Emissions of organic chemicals from consumer articles: ChEmiTecs research programme

How to estimate emissions of organic chemicals from articles – the ChEmiTecs approach

Emission modelling and results

Indoor modelling and pathways

Peter Haglund, Umeå University
Jenny Lexèn, Anna Palm Cousins,
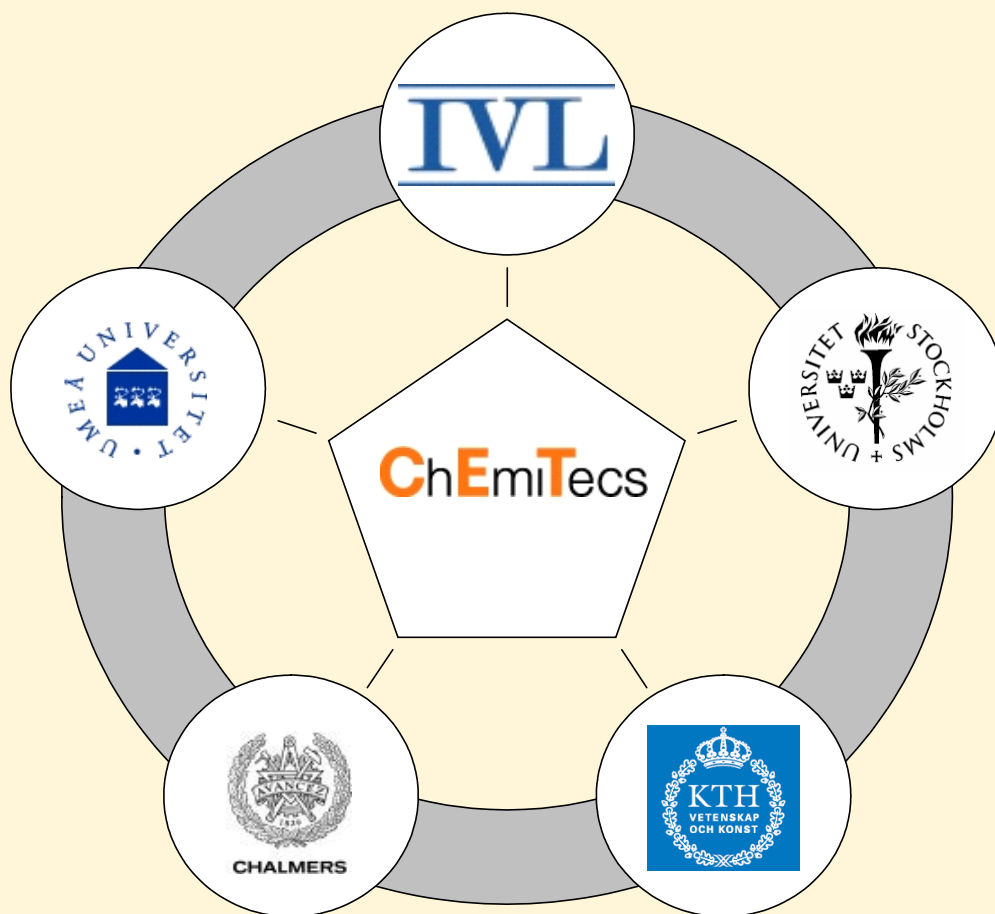*IVL, Swedish Environmental Research Institute*

www.chemitecs.se
(Organic Chemicals Emitted from Technosphere articles)

ChEmiTecs

ChEmiTecs

**Research programme financed by the Swedish EPA
2008-2012**

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Organic <u>Ch</u>emicals <u>Emi</u>tted from <u>Tec</u>hnosphere article<u>s:</u> ChEmiTecs

Overall aim

To increase the scientific understanding of the magnitude of the problem regarding emissions from articles

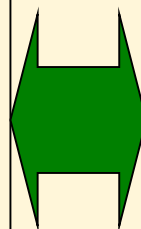Questions raised

How big is the problem?
How dangerous is it?
What can we do about it?

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Integrating domains

Chemicals		**Goods**
• **Chemical Policy - REACH**		• **Product policy - SCP**
• **Environmental Chemistry & Toxicology**	⬌	• **Environmental Systems Analysis & Engineering**
• **Analysis in Nature**		• **Technical System Modeling**
• **"Risk assessment"**		• **"Life cycle assessment"**

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ChEmiTecs research areas

Flow & Stocks

Chemicals

Emissions from goods – problem & actions ?
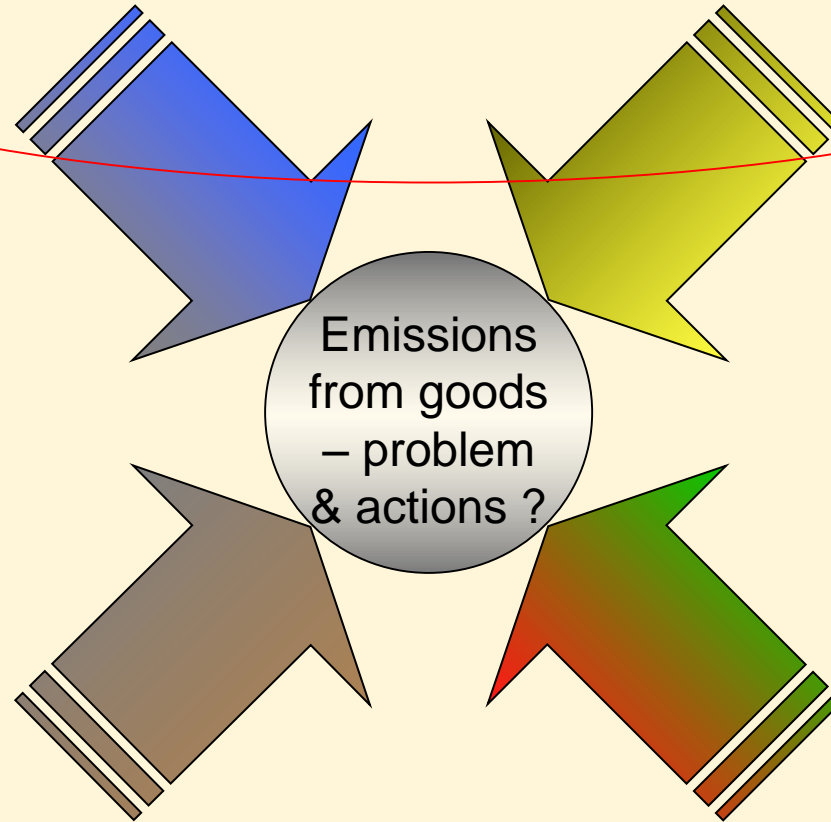
Reduction strategies & instruments

Risk & Perception

Work flow, case studies & quantification

Chemical stability

Reseach on emission mechanisms

Perception, attitudes

Selection of cases

Detailed case studies of 5-10 objects

Emission factors

Model verification monitoring

Concept model

Model to calculate emissions emission divers, exposure scen. etc

Prediction about occurrence

Quantification & Extrapolation Economy-wide Inventory

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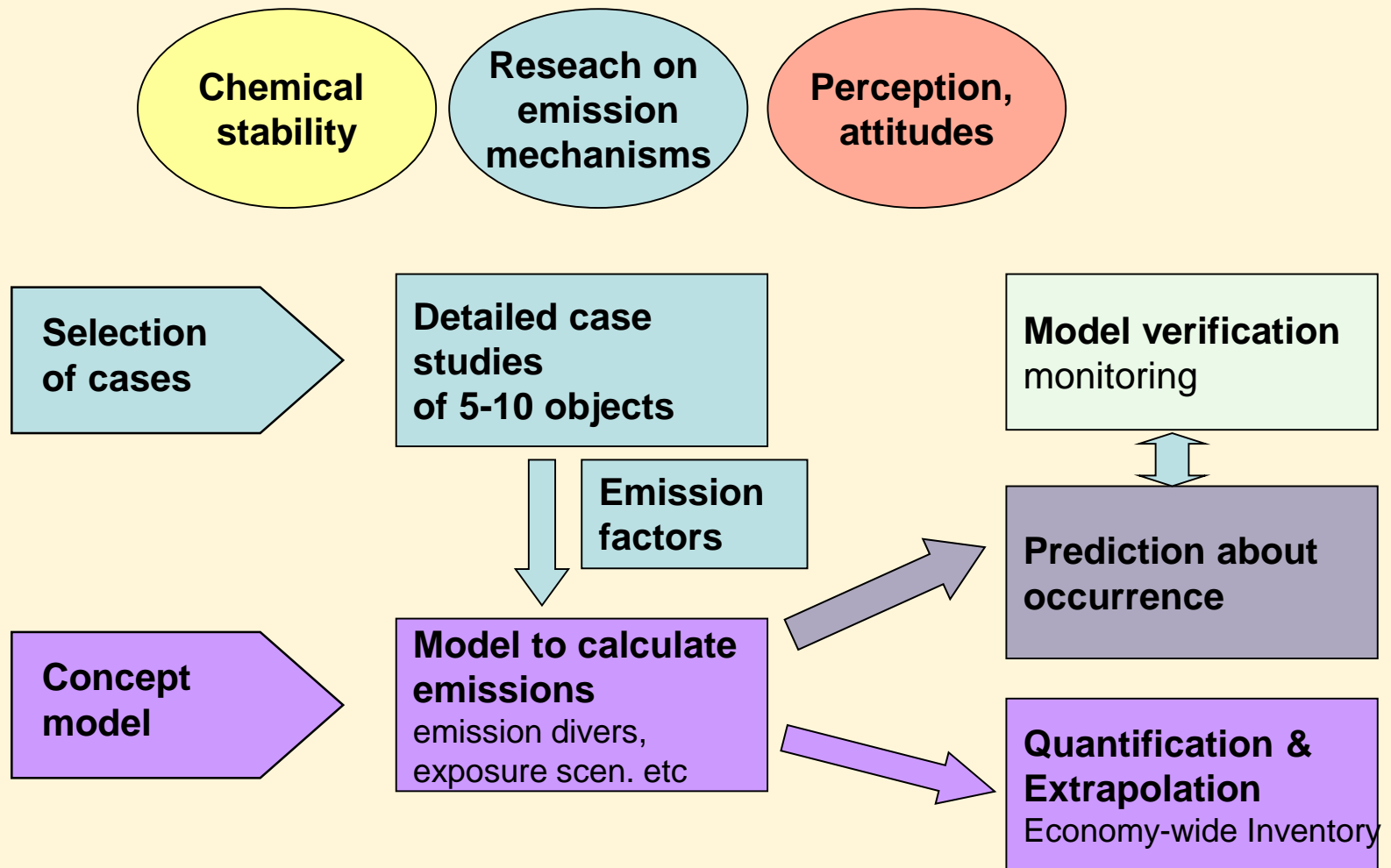
How big is the problem with emissions from articles relation to other sources and pathways ?

Screening studies

- Concentrations in the environment, fill data gaps
- Estimation of pathways and sources
- Selection of case studies

Substance flow analysis (SFA)

- Dimensioning of sources, sinks and flows – what is big and what is small
- Allows for source tracking
- Important information when suggesting management strategies
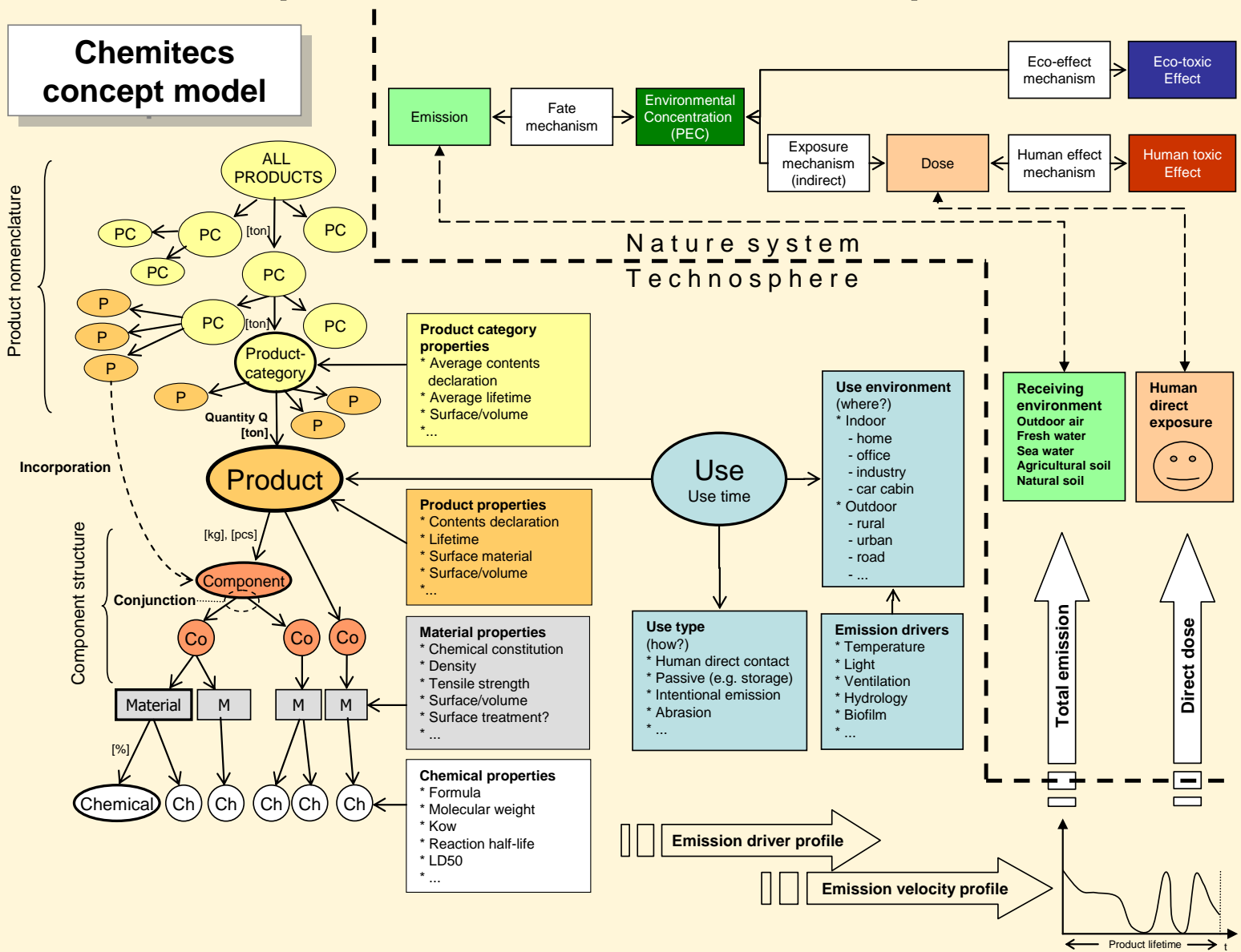
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Generic emission modeling

- Can be used for all organic (neutral) chemicals

- Literature data used for material specific calibration
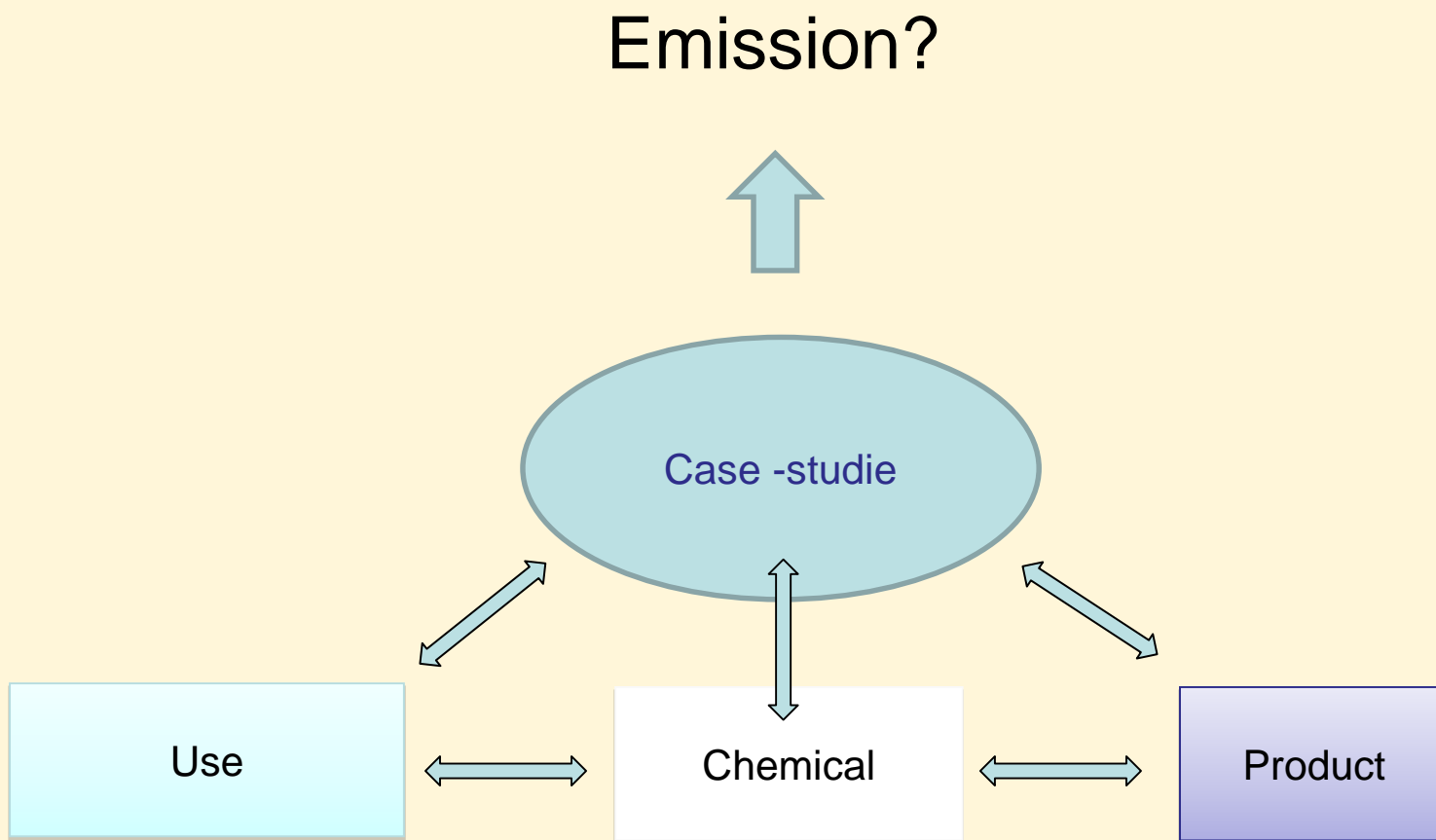
- Can be applied to any emission scenario

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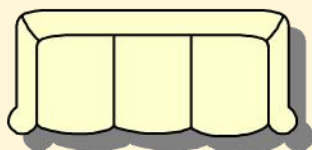# Conceptual model of emissions from products

Chemitecs concept model

Eco-effect mechanism → Eco-toxic Effect

Emission ← Fate mechanism → Environmental Concentration (PEC)

Exposure mechanism (indirect) → Dose ← Human effect mechanism → Human toxic Effect

Nature system

Technosphere

Product nomenclature

ALL PRODUCTS

PC, PC, PC, PC, PC, PC, PC, PC

Quantity Q [ton]

Product-category

Product category properties
* Average contents declaration
* Average lifetime
* Surface/volume
* ...

P, P, P, P, P, P

Incorporation

Product

[kg], [pcs]

Product properties
* Contents declaration
* Lifetime
* Surface material
* Surface/volume
* ...

Use
Use time

Use environment
(where?)
* Indoor
  - home
  - office
  - industry
  - car cabin
* Outdoor
  - rural
  - urban
  - road
  - ...

Receiving environment
Outdoor air
Fresh water
Sea water
Agricultural soil
Natural soil

Human direct exposure

Component structure

Conjunction

Component

Co, Co, Co

Material properties
* Chemical constitution
* Density
* Tensile strength
* Surface/volume
* Surface treatment?
* ...

Material, M, M, M

Use type
(how?)
* Human direct contact
* Passive (e.g. storage)
* Intentional emission
* Abrasion
* ...

Emission drivers
* Temperature
* Light
* Ventilation
* Hydrology
* Biofilm
* ...

Total emission

Direct dose

[%]

Chemical, Ch, Ch, Ch, Ch, Ch

Chemical properties
* Formula
* Molecular weight
* Kow
* Reaction half-life
* LD50
* ...

Emission driver profile

Emission velocity profile

Product lifetime

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Choice of Case Chemicals
(Umeå University: P. Andersson, S. Rännar)

Emission?

Case -studie

Use

Chemical

Product

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Prioritization

Prio =
Area × Chemical content × Emission drivers

(various uses)

Furniture

Electronics

Clothes & shoes

Building materials

Vehicals
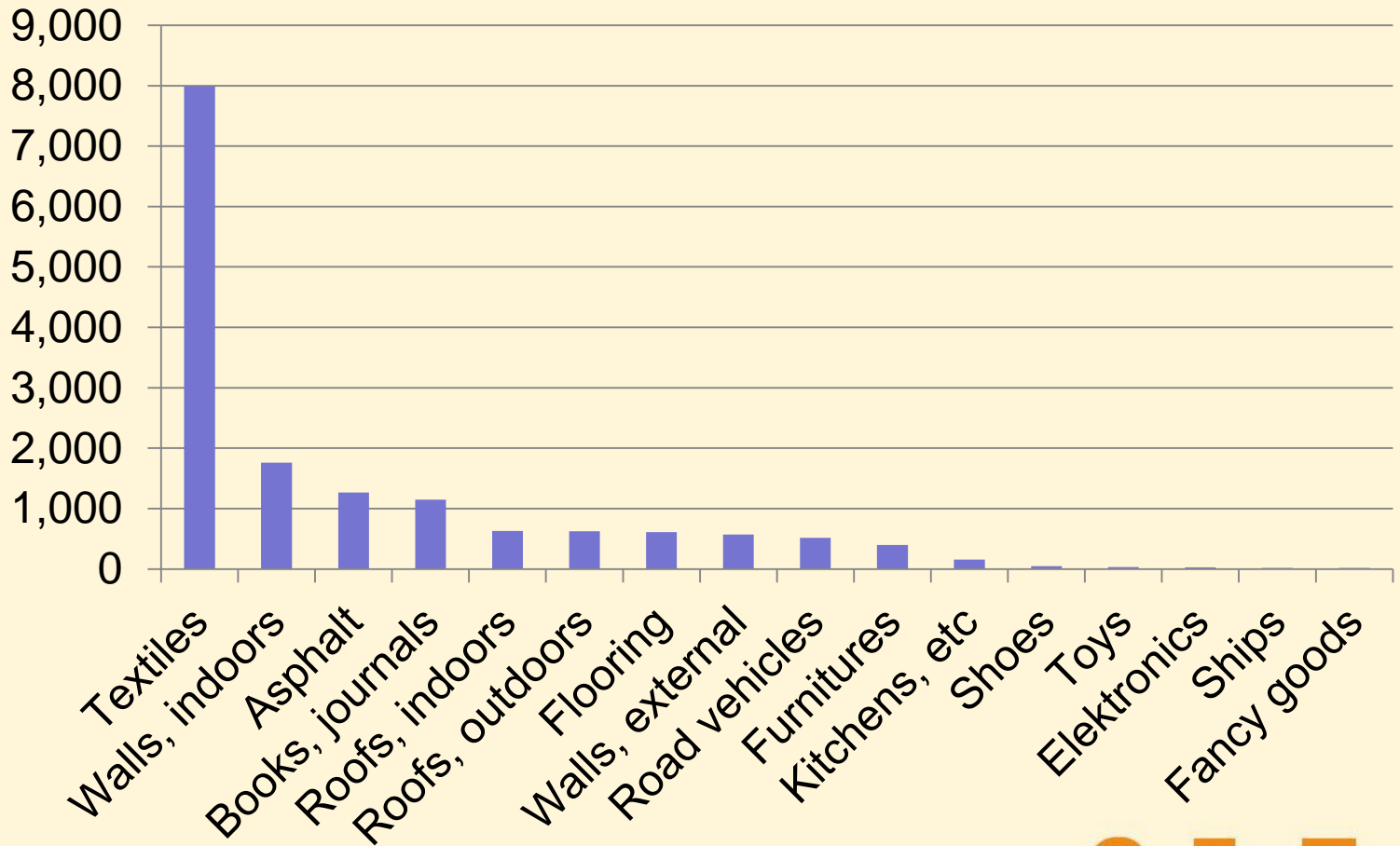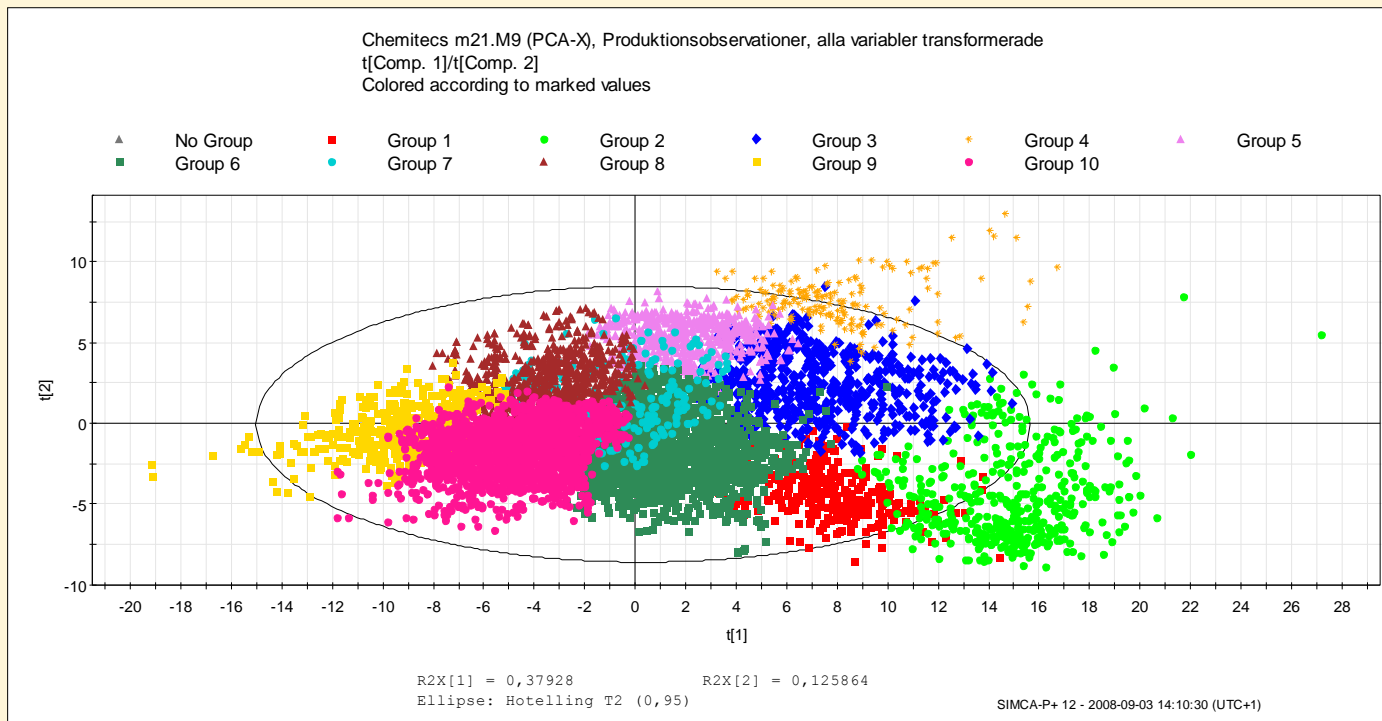
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Area calculations

Total area (km^2)

Category	Value
Textiles	8,000
Walls, indoors	~1,750
Asphalt	~1,250
Books, journals	~1,150
Roofs, indoors	~600
Roofs, outdoors	~600
Flooring	~600
Walls, external	~550
Road vehicles	~500
Furnitures	~400
Kitchens, etc	~150
Shoes	~50
Toys	~50
Elektronics	~25
Ships	~10
Fancy goods	~10

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Selected produkt categories
(Custum stat, SCB; 14430 KN nummers)

KN-nummer	Description
39	Plastic
40	Rubber
44	Wood
59	Coated textiles
62	Clothes
64	Shoes
85	Electronics
87	Vehicles
94	Furniture
95	Toys

Independent expert judgement

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Selection of Case Chemicals

Chemitecs m21.M9 (PCA-X), Produktionsobservationer, alla variabler transformerade
t[Comp. 1]/t[Comp. 2]
Colored according to marked values

- Cluster analys was used to create 10 groups of chemicals (with similar properties within group).

Stefan Rännar och Patrik Andersson

5 case studies

-Wear
-Surface/Mass
-Ageing
-Frequence
-Temp, UV
-etc

Life "cycles" & episodes

Other factors, **e.g.**
-Analytical properties
-Data availability / effects
-Subst. with known occurrence
-Subst. of specific interest
-Representativity + Diversity

Goods, e.g.
Building(s)
Roads/vehicles
Polymers
Textiles, shoes
Electronics

Relevant objects - "of concern"

Case selection

-Production,
-Import, Export,
-Waste
-ServiceLife,
-Stock
-Composition
-Free amount

Chemicals

-Org subst
-H/LPVC (7160 st)
-Priolist subst
-PB
-LRTP
-Mw <1000

TBP

DINP

MBT

HS

PFCs

TPP

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Emission modeling

Convection mass transfer coefficient, h_m

$$h_m = \frac{D_a}{x} 0.664 \left(\frac{u_m \rho_a x}{\mu_a} \right)^{1/2} \left(\frac{\mu_a}{D_a \rho_a} \right)^{1/3}$$
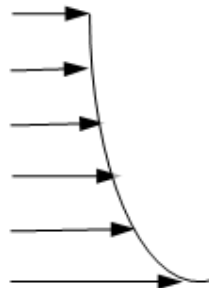
Partition in equilibrium at boundary layer, $K_{M/A}$

$$RT \ln K_{M/A} = c + aA + bB + eE + sS + lL$$

Diffusion in material, D

$$D = \exp \left(Ap - 0.1351 (Mw)^{2/3} + 0.003 Mw - \frac{10450}{T} \right)$$

Holmgren, et al.
A generic emission model to predict release of organic substances from materials in consumer goods   *Science of the Total Environment, 437: 306-314*

ChEmiTecs

Emission modeling

Convection mass transfer coefficient, h_m

Air velocity dependent

$$h_m = \frac{D_a}{x} 0.664 \left(\frac{u_m \rho_a x}{\mu_a} \right)^{1/2} \left(\frac{\mu_a}{D_a \rho_a} \right)^{1/3}$$

Partition in equilibrium at boundary layer, $K_{M/A}$

Very compound dependent

$$RT \ln K_{M/A} = c + aA + bB + eE + sS + lL$$

Diffusion in material, D

Very material dependent

$$D = \exp \left(Ap - 0.1351(Mw)^{2/3} + 0.003Mw - \frac{10450}{T} \right)$$

Holmgren, et al.
A generic emission model to predict release of organic substances from materials in consumer goods   *Science of the Total Environment, 437: 306-314*
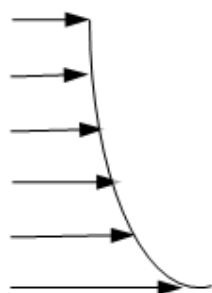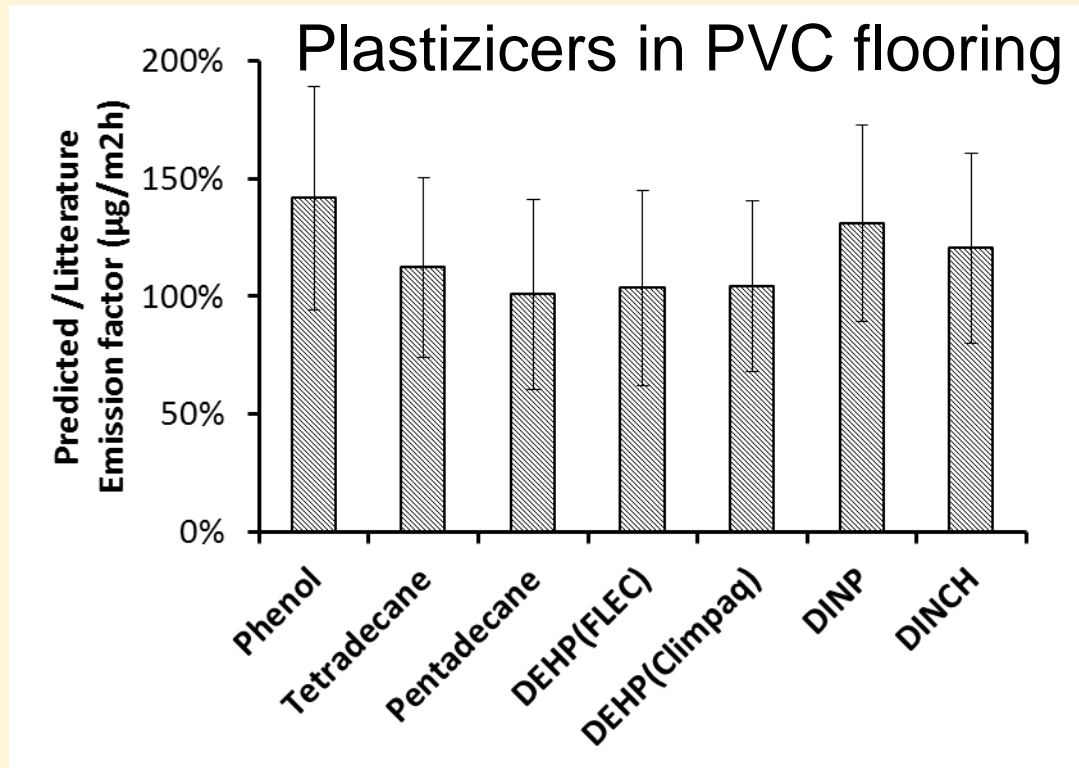
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1 m³ chamber

Temperature control
- Up to 100 ±1 ° C (air)
- Up to 300 ° C (walls)

Sampling on adsorbent

Method validation

Plastizicers in PVC flooring

Method comparison

Emissions of plastic additives

Chart comparing OECD and ChEmiTecs x 70 emission values for plastic additives:

Additive	OECD	ChEmiTecs x 70
2,4-Dibromfenol	~48000	~49000
Pentabromobenzyl acrylate	~39000	~9500
Trifenylfosfat	~27500	~29000
Dibutylftalat	~24500	~24500
2,4,6-Tribromfenol	~27500	~34500
Bensylbutylftalat	~19000	~24000
Di(n-hexyl)phtalate	~16500	~24000
Triethyl phosphate	~14000	~3000
12H-Phthaloperin-12-one	~18000	
Di(etylhexyl)ftalat	~14500	~22000
Dechlorane Plus	~16500	
Di(2-etylhexyl)adipat	~13000	~23000

Legend: OECD (light blue), ChEmiTecs x 70 (dark blue)

ChEmiTecs

Retrospective/furure time trends
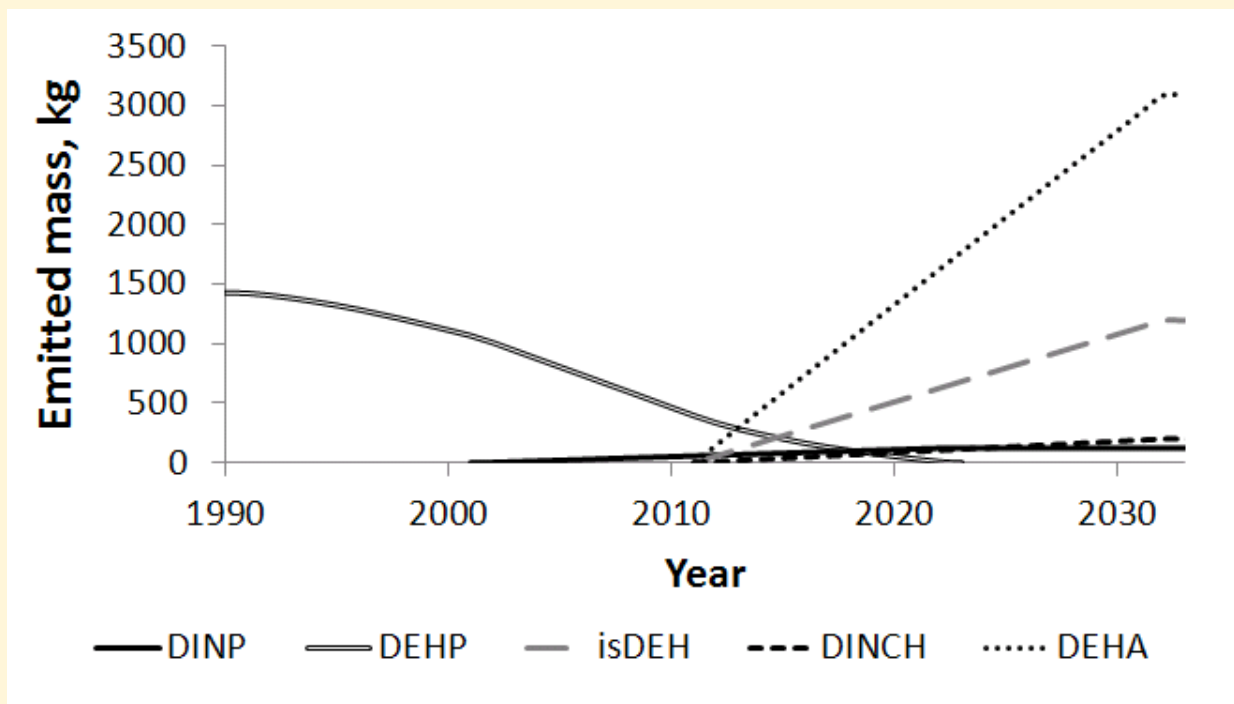

DEHP: Di(2-ethylhexyl)phthalate
DINP: Di-*iso*-nonyl phthalate
DEHA: Di(2-ethylhexyl)adipate
DINCH: Di-*iso*-nonyl-1,2-cyclohexanedicarboxylic acid ester
isDEH: Di-*iso*-nonylphthalate diethyl hexyl-*iso*-sorbide

	2012 (kg)	
DEHP	DINP	DINCH
210	40	3.6

ChEmiTecs

Further developments

Homogenous and stable materials → Particulate emissions (from wear particles) → Partitioning to other recipients (settling dust, water or human skin) → Multi-layer materials → Effects of cleaning (abrasion, surfactants etc.) → "Blooming" materials

ChEmiTecs
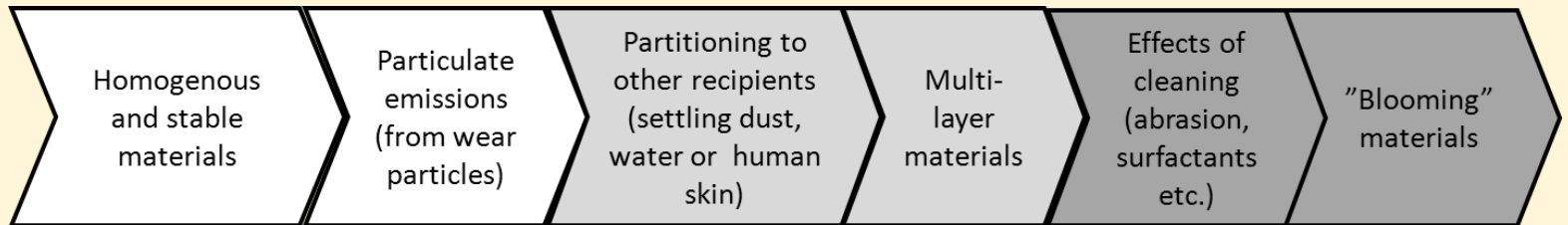
First Comprehensive Test:
One article/use, all chemicals

Total area /product group

Painted inner walls

Area (m²)

y-axis values
9,0E+09
8,0E+09
7,0E+09
6,0E+09
5,0E+09
4,0E+09
3,0E+09
2,0E+09
1,0E+09
0,0E+00

Textiles, Inner walls, Pavements, Furniture and fixed furnishing, Books and papers, Plastic films, Ceilings, Roofs, Floors, Outer walls, Motor vehicles on wheels, Consumer electronics, Shoes, Toys

ChEmiTecs
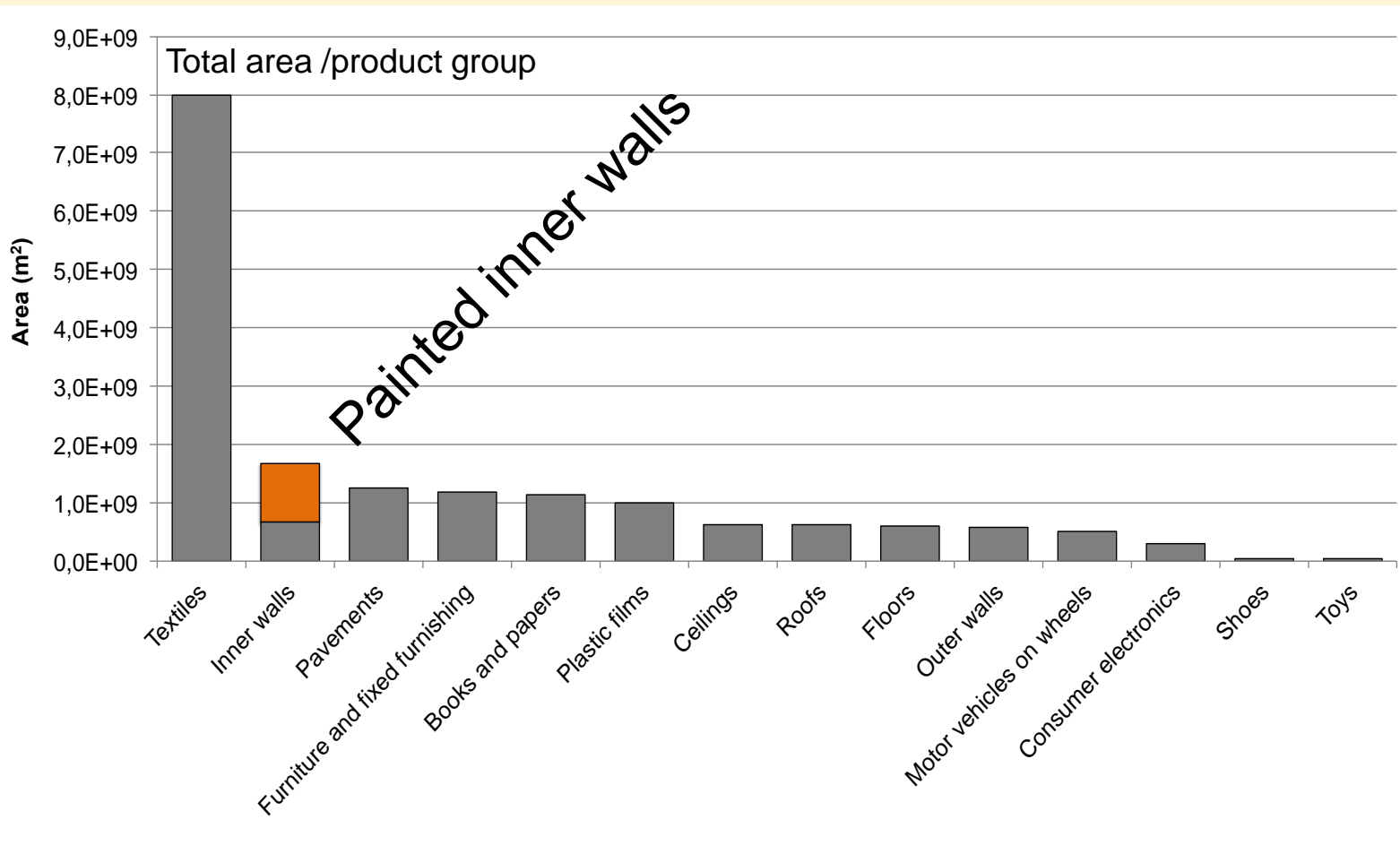
What chemicals are included in calculations?

Chemiclas in water based paint

71 polymerers
103 additives
54 Solvents

Type of additive

43 inorganic
43 organic
17

organo-metalic

To emission calculations

37 compounds in model domain

6 compounds outside model domain

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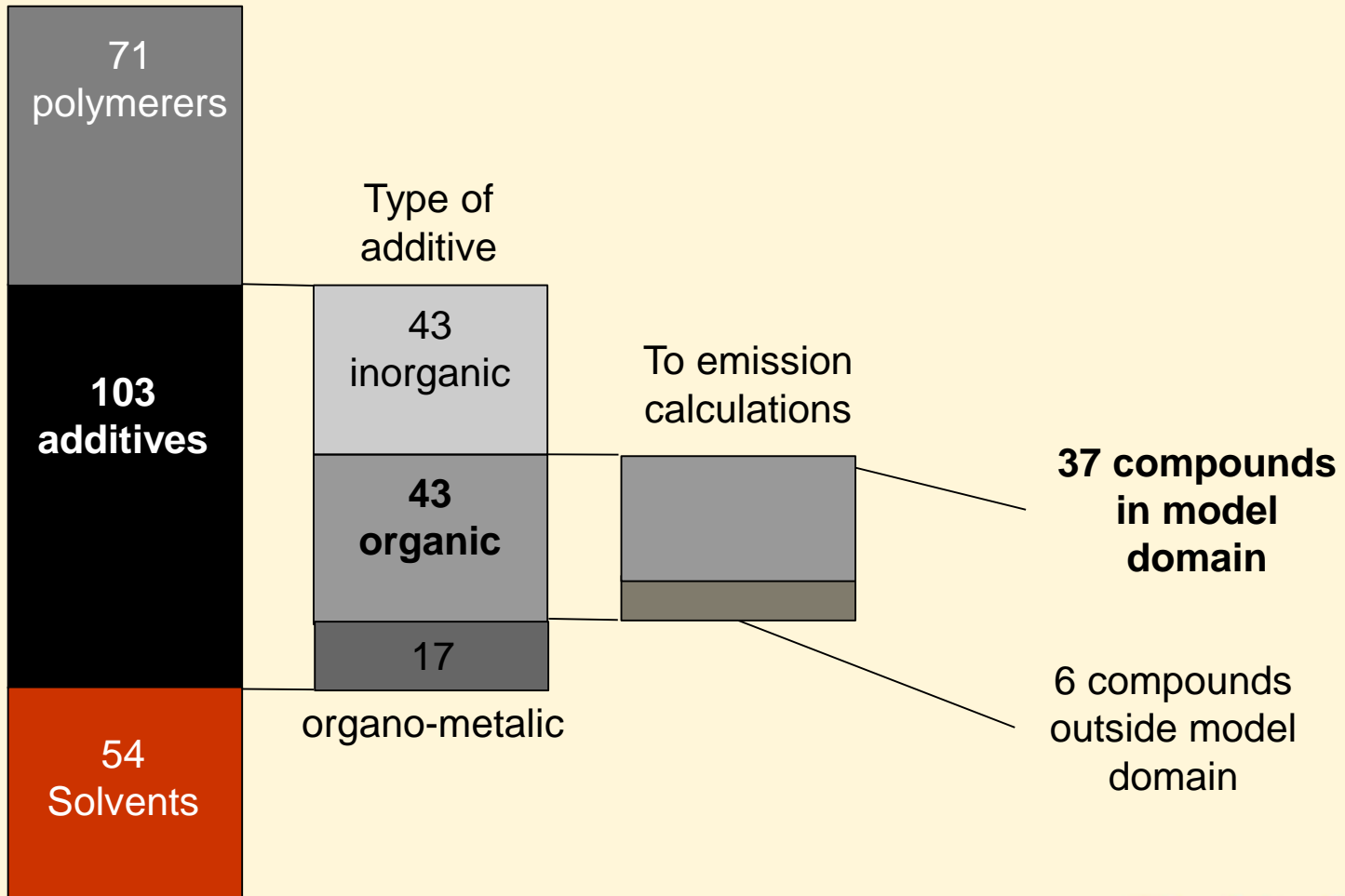
Wall paint emissions, Sweden, per yr

Compound	Class	g per yr
1,2-Benzisothiazol-3(2H)-one	Biocide	17 000
Carbamic acid, butyl-, 3-iodo-2-propynyl ester	Biocide	5 300
3(2H)-Isothiazolone, 2-octyl-	Biocide	4 200
3(2H)-Isothiazolone, 4,5-dichloro-2-nitro-	Biocide	1 700
1,3-Propanediol, 2-bromo-2-nitro-	Biocide	1 400
Diuron	Biocide	1 300
2-Amino-2-methylpropanol (AMP)	Dispergent	960
Diethanolamine	Dispergent	960
Carbamic acid, 1H-benzimidazol-2-yl-, methyl ester	Biocide	860
3(2H)-Isothiazolone, 2-methyl-	Biocide	760
2-Butanone, oxime	Biocide	660
3(2H)-Isothiazolone, 5-chloro-2-methyl-	Biocide	370
5,8,11,13,16,19-Hexaoxatricosane	Plasticizer	370
Isothiazolinone	Biocide	250
Terbutryn	Biocide	150
Triethanol amine (TEA)	Dispergent, Biocide	110
Poly(oxy-1,2-ethanediyl), a-hydro-omega-hydroxy-	Nonylfenol(etoxylat)	64
Paraffin waxes and hydrocarbon waxes		21
Poly[oxy(methyl-1,2-ethanediyl), a-butyl-omega-hydroxy-	Nonylfenol(etoxylat)	15
Poly(oxy-1,2-ethanediyl), a-nonylphenyl-omega-hydroxy-	Nonylfenol(etoxylat)	14
Poly[oxy(methyl-1,2-ethanediyl), a-hydro-omega-hydroxy-	Nonylfenol(etoxylat)	12
Acetamide, 2-chloro-N-(hydroxymethyl)-	Pesticid	9.8
Urea		8.5
1-Decanaminium, N-decyl-N,N-dimethyl-, chloride	Pesticid	5.8

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Emissions kg/year of all organic compounds

Sofas
Beds
Foam matresses
Office chairs
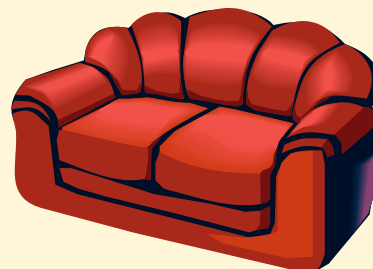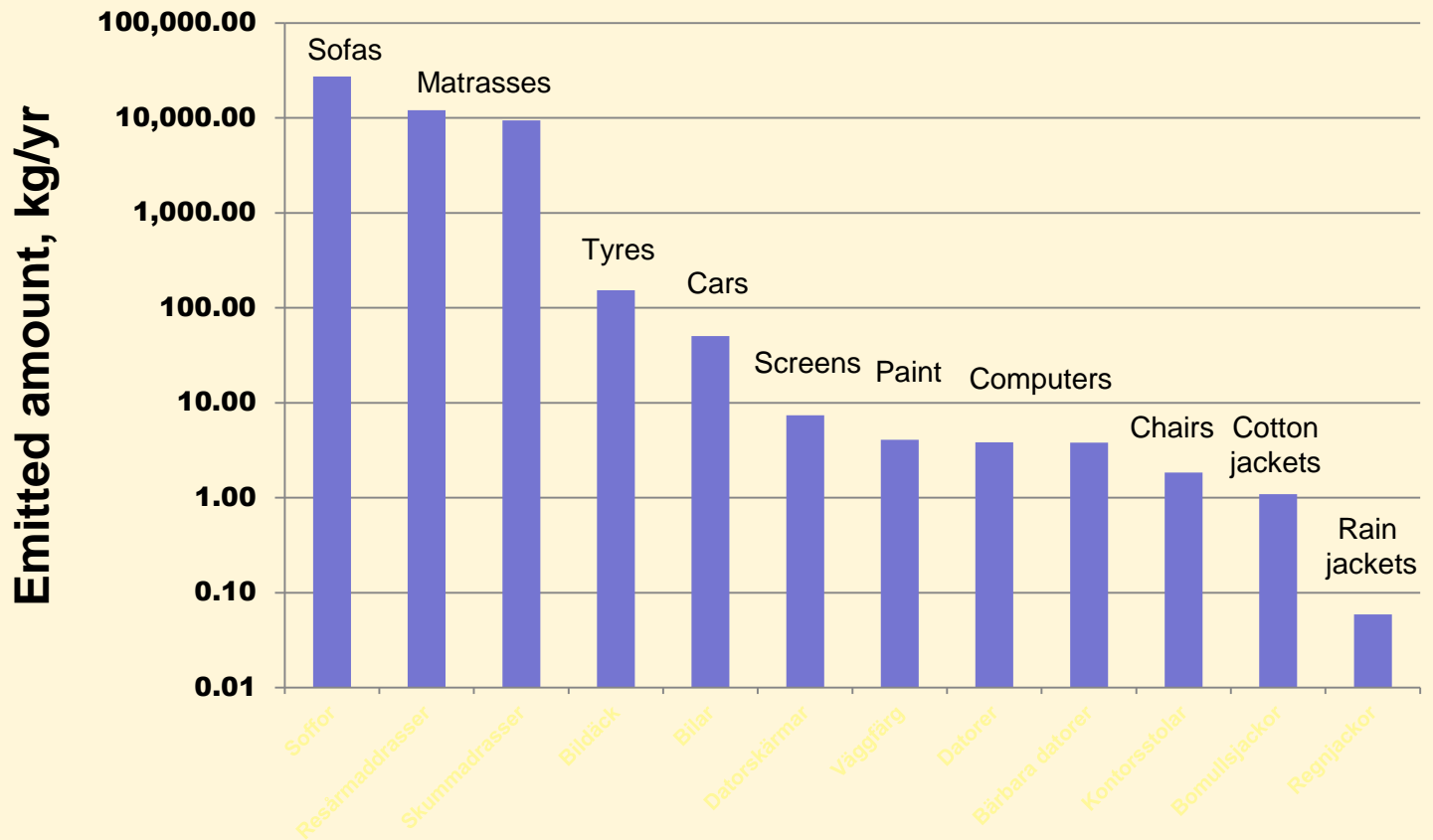
Computers
Laptops
Screens
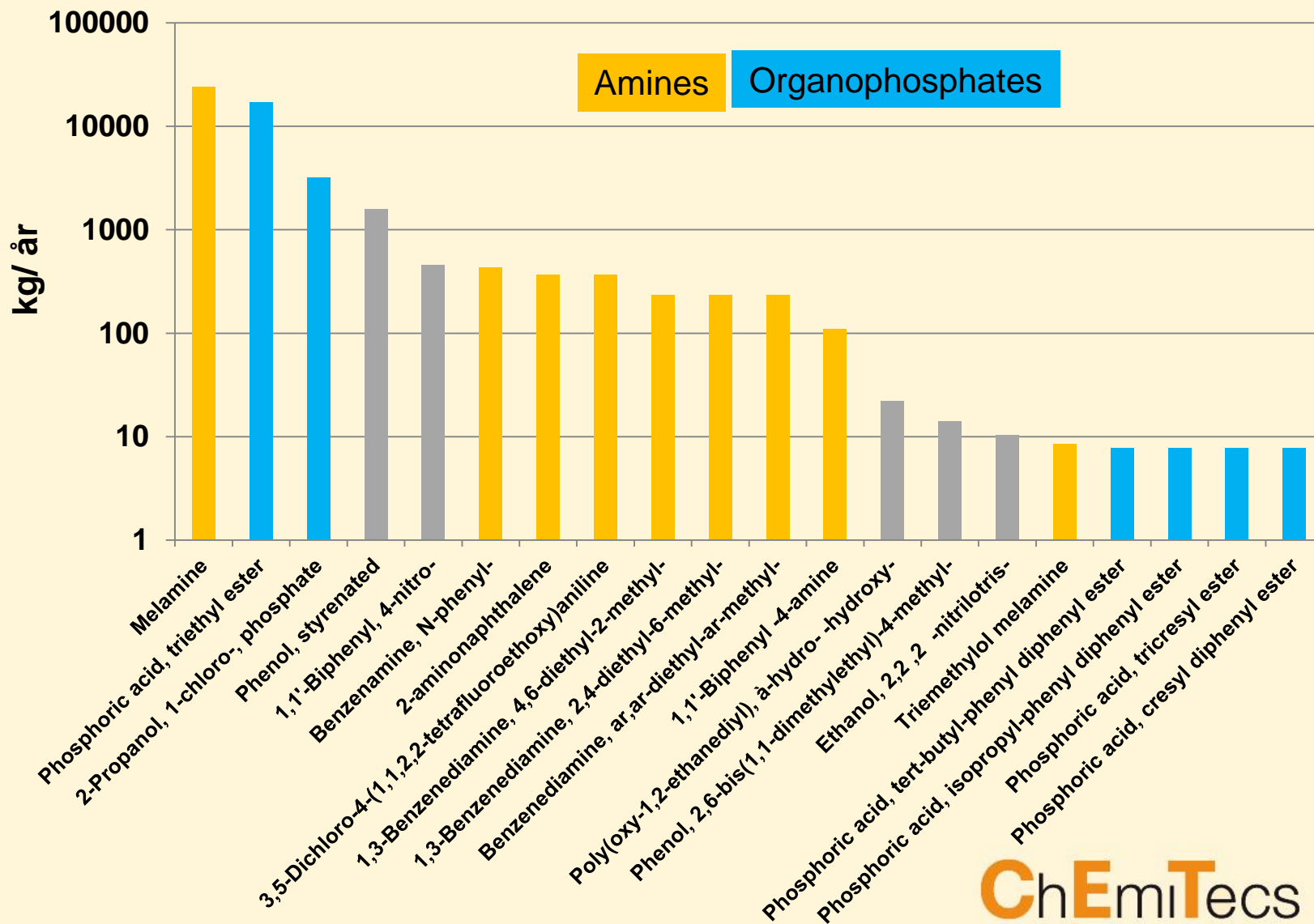
Cars
Tyres

Cotton jackets
Rain jackets

Wall paint

ChEmiTecs

Input, total 37000 rows

Article   **Material**   **Chemical**   **Use / Envi.**   **Emission**

Total emissions kg/yr

Emitted amount, kg/yr

Sofas
Matrasses
Tyres
Cars
Screens
Paint
Computers
Chairs
Cotton jackets
Rain jackets

Soffor
Resармaddrasser
Skummadrasser
Bildäck
Bilar
Datorskärmar
Väggfärg
Datorer
Bärbara datorer
Kontorsstolar
Bomullsjackor
Regnjackor

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Emissions from "soft" furnitures

Linked fate model gives levels in indoor and outdoor environments

Properties

Emissions

SMURF Model

Air

Indoor air surfaces

Urban
Indoor Module

Soil

Water

Sediment

Emission
Intermedia transport
Advection/removal/burial
Degradation

Cousins, 2012

Predicted concentrations

Monitoring data

?

Cousins A.P. 2012. Sci. Tot . Environ. 438, 233-241

Emission optimization

UNCERTAINTY ANALYSIS
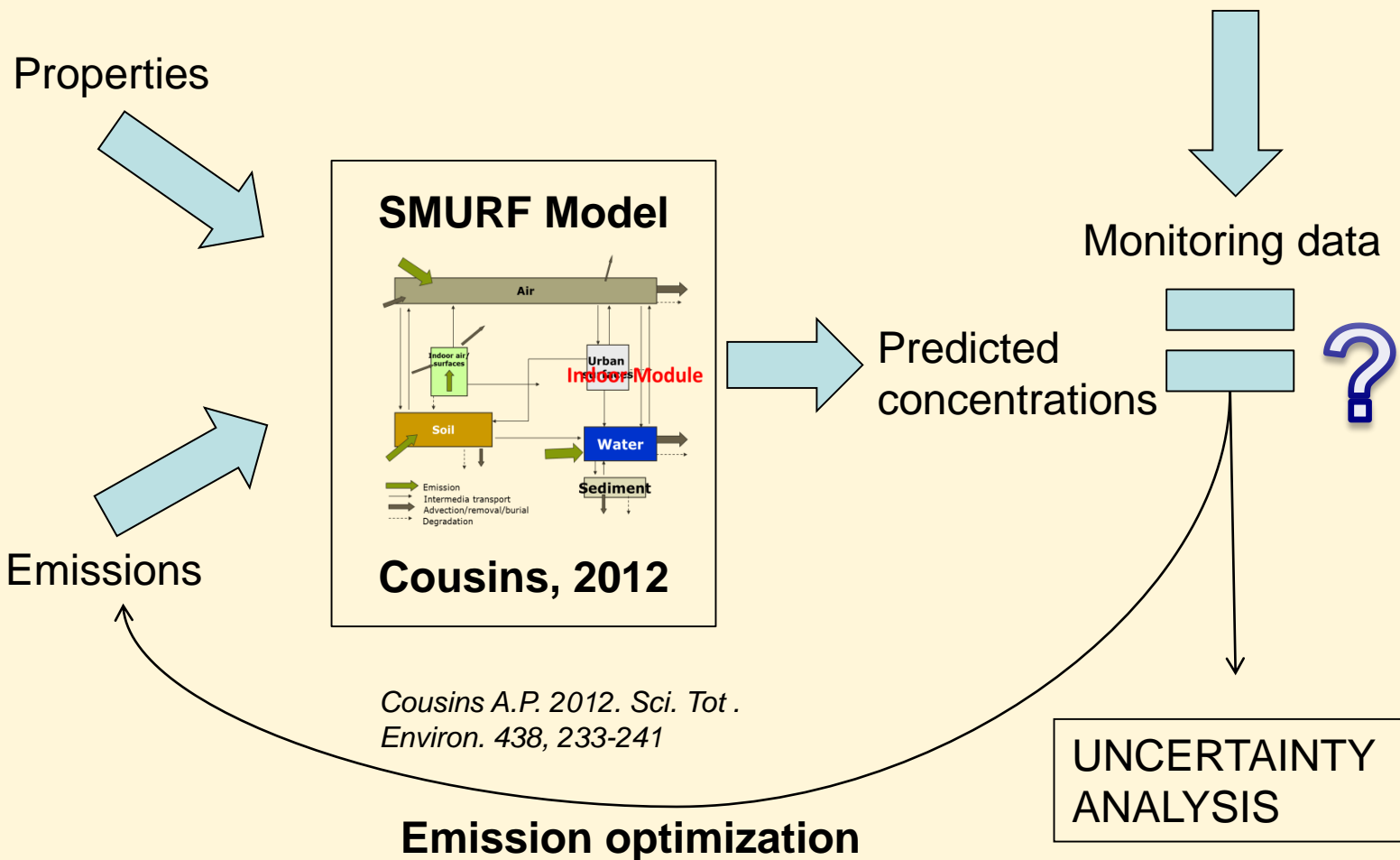
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Annual Economy Wide Emissions

- Prioritized goods 🙂

- Data collection
    - Surface area 🙂
    - Average material composition 😐
    - Average chemical composition 😐

- Generic modeling 🙂

- Dimensioning 🙂

- Actions?

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? ? ?

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