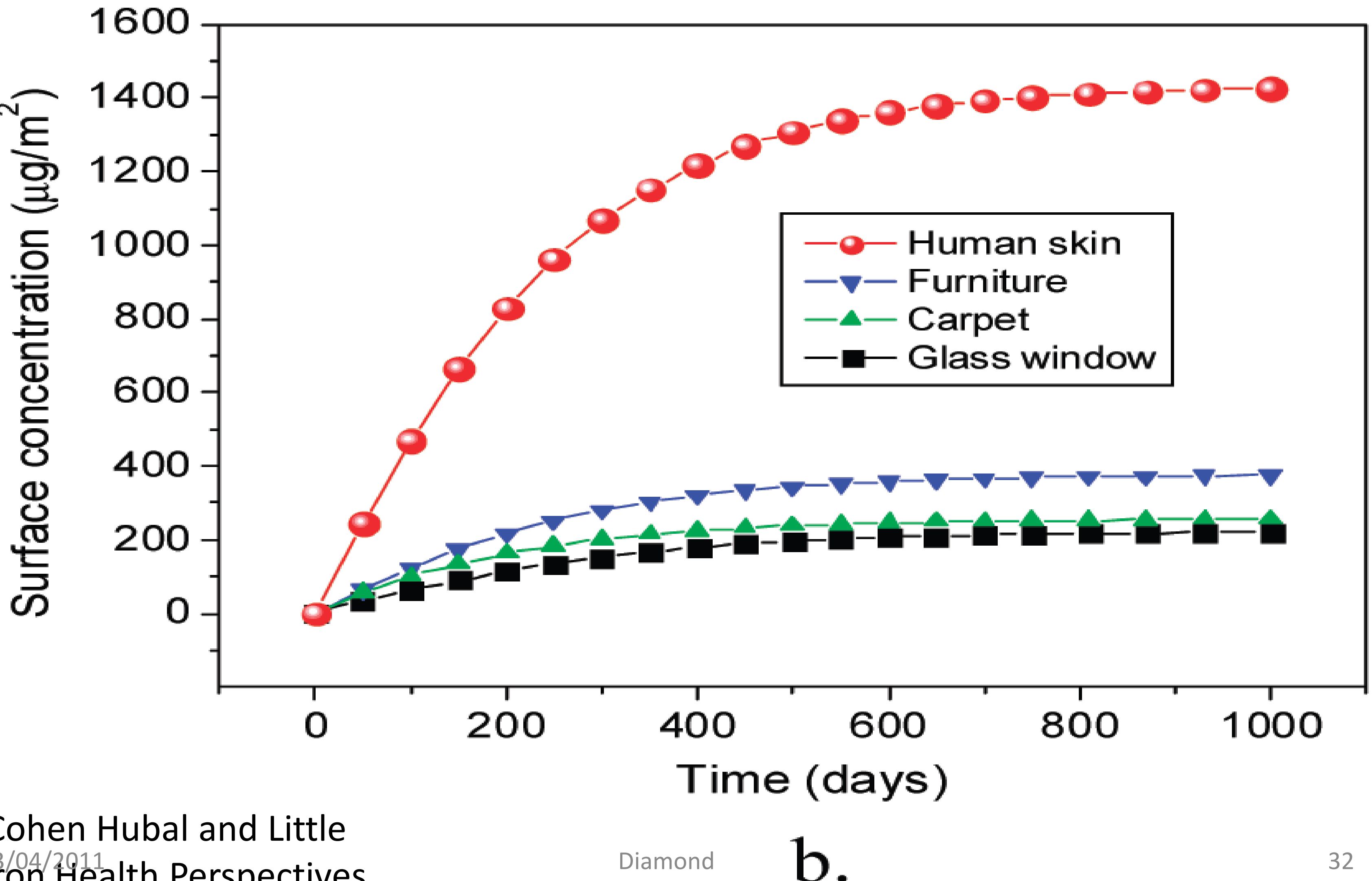
Phthalate Partitioning

- Data from CTEPP Study



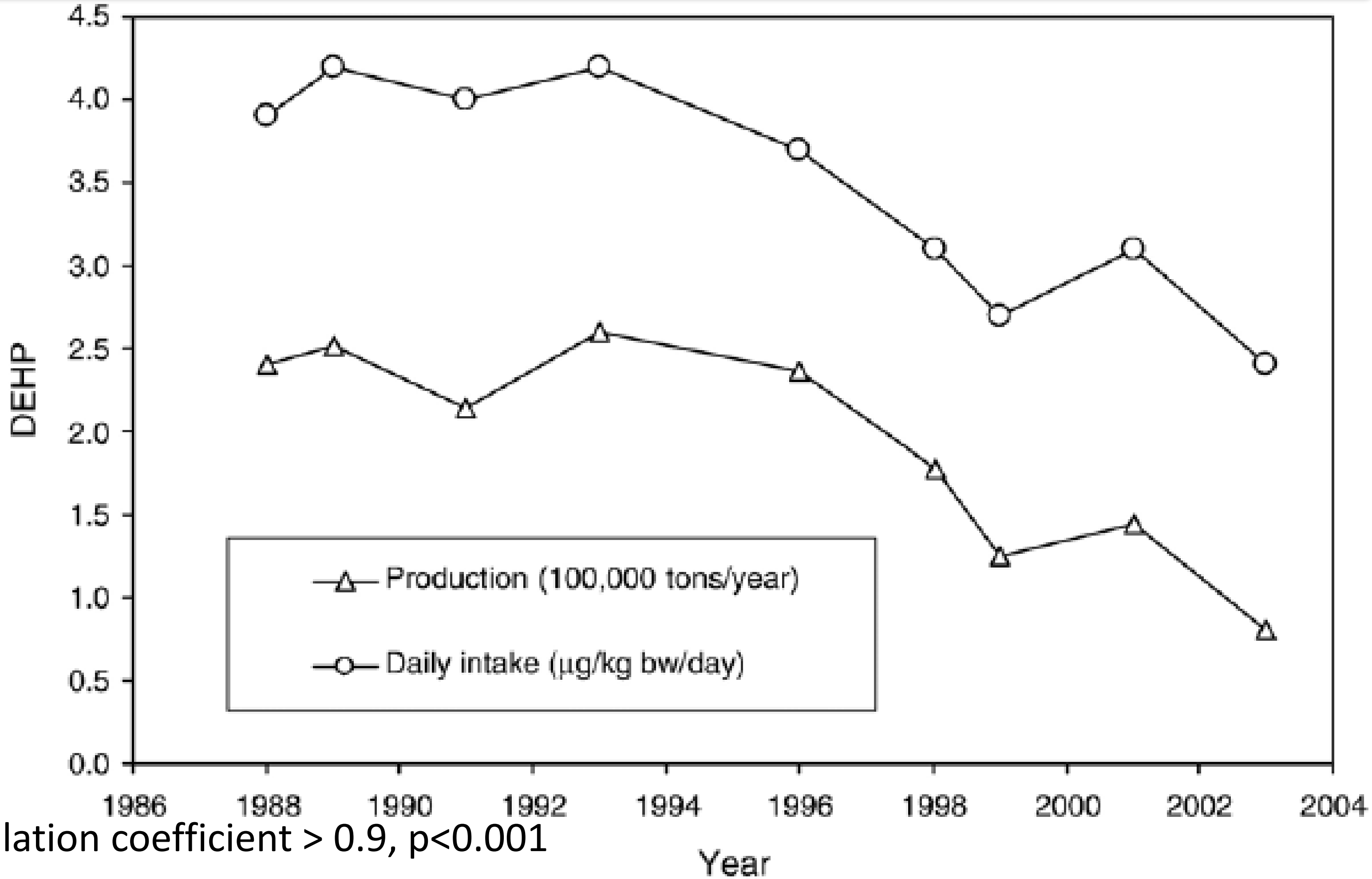
Xu, Cohen Hubal and Little
Environ Health Perspectives

Use of Partition Coef to Predict Concentrations



Xu, Cohen Hubal and Little
Environ Health Perspectives

Population Scale Correlation between Intake and Production



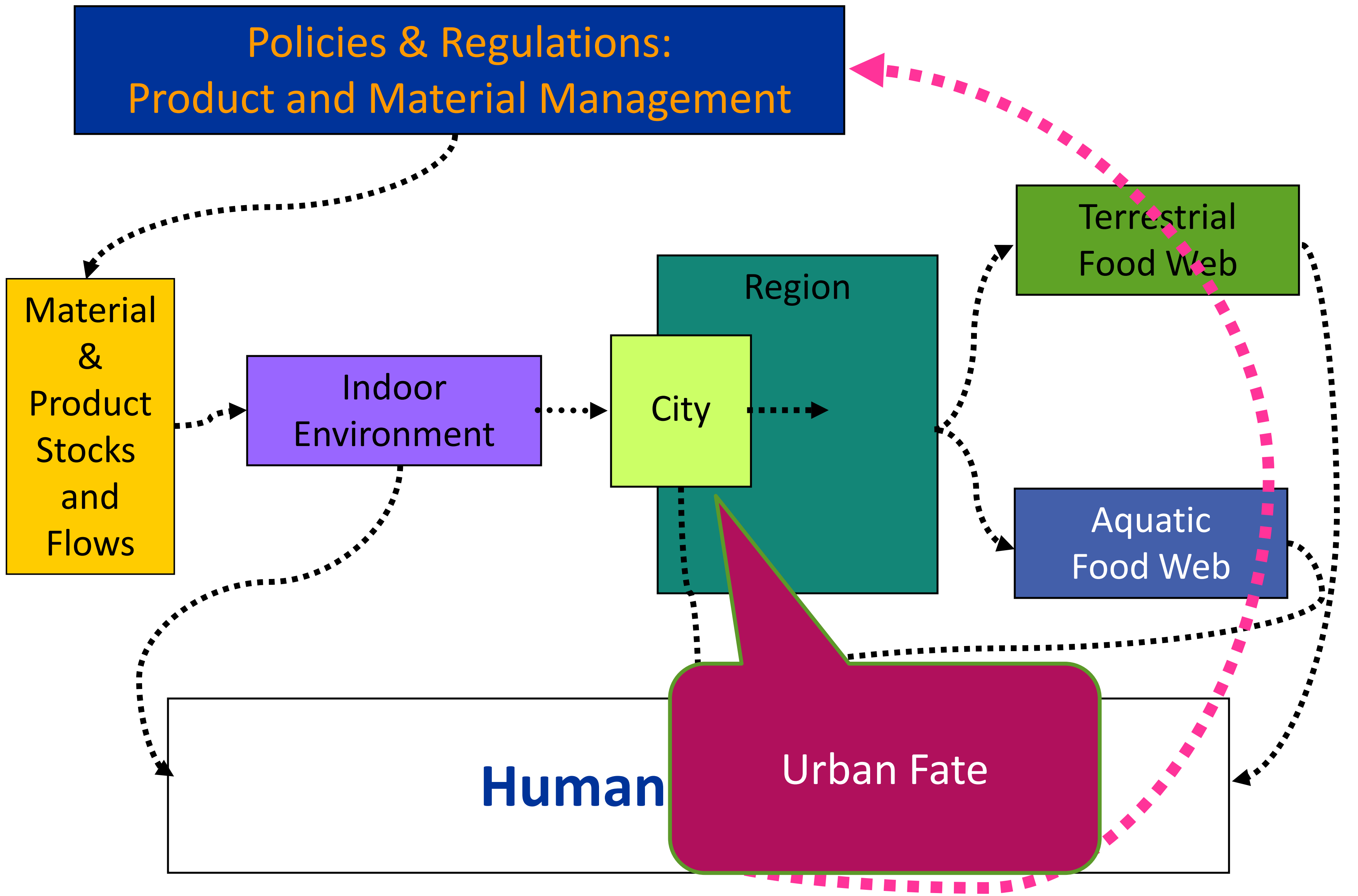
Correlation coefficient > 0.9, p<0.001

Helm D.2007 Correlation between production amounts of DEHP and daily intake. Sci Total Environ 388:398-391.

Chemical	Indoor Emission (ug/m^2 d)	Chemical Mass (mg)	Residence Time (y)	Annual Release (%)
BPA	1.2-2.5	240	76	1.3
BBP	0.4-13.3	22	27	4
DEHP	4.3-7.7	17000	1175	0.1
PCB	0.8	600	800	0.1
PBDE	0.03-0.2	4.6		0.001

Take Home Messages

- Indoor environment has many emission sources
- Very small fraction of total mass is emitted
- Emitted chemicals can have relatively high concentrations & long residence times
  - Minimal loss mechanisms
  - Magnifying glass
- Concentrations (related to exposure) are a function of:
  - Emissions (sources & source strength)
  - Physical-chemical properties
  - Room characteristics
  - Within room partitioning & loss mechanisms (sinks)


Policies & Regulations:
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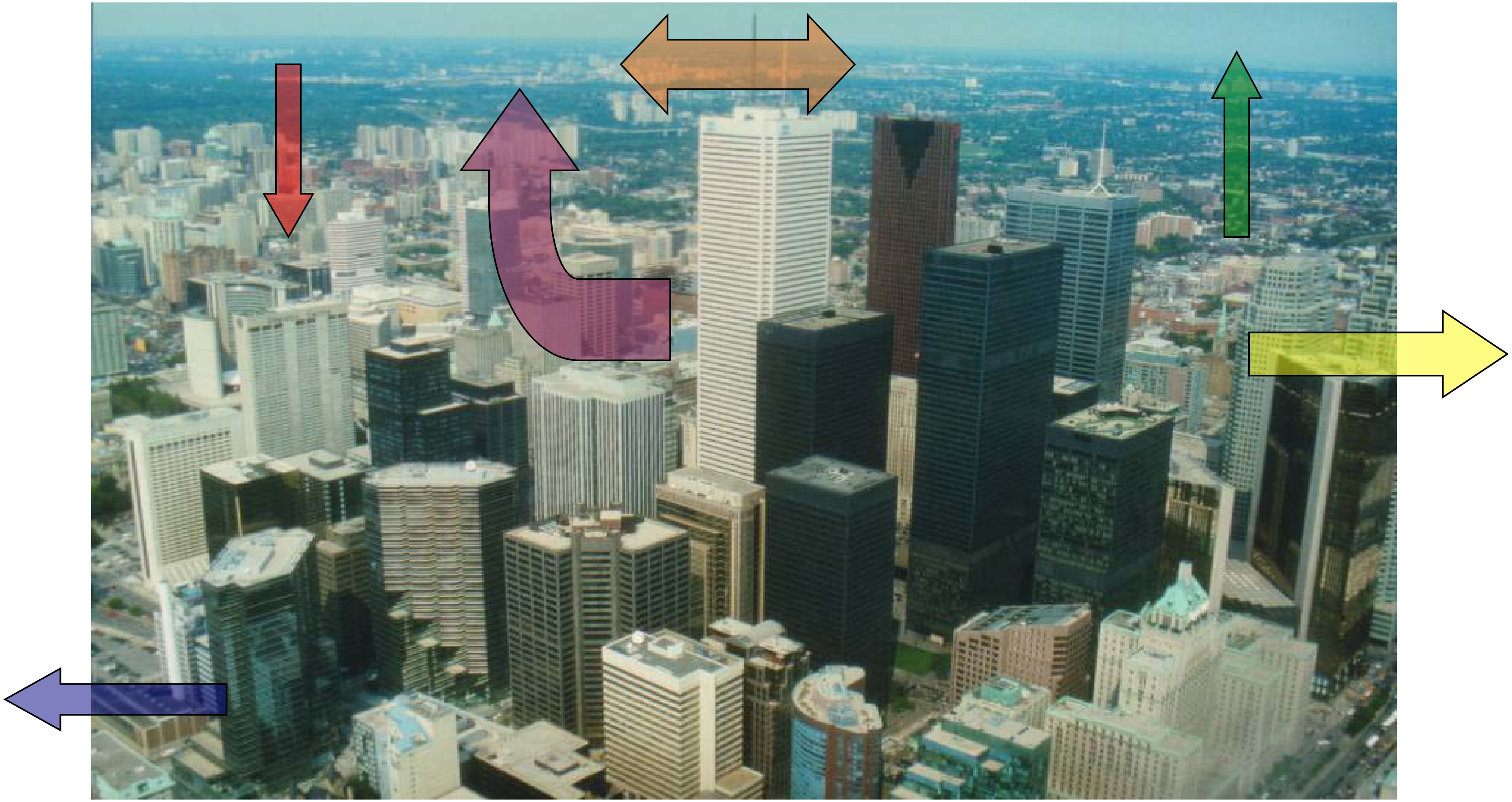
Human
Urban Fate

Chemical Fate

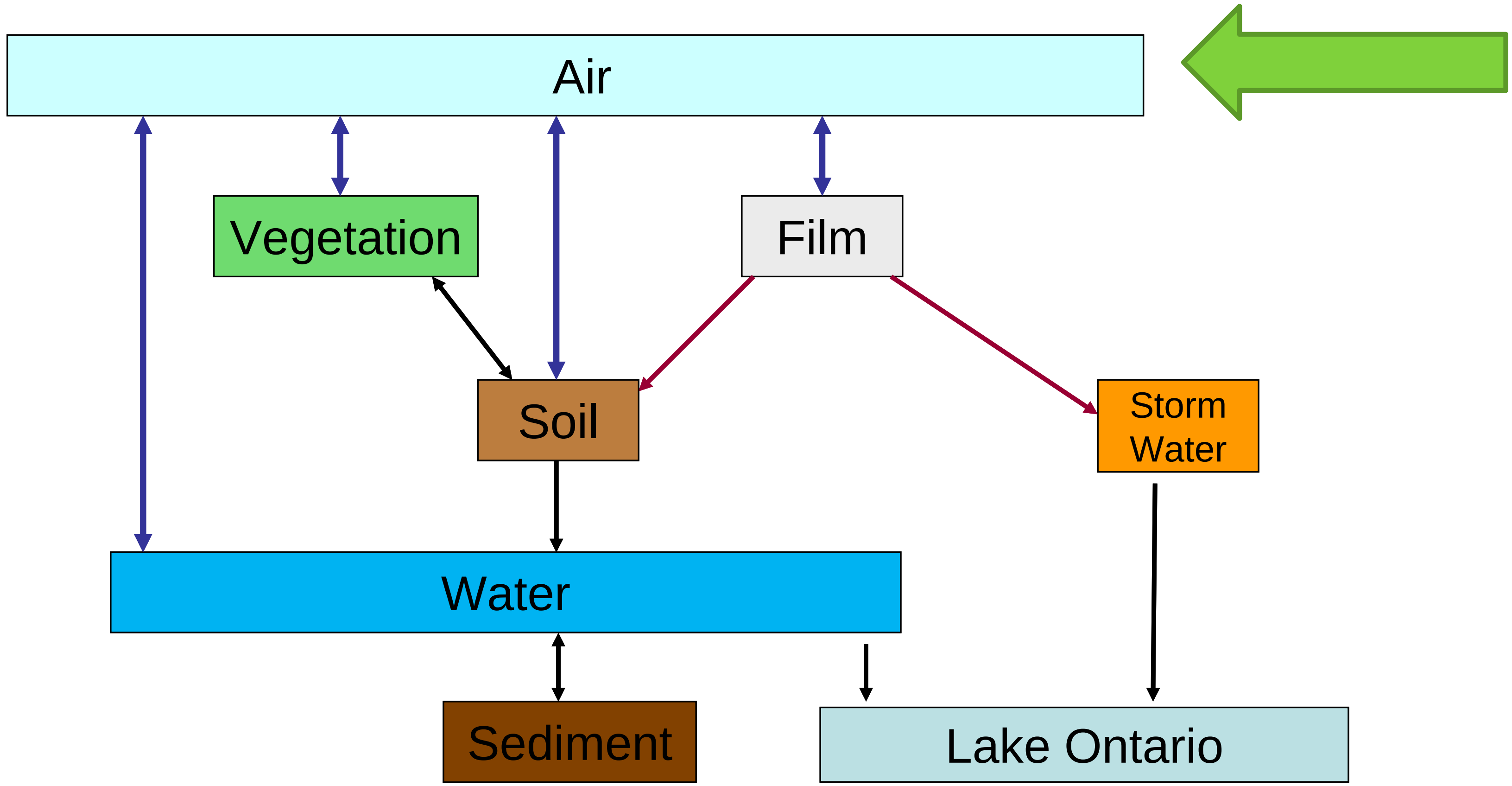


Wu, Harner, et al. 2005

Chemical Fate in Cities

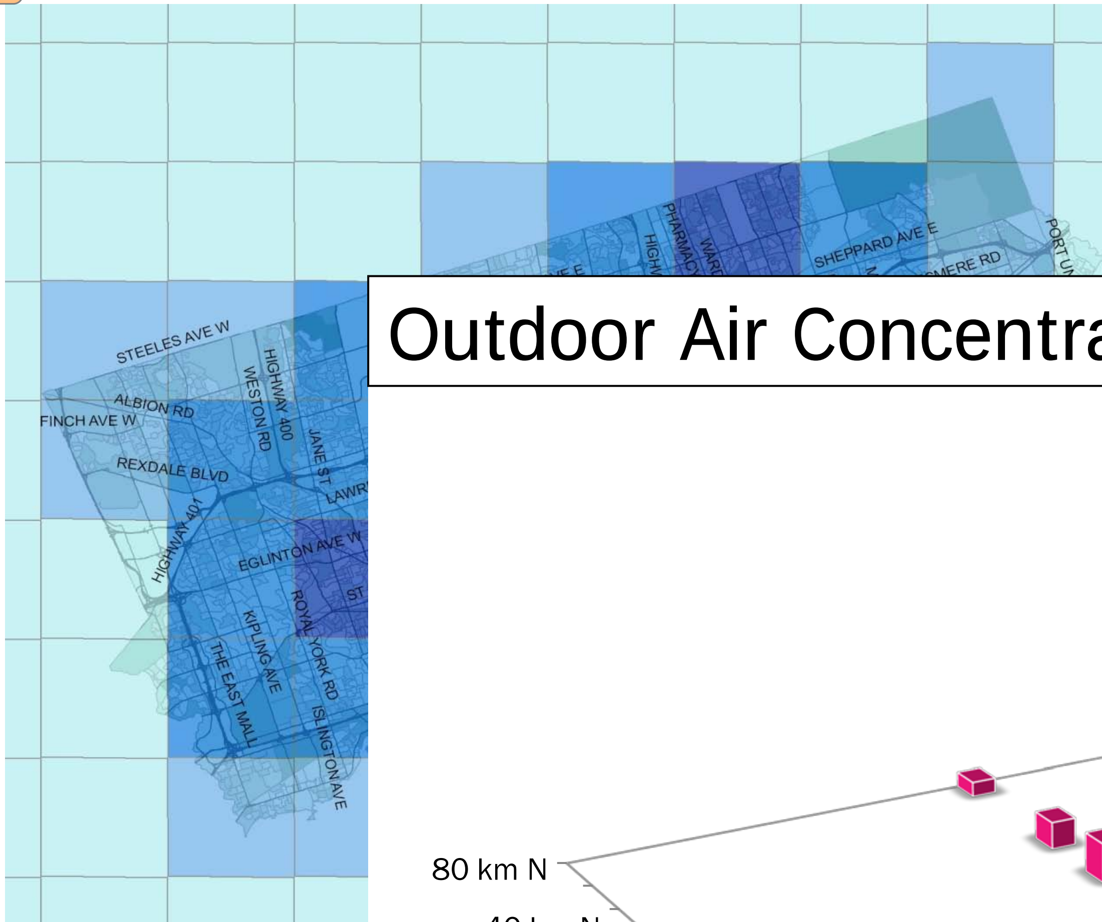
- Numerous emissions into a relatively small geographic area
- Area is highly disturbed
  - Impervious surfaces
  - Altered drainage system that maximizes rapid water conveyance and not storage
  - Compacted soils with elevated contaminant levels
  - Simple vegetative community

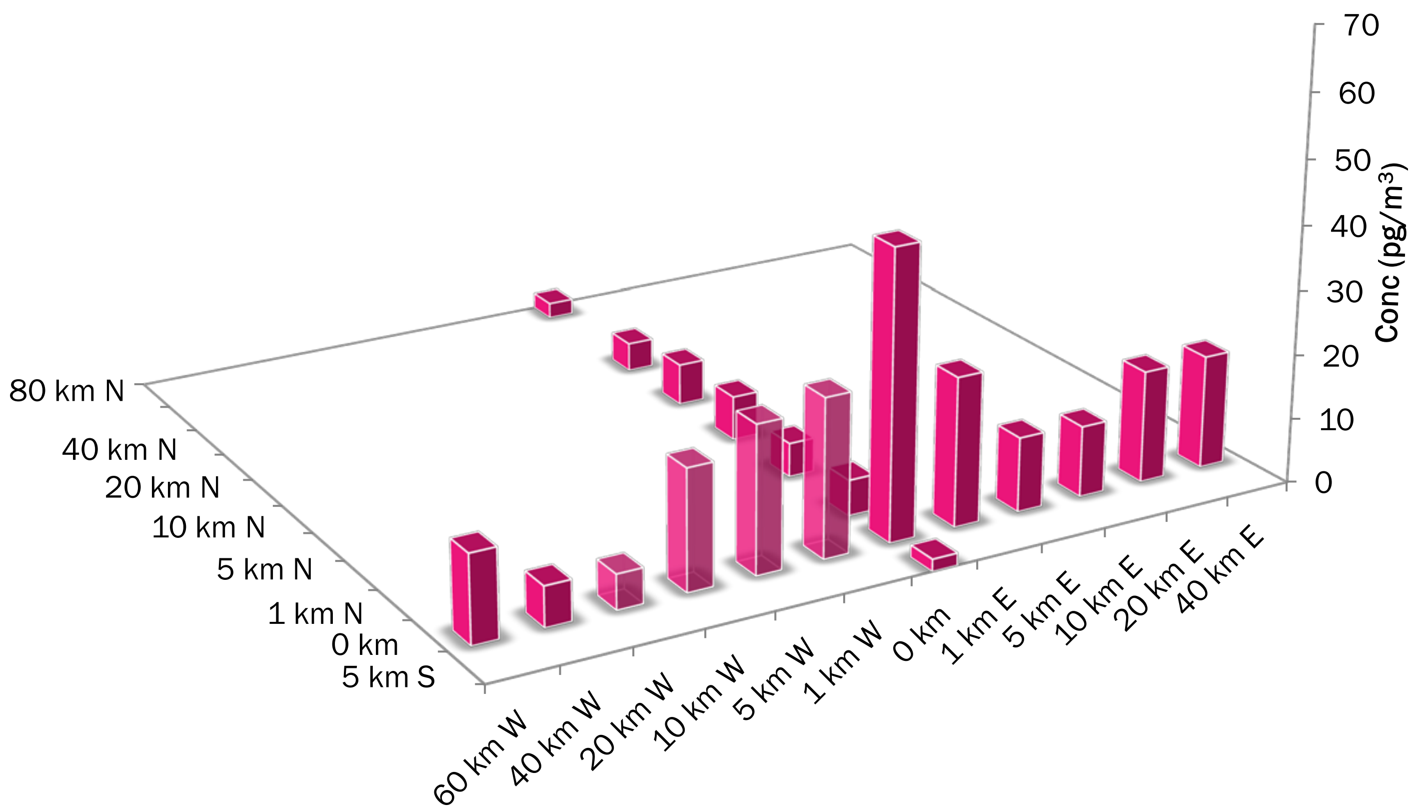
Environmental Compartments in City



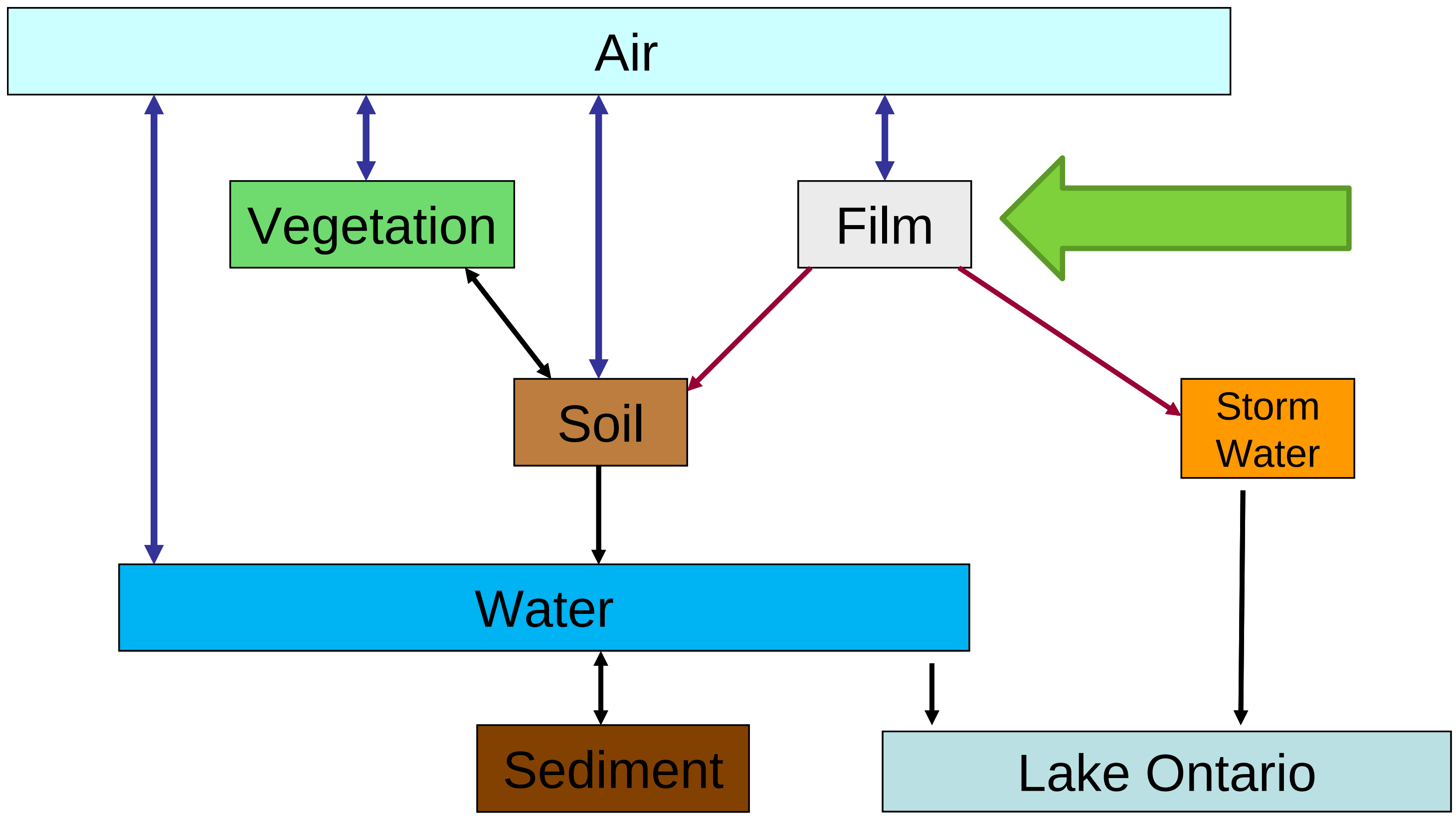
Diamond et al. 2001. Chemosphere, Priemer & Diamond 2002. ES&T
S.A. Csiszar, M.L. Diamond, L. Thibodeaux
Modelling urban films using a dynamic Multimedia Urban Model. In prep.

Outdoor Air Concentrations pg/m³



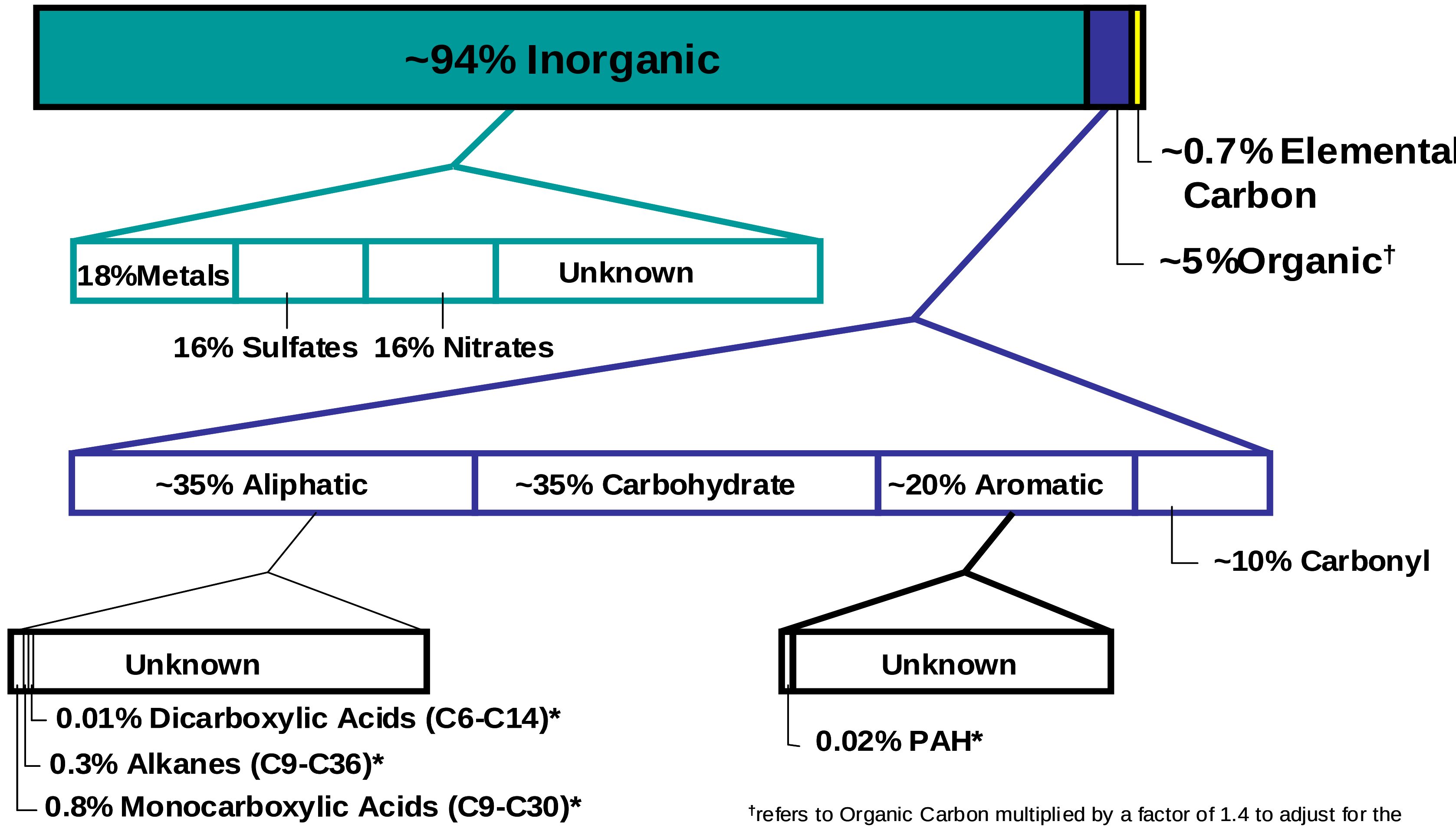


Environmental Compartments in City



Diamond et al. 2001. Chemosphere, Priemer & Diamond 2002. ES&T
S.A. Csiszar, M.L. Diamond, L. Thibodeaux
Modelling urban films using a dynamic Multimedia Urban Model. In prep.

Mass Balance Of Urban Surface Films

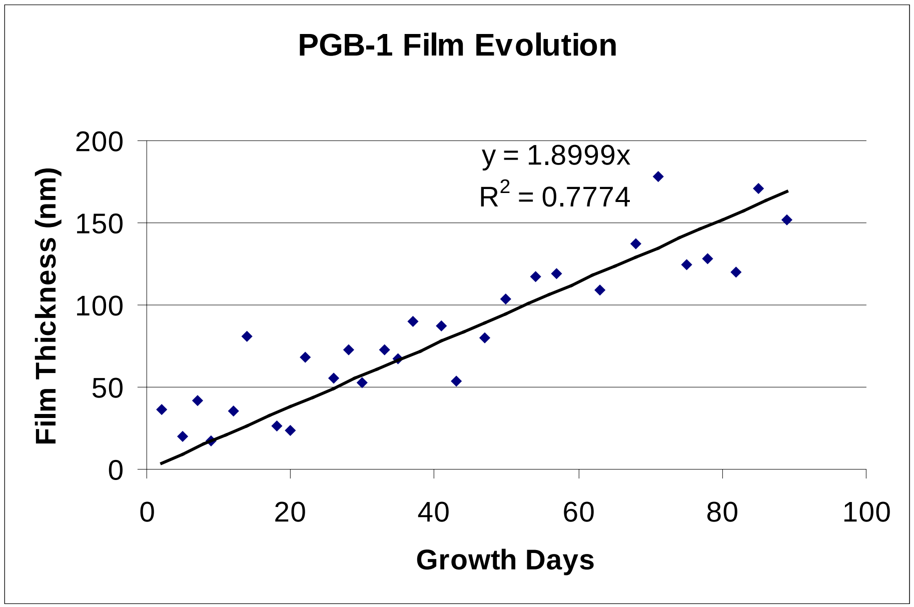


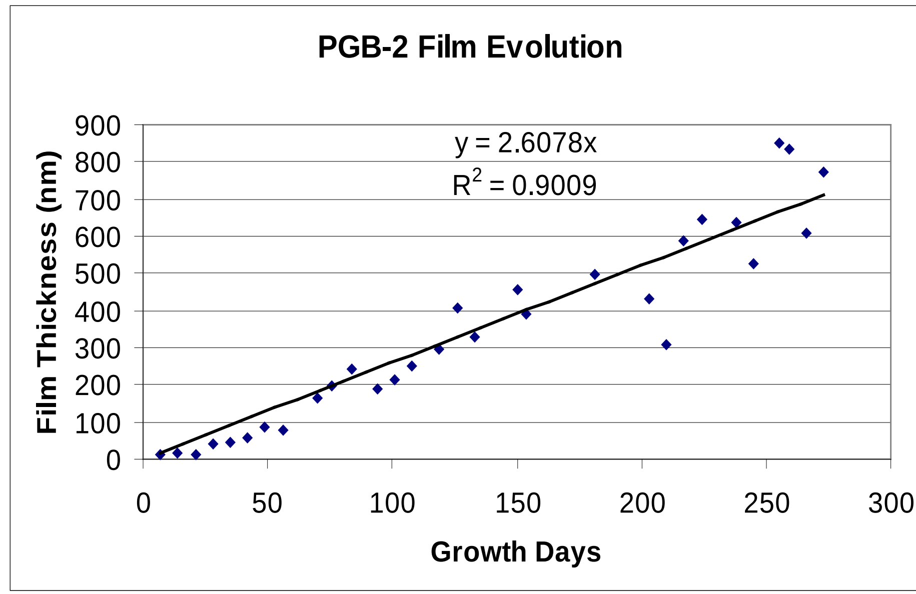
†refers to Organic Carbon multiplied by a factor of 1.4 to adjust for the molecular form of carbon species

*values compiled from previous studies

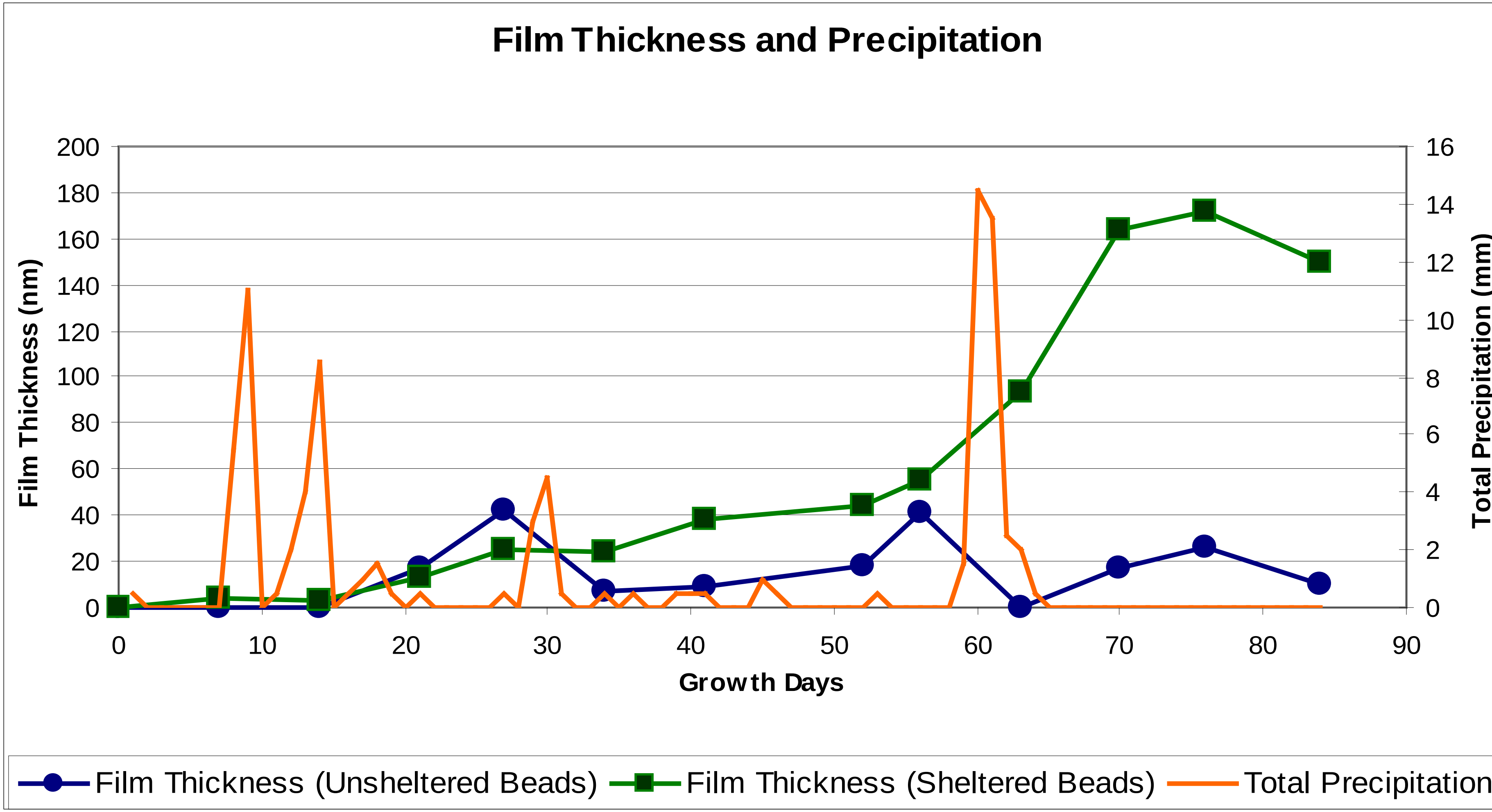
Lam et al. 2005 *Atmos Environ* 39: 6578–6586

Film Accumulation



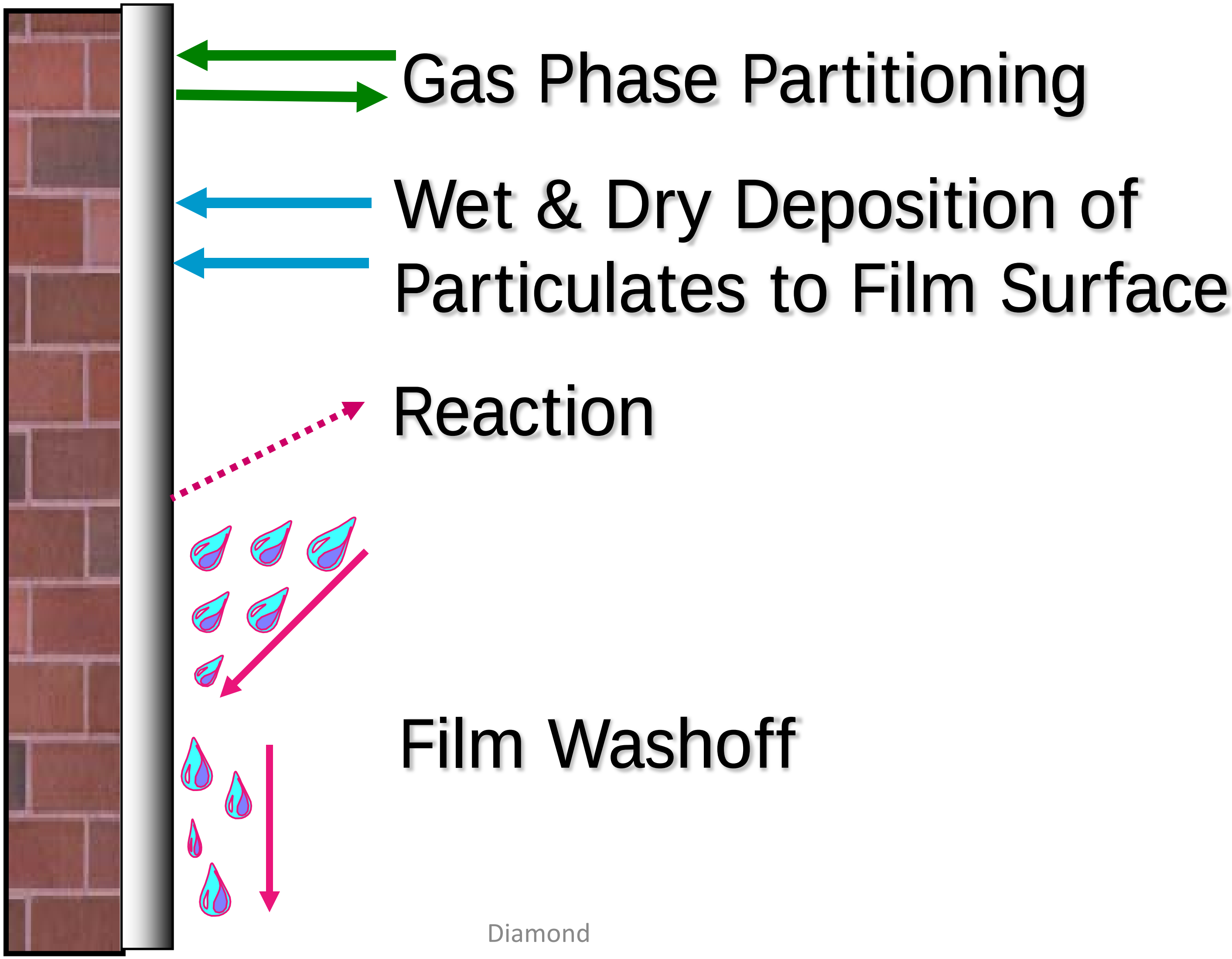


Wu et al. 2008 *Atmos. Environ*. 42: 5696-5705

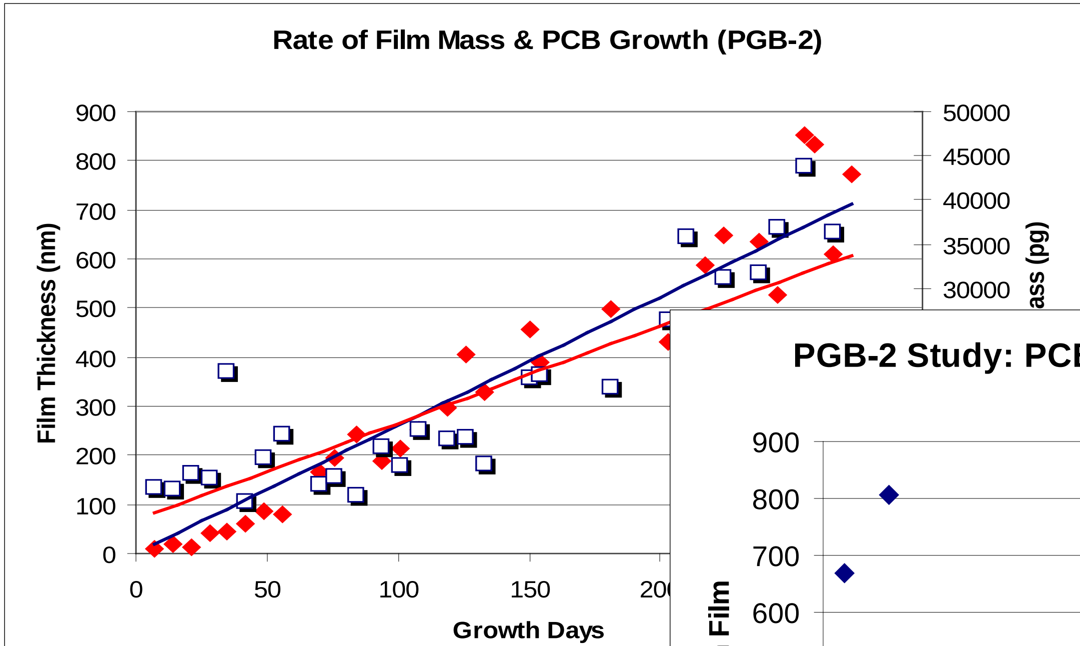


Wu et al. 2008 *Atmos. Environ*. 42: 5696-5705

Organic Film

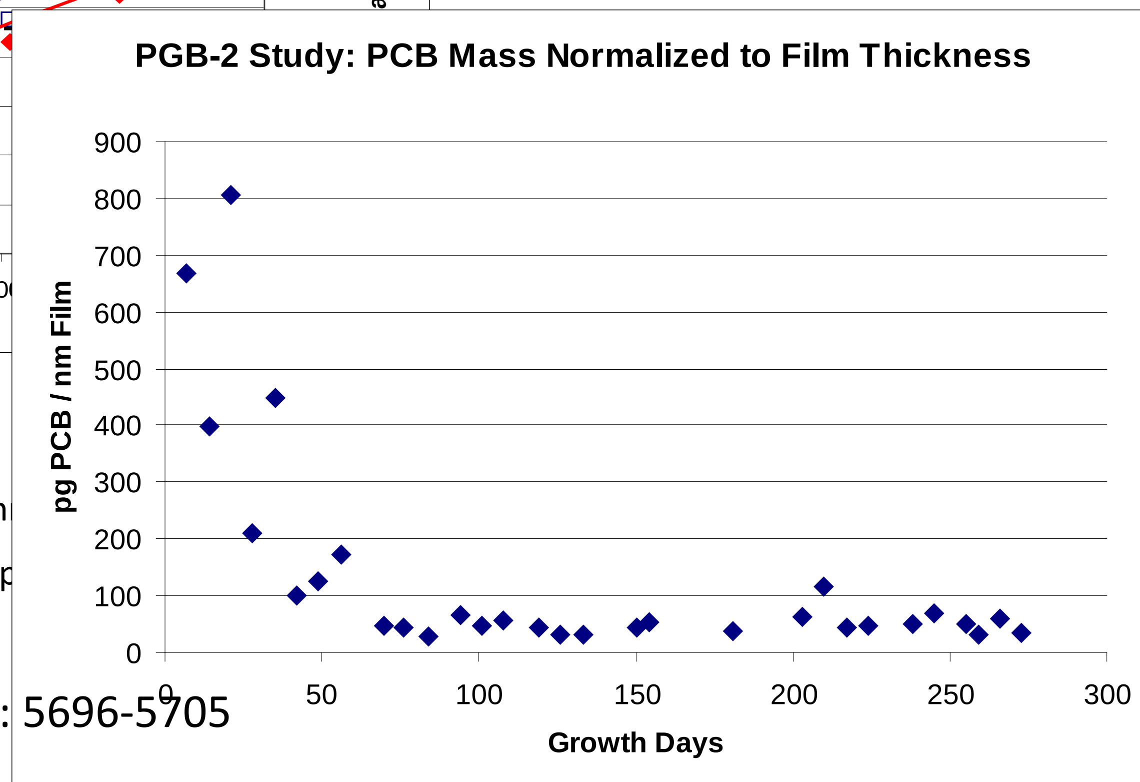


PCBs in Film



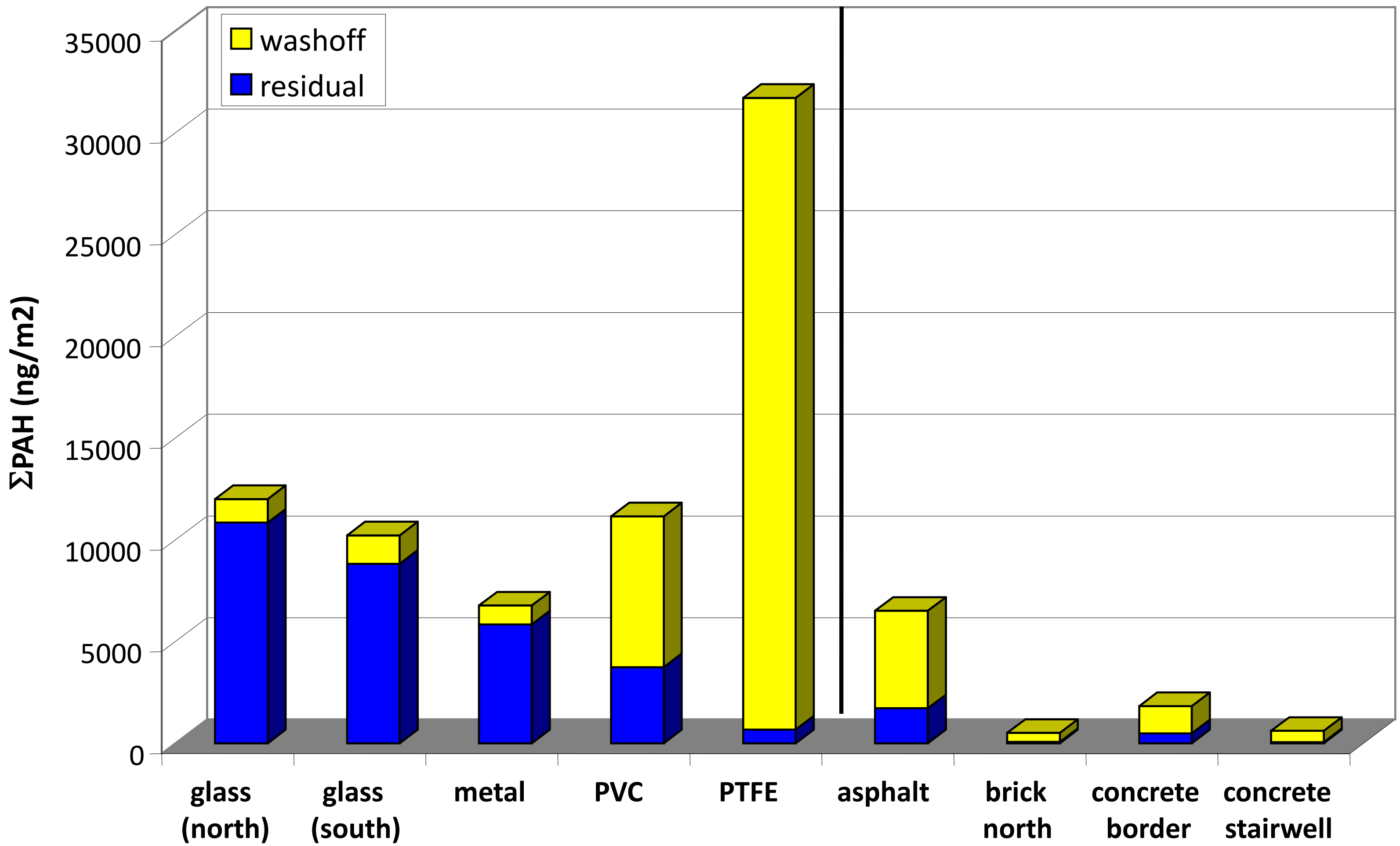
Legend: Film Thickness (n

Total PCB Mass (p



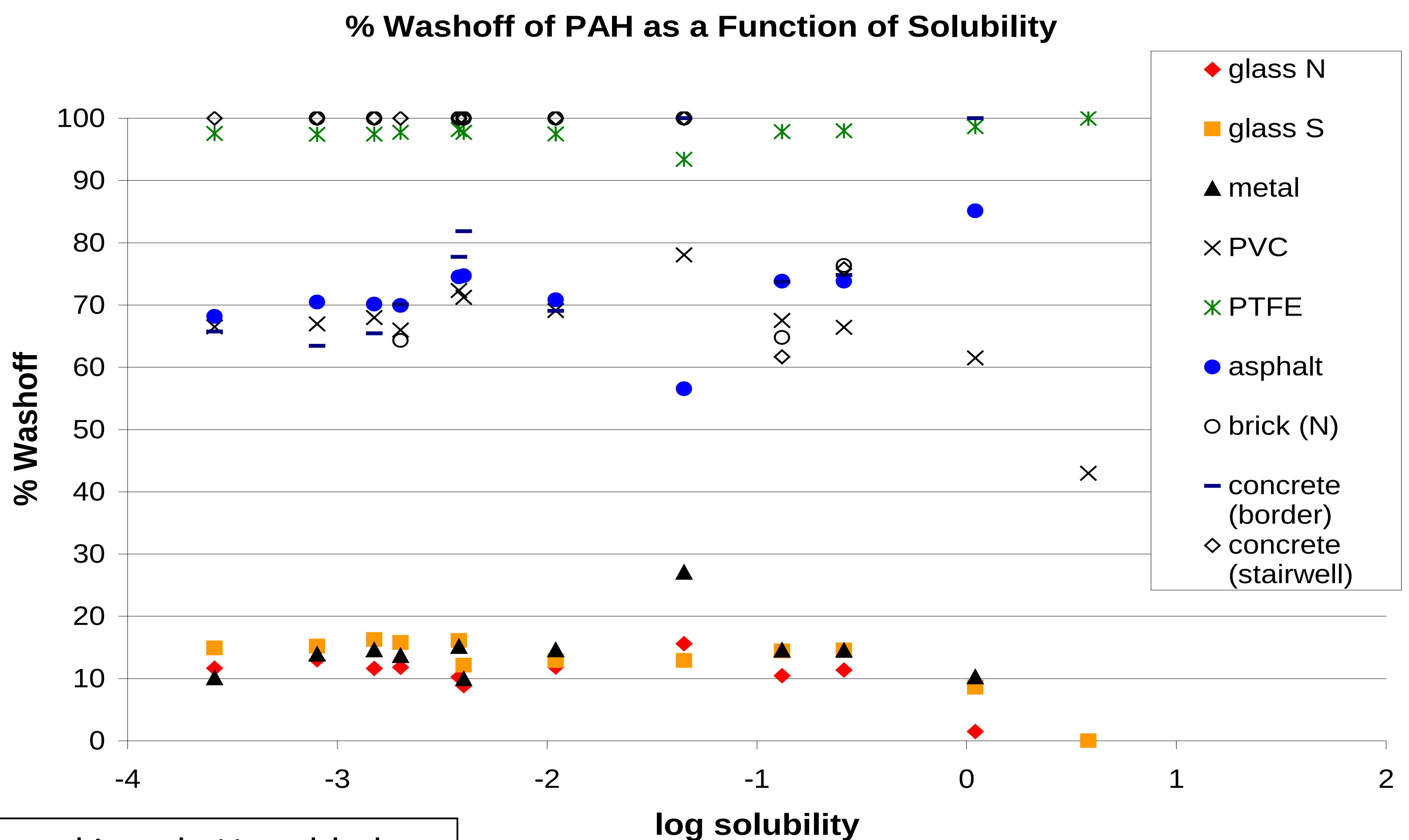
Wu et al. 2008 *Atmos. Environ*. 42: 5696-5705

Accumulation & Removal



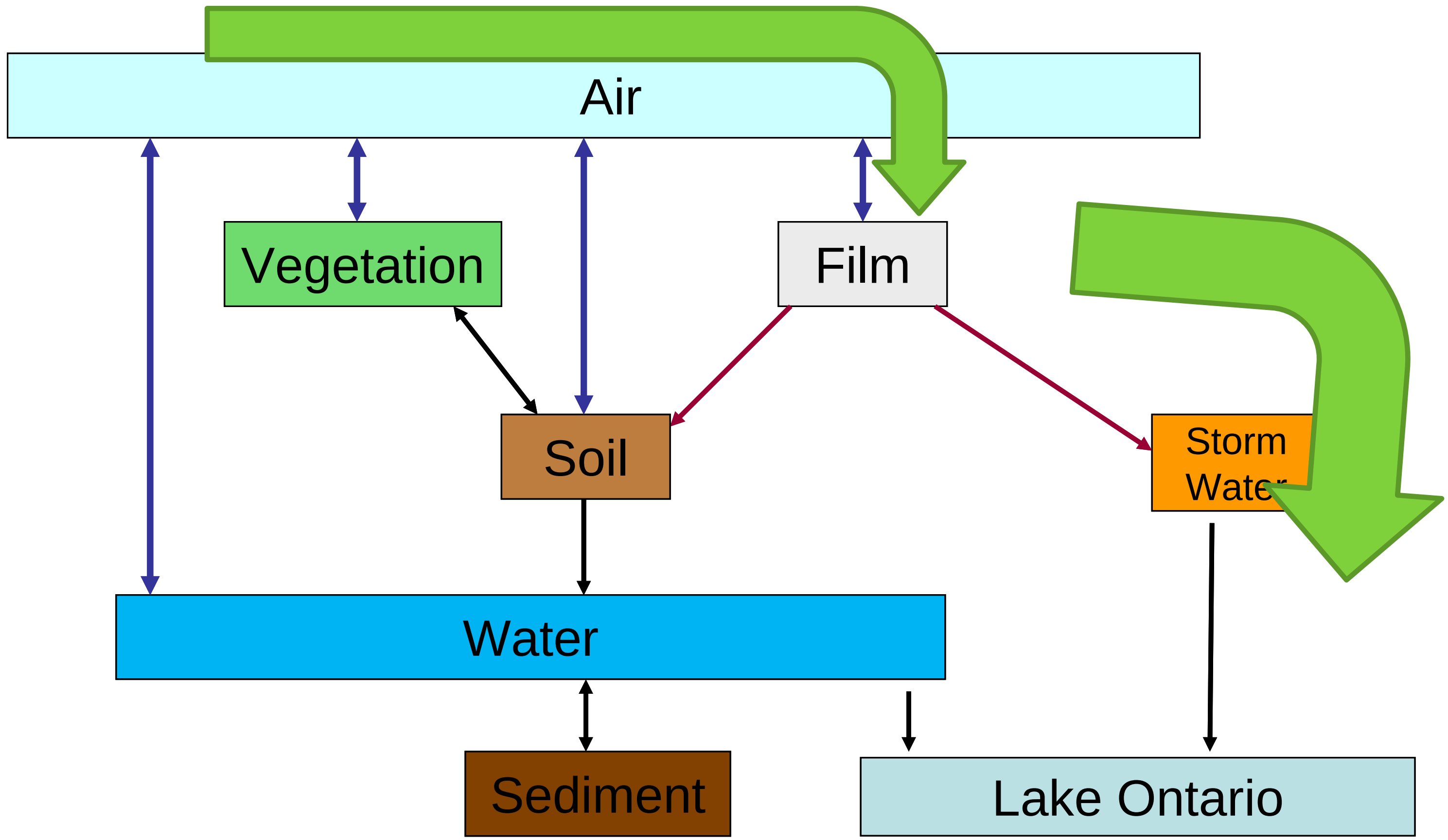
Labencki et al. Unpubl. data

Wash-off & Solubility



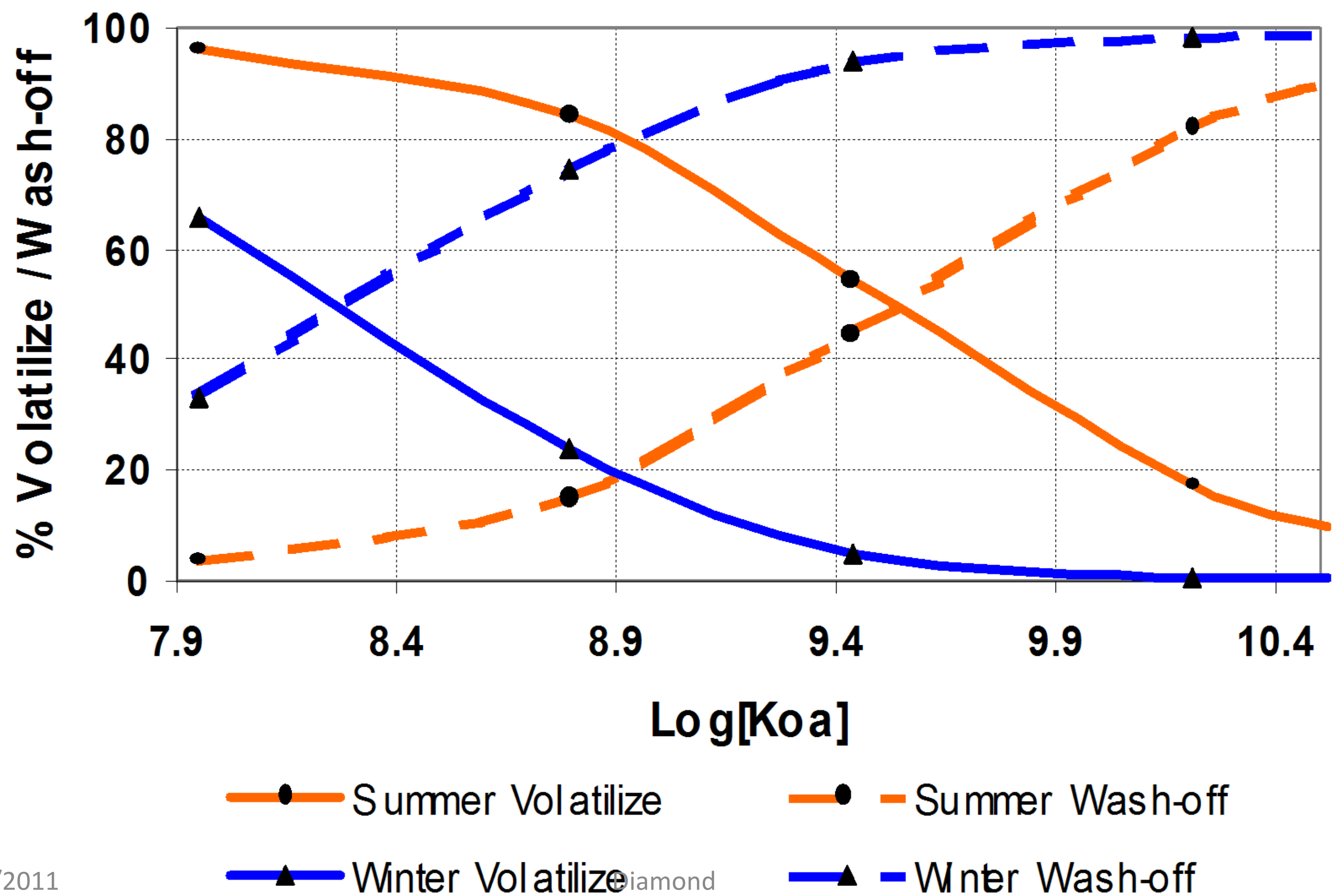
Labencki et al. Unpubl. data

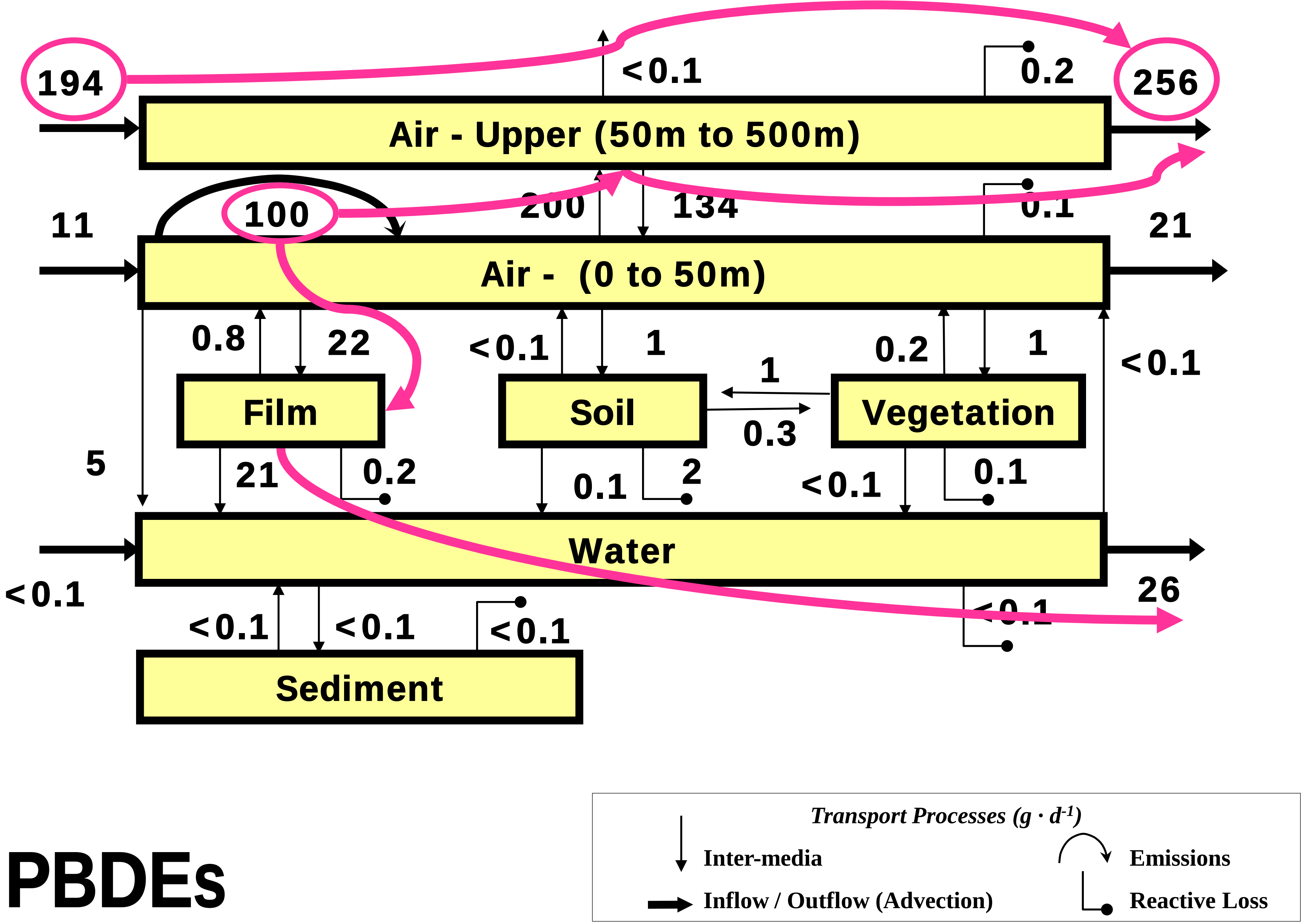
Movement of PBDEs



Diamond et al. 2001. Chemosphere, Priemer & Diamond 2002. ES&T
S.A. Csiszar, M.L. Diamond, L. Thibodeaux
Modelling urban films using a dynamic Multimedia Urban Model. In prep.

Chemical Transport from Film

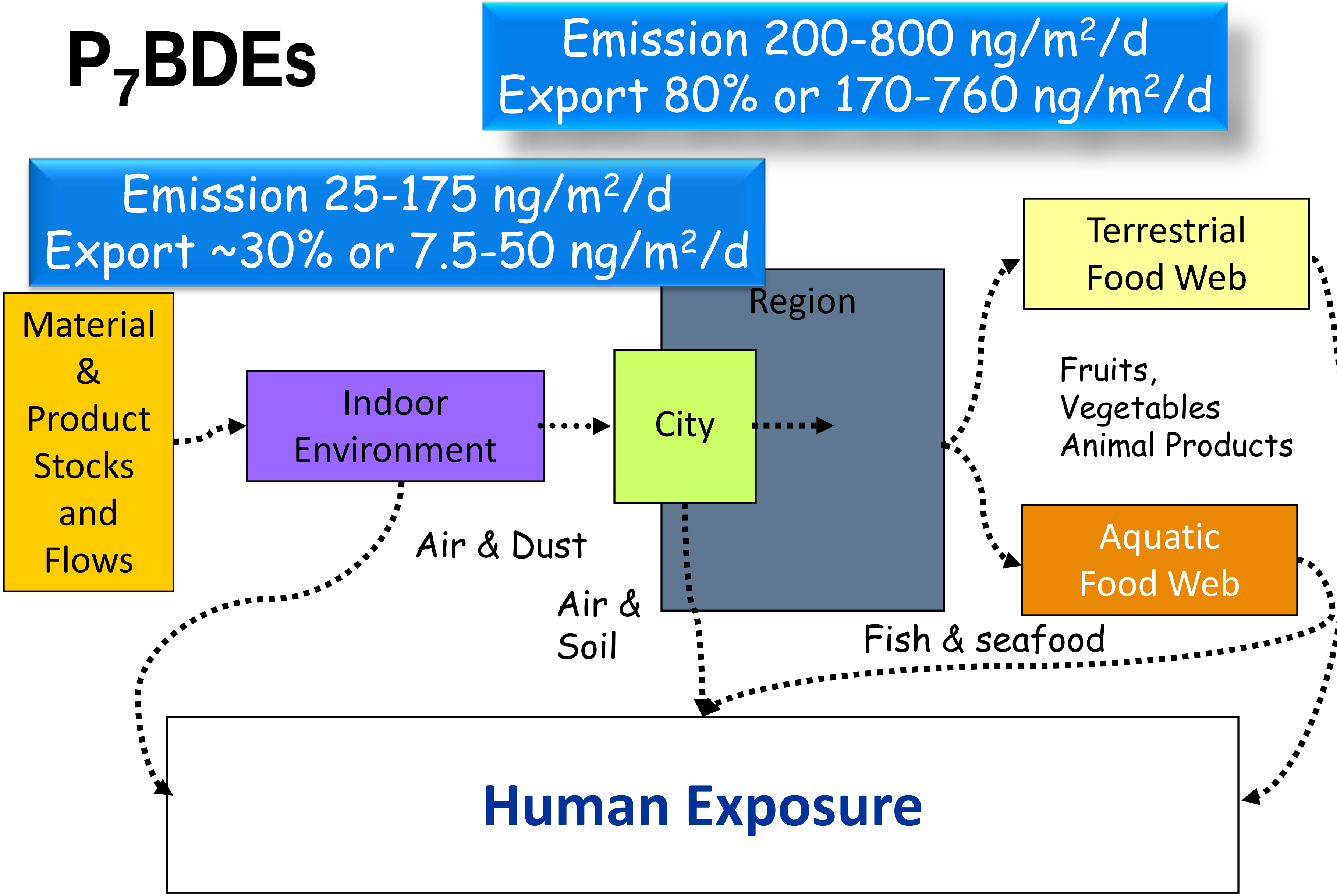




PBDEs

Jones-Otazo, Clarke et al. 2005 *Enivon Sci & Technol* 39: 5121-5130

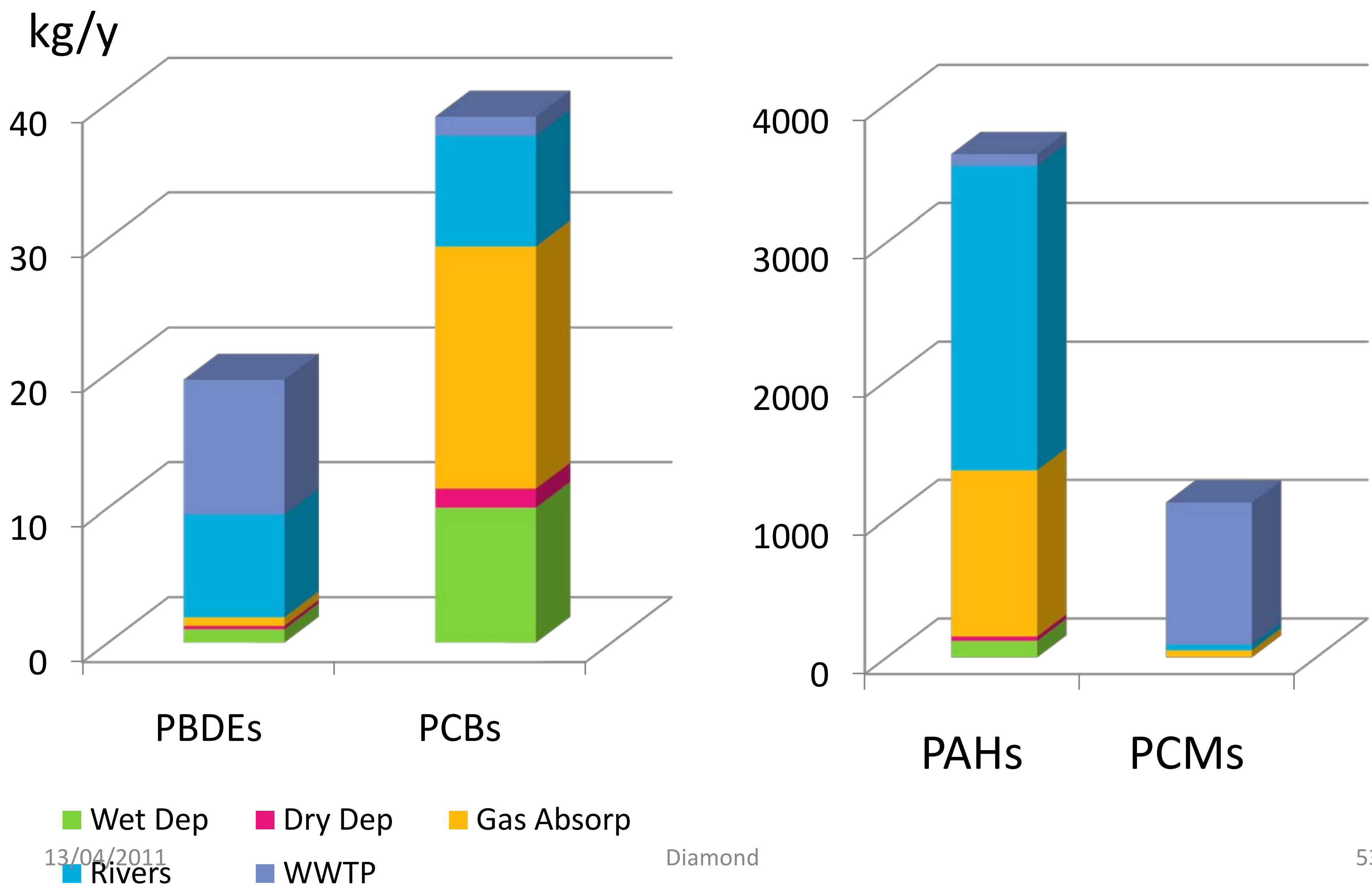
P_7BDEs



Jones-Otazo, Clarke et al. 2005 *Enivon Sci & Technol* 39: 5121-5130

Zhang et al. 2009 *Environ Sci Technol* 43: 2845-50

Comparison of Loadings to Lake Ontario



Summary: Material Flow Analysis

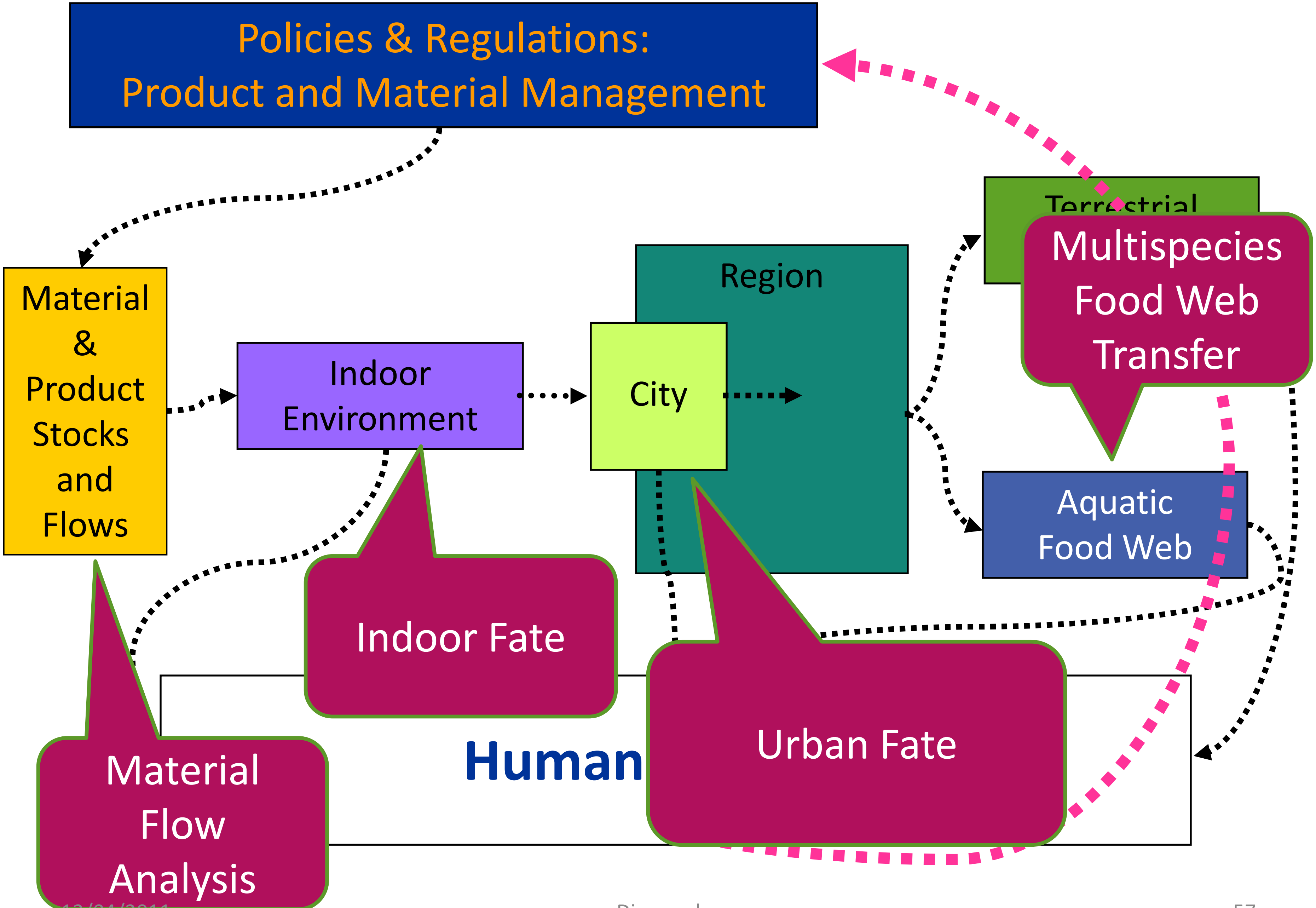
- Mass balance of products, chemicals, etc., across a boundary
- Used here to quantify <u>mass of products and/or materials </u>containing chemical of interest AND <u>mass of chemical of interest</u>
- Need to know mass or inventory AND inputs and outputs

Summary: Indoor Environment

- “concentrator” of emissions because of numerous chemical emission sources and limited loss processes (e.g., minimal air exchange rate)
- Important to understand chemical sources AND sinks (e.g., PUF furniture, carpet)
- Tiny fraction of SVOC is emitted from a very large inventory (or mass)

Summary: Cities

- Cities are geographic “concentrators” of resources, hence elevated concentrations in all media (air, soil, water)
- Impervious surfaces are coated with thin film that “collects” atmospherically deposited chemicals and facilitates movement back to air or to surface water
- Most chemicals emitted to air in cities is lost by advection, but also impervious surfaces promote chemical mobility in comparison to soils that are efficient chemical sinks


Policies & Regulations:
Product and Material Management
Material & Product Stocks and Flows
Indoor Environment
City
Region
Terrestrial
Multispecies Food Web Transfer
Aquatic Food Web
Indoor Fate
Urban Fate
Human
Material Flow Analysis