Emerging contaminants in the indoor environment

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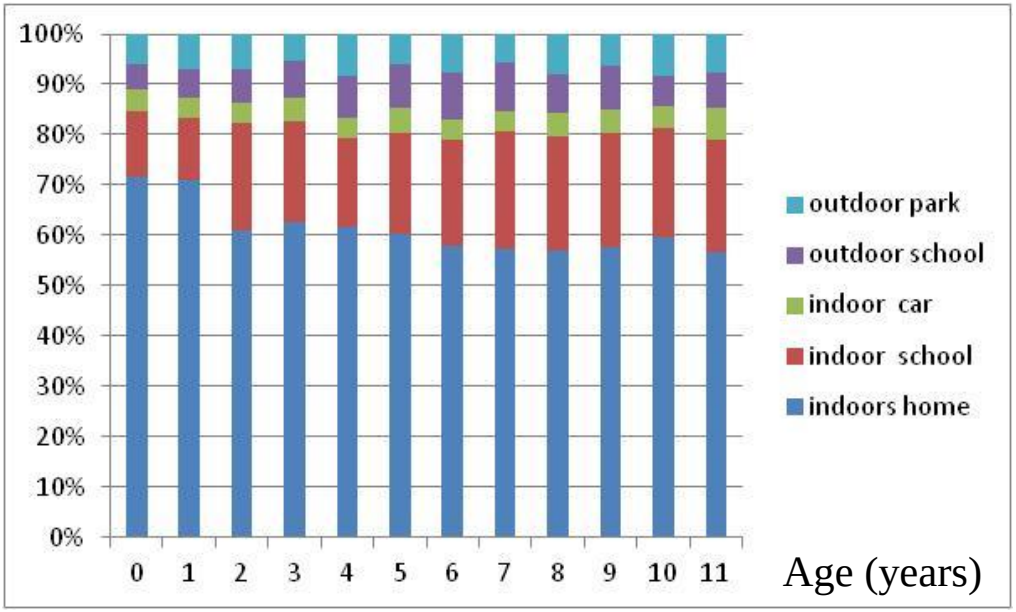
Indoor environment

We spend in average 85-90% of our time indoors

- Home (house, appartment..)
- Car/public transport (bus, train, airplane..)
- School/ kindergarten
- Office
- Restaurant
- Library
- Hotel
-....

= non-industrial



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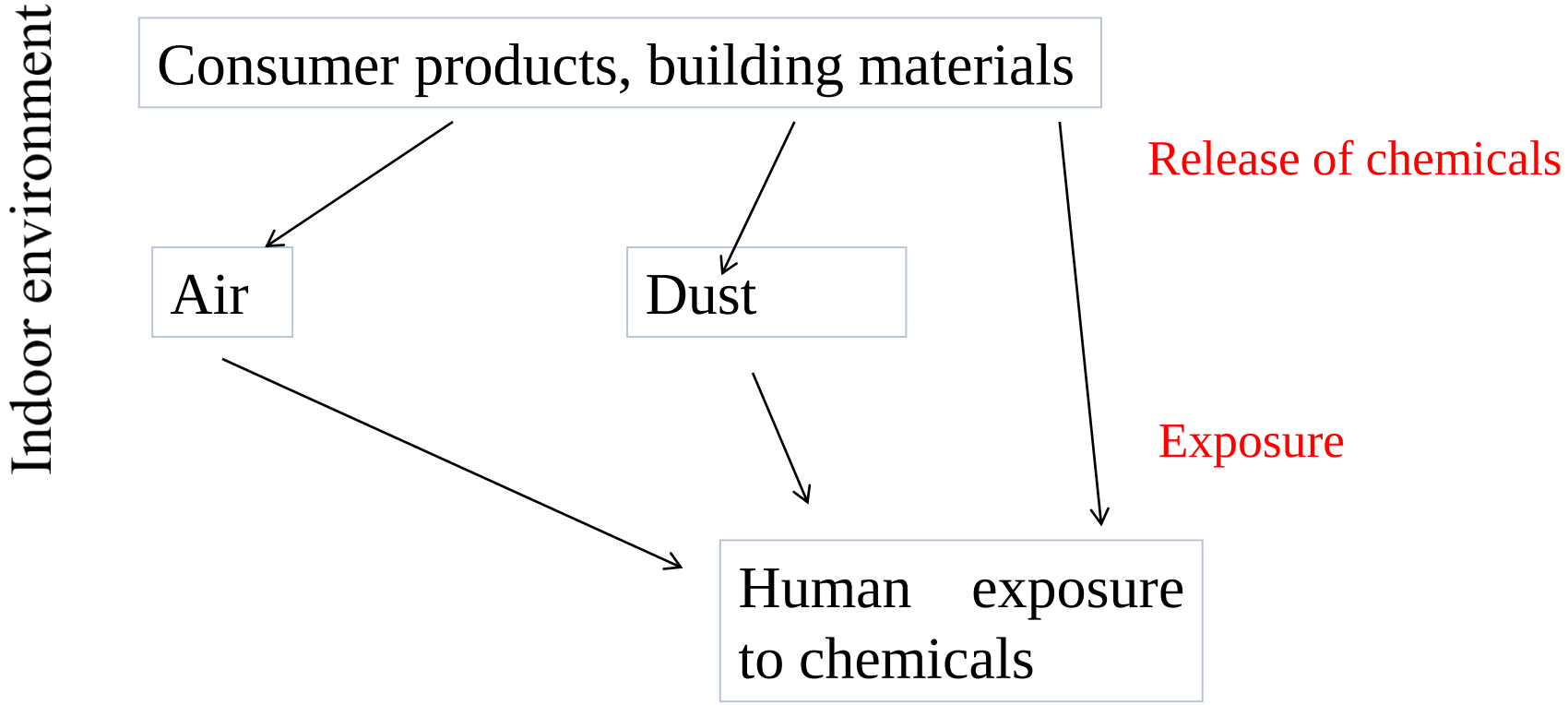
Cohen-Hubal et al., EHP 2000

Why are we interested in the indoor environment?



Contaminants

Chemicals – once they are a problem/issue to humans = contaminants

- Classical / legacy / old contaminants
- Emerging / new / novel contaminants

Emerging contaminants:

- chemicals which are newly/recently observed in the environment

- chemicals that are not currently regulated and potentially pose significant ecological or human health risks

- chemicals not commonly monitored in the environment, but have the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects

Emerging / new / novel contaminants - NORMAN

Emerging environmental substances are not necessarily new chemicals. They are substances that have often long been present in the environment, but whose presence and significance are only now being investigated/elucidated.

- **"Emerging substances"** can be defined as substances that have been detected in the environment, but which are currently not included in routine monitoring programmes at EU level and whose fate, behaviour and (eco)toxicological effects are not well understood.

These chemicals may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects and public perception and on monitoring data regarding their occurrence in the various environmental compartments.

NORMAN

- systematic collection of data in the EMPODAT database monitoring data
- assignment of priority

Indoor contaminants

- volatile - VOCs
- semi-volatile - SVOCs (classical and emerging)
- non-volatile - NVOCs (including metals and their oxides/salts)
- polymers – polymeric chemicals
- degradation / transformation products

Consumer products and building materials

Chemicals used in the products

- As additives
- As monomers

Screening of chemicals

- Non-destructive techniques
    - (electron microscopy, XRF, FTIR)
- Destructive techniques (GC/LC-MS)
- Direct probe TOFMS

Air

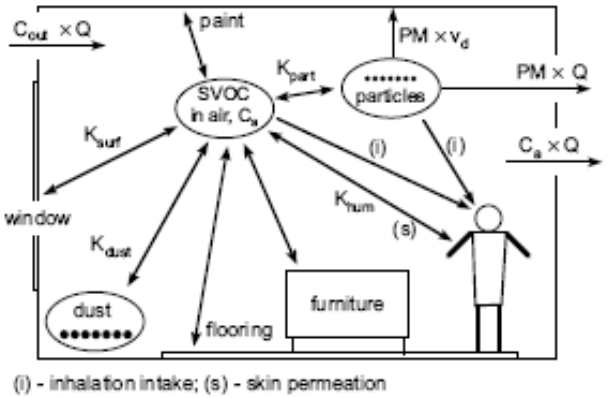
- VOCs (gas phase)
- Part of the SVOCs (too!) – properties + uses

Presence of particulate matter

Sampling
- active vs passive vs personal

Active sampling (low vs high volume) – fct concentration of contaminants

Dust



Integrates exposure in a room:

-Dust ingestion
-Dust inhalation
-Dermal contact (with dust)

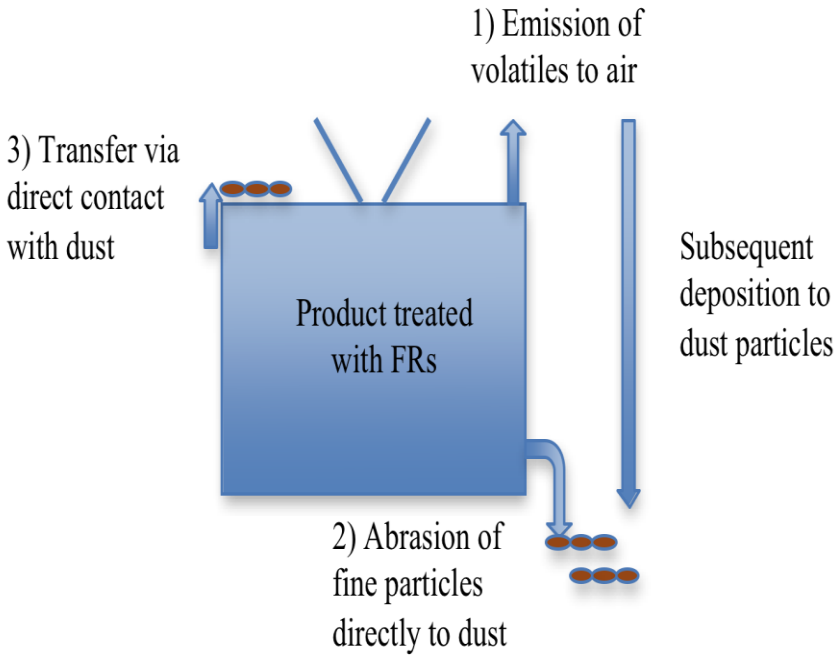
-Such exposure pathways are mostly relevant for SVOCs – with larger and higher MW – and/or NVOCs

Lioy et al., EHP 2002

Dust

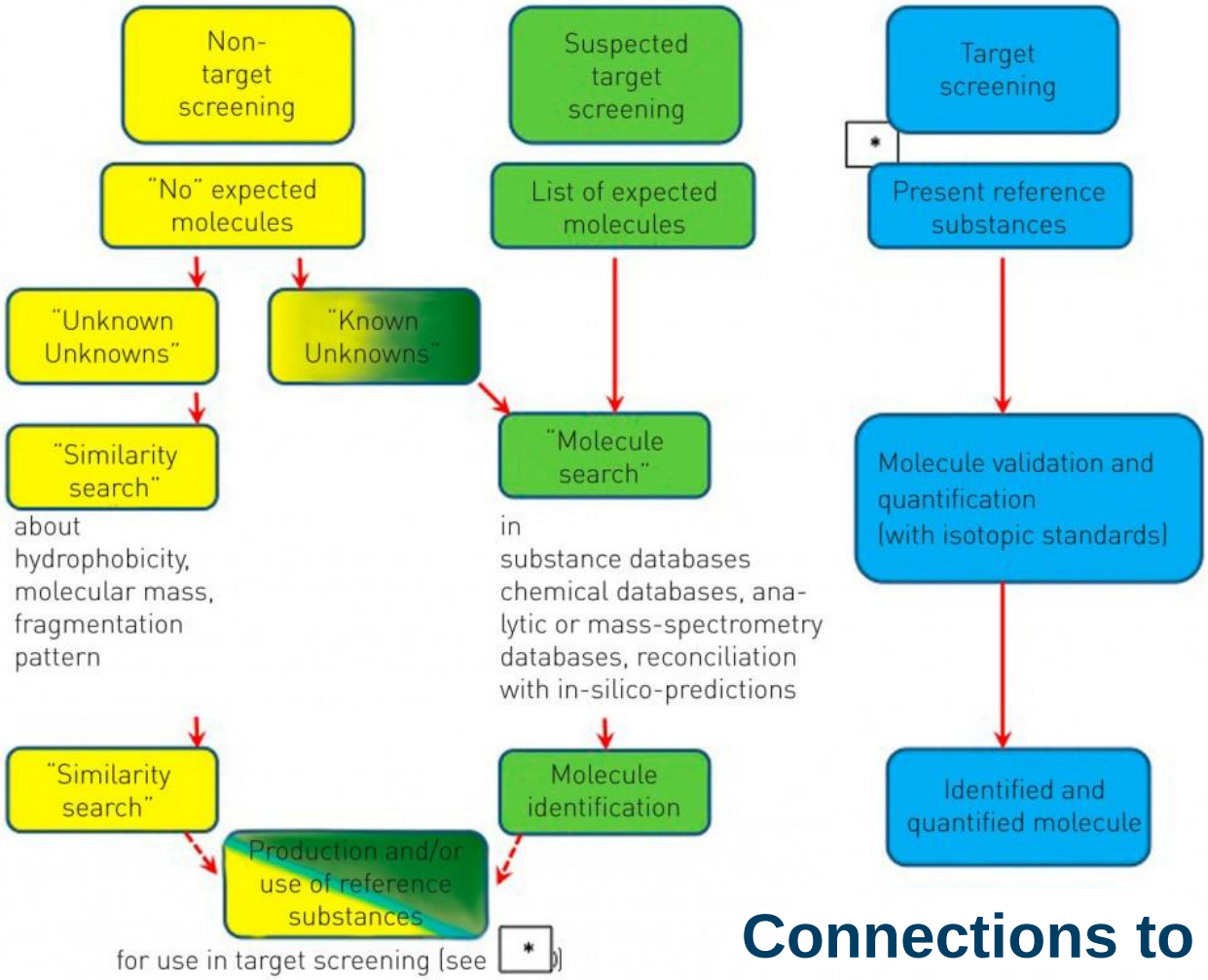
Mechanisms of accumulation of SVOCs in dust

1) Volatilisation
2) Abrasion
3) Direct contact



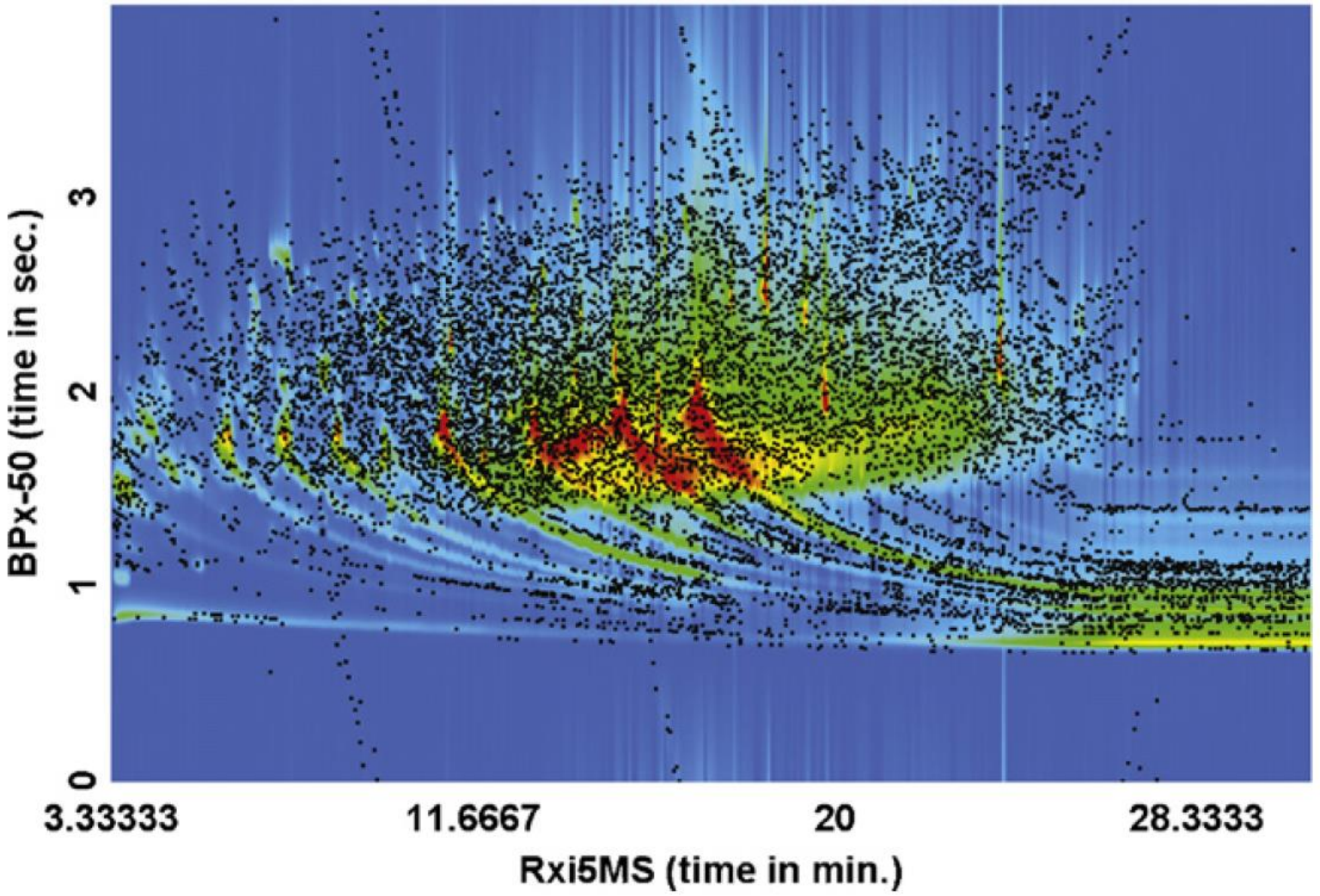
Courtesy of Stuart Harrad

Analysis (air, dust, products)



Connections to WGs of NORMAN

GCxGC-ToFMS of an hexane extract of dust



Hilton et al., J. Chromatogr A, 2010

INTAKE

Air

METABOLISM

BIOMONITORING

(Food)

Dust

Consumer Products

Serum/Blood

Urine

Humans

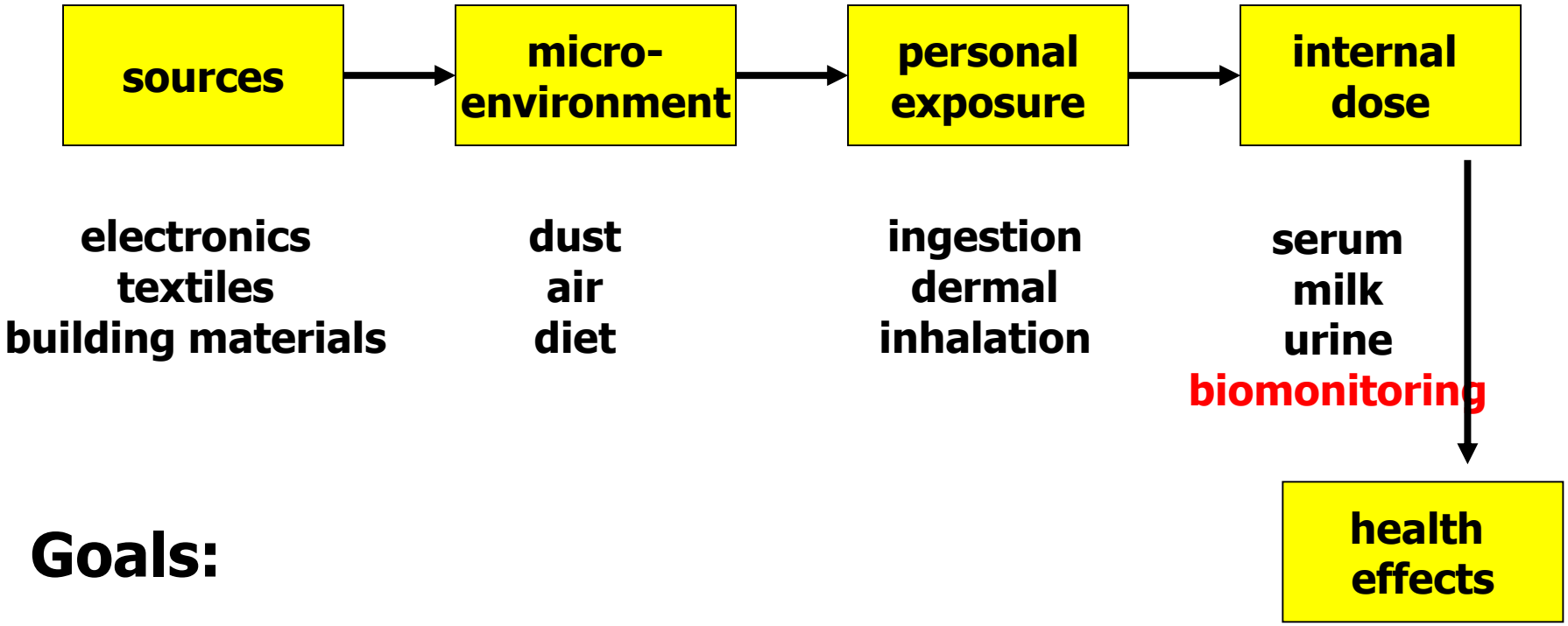
Routes of exposure

- Inhalation (gas phase vs particules)
- Ingestion (dust)
- Dermal exposure
- Food

Absorbtion (bioaccessibility and bioavailability)
Distribution in the body (fct of properties)
Metabolism (liver, serum, epiderm) + Phase II
Excretion

BIOMONITORING **Toxicity!!**

Human exposure to indoor contaminants



Goals:

-understanding exposure to indoor contaminants from *product* to *person*

-linking exposure to possible adverse effects

Classical indoor contaminants

-Polycyclic aromatic hydrocarbons (PAHs)

-Polychlorinated biphenyls (PCBs)

-Pesticides and biocides

-Alkanes

-Hydrocarbons

-VOCs

-Metals

Emerging indoor contaminants

-Flame retardants

-Plasticizers (e.g. phthalates, adipates, citrates....)

-Bisphenols (including BPA)

-Perfluorinated compounds (PFCs)

-Pesticides and biocides

-Personal care products (!!)

-Antioxidants (in plastics, based on aniline or t-butylphenols)

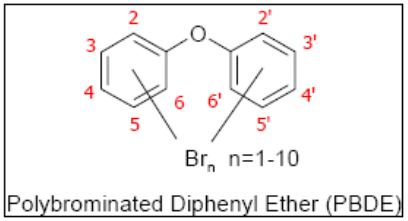
-Siloxanes

-Others!!!

Flame retardants

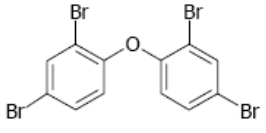
Brominated flame retardants

PBDE Nomenclature

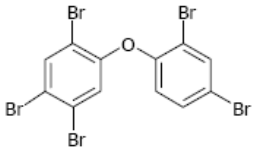


Polybrominated Diphenyl Ether (PBDE)

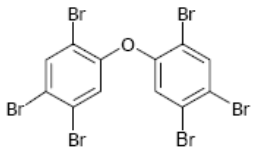
PentaBDE Congeners:


2,2',4,4'-tetrabromodiphenyl ether

BDE-47

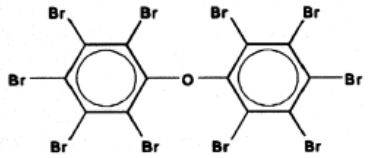

2,2',4,4',5-pentabromodiphenyl ether

BDE-99

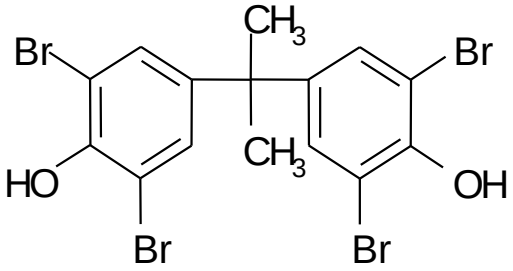

2.2',4,4',5,5'-hexabromodiphenyl ether

BDE-153

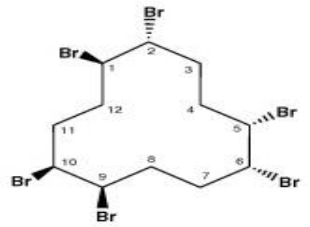
DecaBDE:

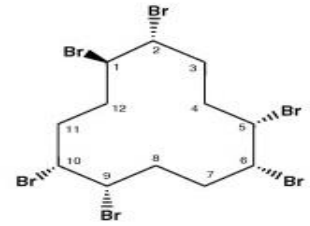

BDE 209

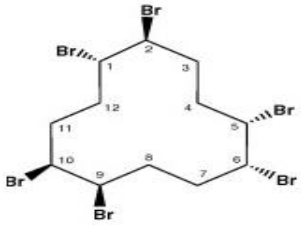
Polybrominated diphenyl ethers (PBDEs)



TBBP-A


(-) α -HBCD
(1R,2R,5S,6R,9R,10S)


(-) β -HBCD
(1R,2R,5S,6R,9S,10R)


(-) γ -HBCD
(1S,2S,5S,6R,9R,10S)

HBCDs

- used as additive FRs at concentrations of 2-30% in polymers

Applications of BFRs

- **Penta-BDE:** **Flexible polyurethane foam**

  Upholstery textile in furniture

- **Octa-BDE:** **Electronic and electrical equipment**

  - housing and small components

- **Deca-BDE:** **Electronic and electrical equipment**

  - housing and small components

  Upholstery textiles

- **HBCDs:** **Polystyrene (roof isolation) and textile backcoating**
- **TBBP-A :** **Electrical and electronic equipment**

  - printed circuit boards and housing

Health hazards identified in animal models

PBDEs

* disrupt thyroid hormone pathways (decrease of T4 levels)
* low estrogenic activity
* neurotoxicity and neurodevelopmental disorders
* decreased IQ in offspring, hyperactivity

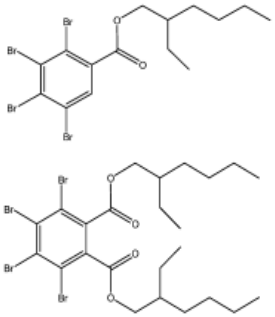
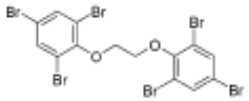
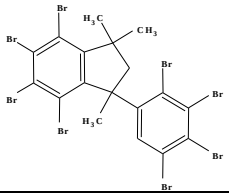
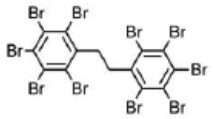
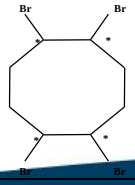
HBCDs

* antagonistic effect on detoxification enzymes
* disrupt the thyroid hormone system
* alter the normal uptake of the neurotransmitters in rat brains
* neonatal exposure can induce developmental neurotoxic effects, such as aberrations in spontaneous behaviour, learning, and memory function.

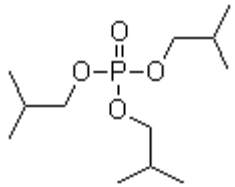
TBBP-A

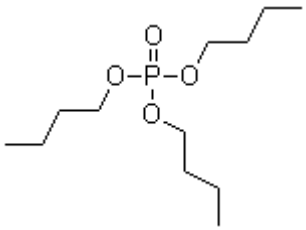
* thyroid hormone-like and estrogen receptor-mediated effects
* immunotoxic
* neurotoxicity through *in vitro* inhibition of dopamine uptake

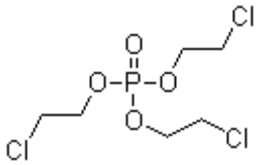
Alternative/Novel BFRs

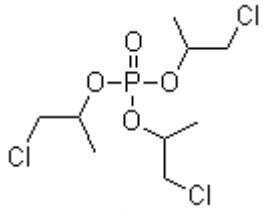
Short name	Chemical name	Technical name	Structure	Potential substitute for
TBB + TBPH	TBB: 2-ethylhexyl 2,3,4,5-tetrabromobenzoate TBPH: (2-ethylhexyl) tetrabromophthalate	FR 550		Penta-BDE
BTBPE	1,2-bis(2,4,6-tribromophenoxy) ethane	FR680		Octa-BDE
OBIND	Octabromotrimethyl-phenylindane			Octa-BDE
DBDPE	Decabrominated diphenyl ethane	SAYTEX 8010		Deca-BDE
TBCO	1,2,5,6-tetrabromocyclooctane			HBCD

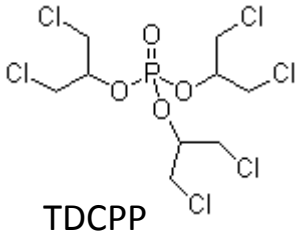
Organophosphorus flame retardants (PFRs)

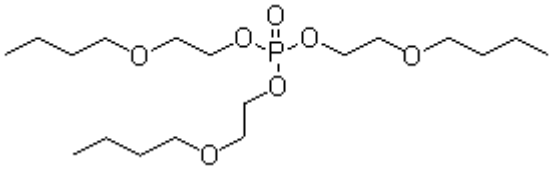

TiBP

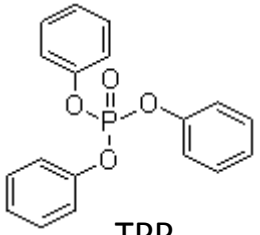

TBP

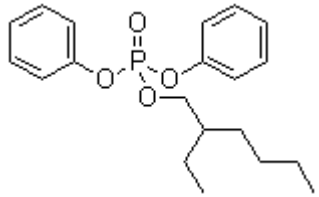

TCEP

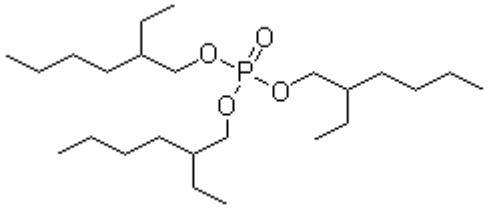

TCPP

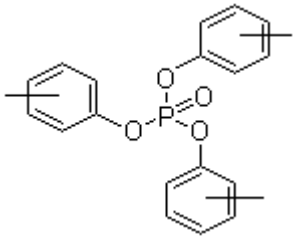

TDCPP

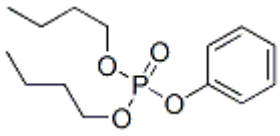

TBEP

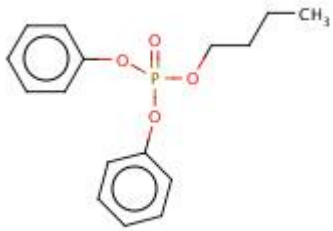

TPP


EHDPP

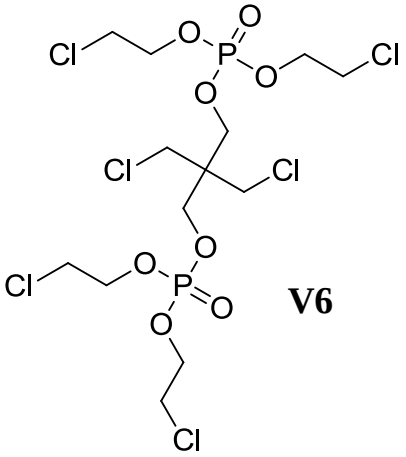

TEHP


TCP

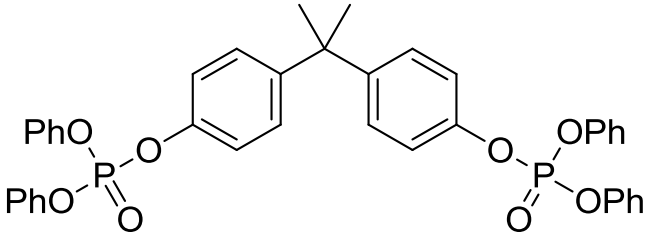

DBPhP


DPhBP

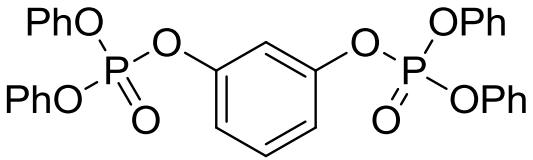
More.... PFRs



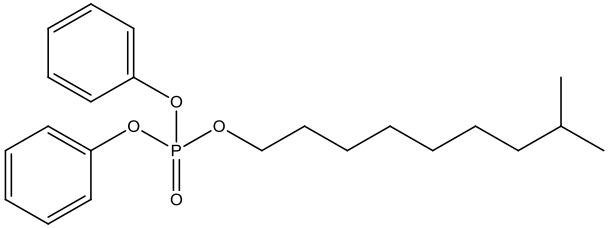
V6



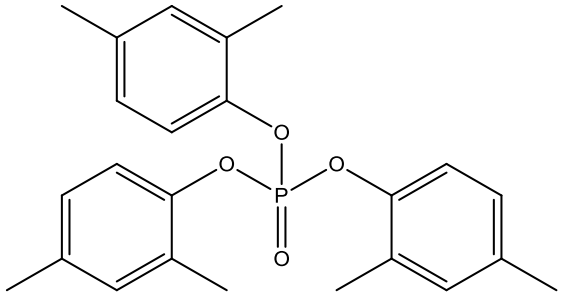
BDP



RDP

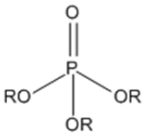


Isodecyl diphenyl phosphate (iDPP)



Trixylenyl Phosphate (TXP)

PFRs



- TCEP - in cellulose esters (linked to cancer)
- TCIPP – in polyurethane foams (replacement of Penta-BDE)
- TDCIPP (chlorinated TRIS) in polyurethane foam, resins, latex
  - banned for use in children's pajamas (1977)
  - found in foams for baby products
- TPHP - plasticiser, flame retardant in polyurethane foam (component of Firemaster 550), PVC, …
- TBOEP – mostly as plasticiser
  - lacquers, rubber, floor polish

Suggested endocrine disruptive effects

- *In vitro* inhibition of androgen, estrogen, glucocorticoid, and PPAR-γ receptor
- Association with reduced male fertility *in vivo*

Kojima et al. 2013, Pillai et al. 2014, Dodson et al. 2012, Meeker and Stapleton 2010

van der Veen and de Boer, Chemosphere 2012

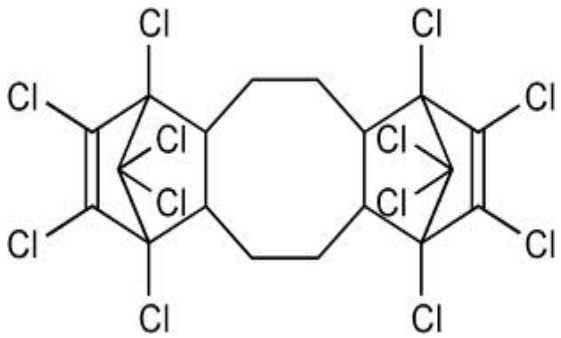
Chlorinated FRs

Polychlorinated parrafins (CPs)

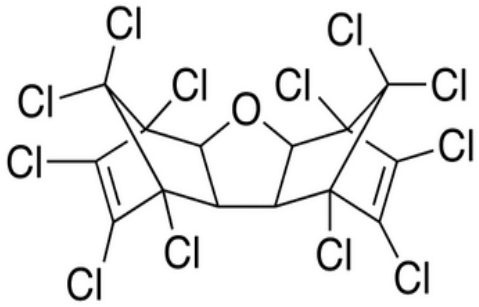
Chlorination degree of CPs can vary between 30 and 70%.

- CPs are subdivided according to their carbon chain length:
- short chain CPs (SCCPs, $C_{10\text{-}13}$)
- medium chain CPs (MCCPs, $C_{14\text{-}17}$)
- long chain CPs (LCCPs, $C_{>17}$)

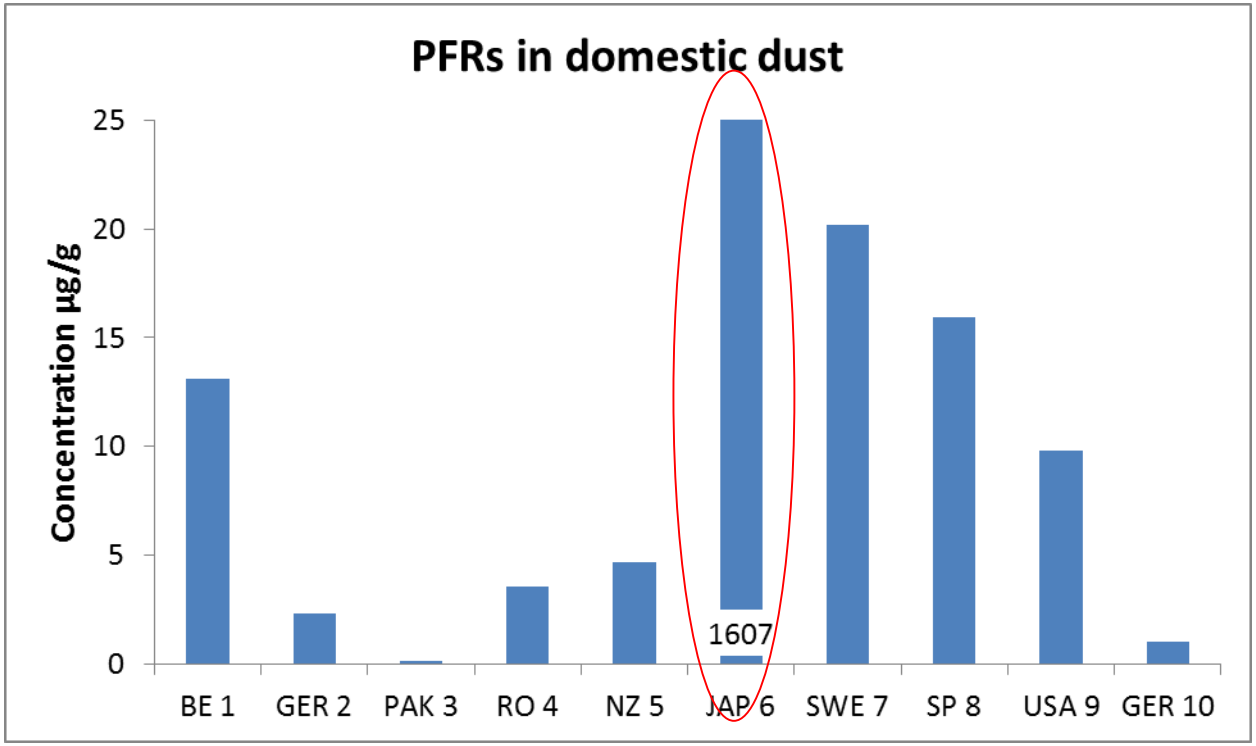
Dechlorane Plus



Dechlorane 602

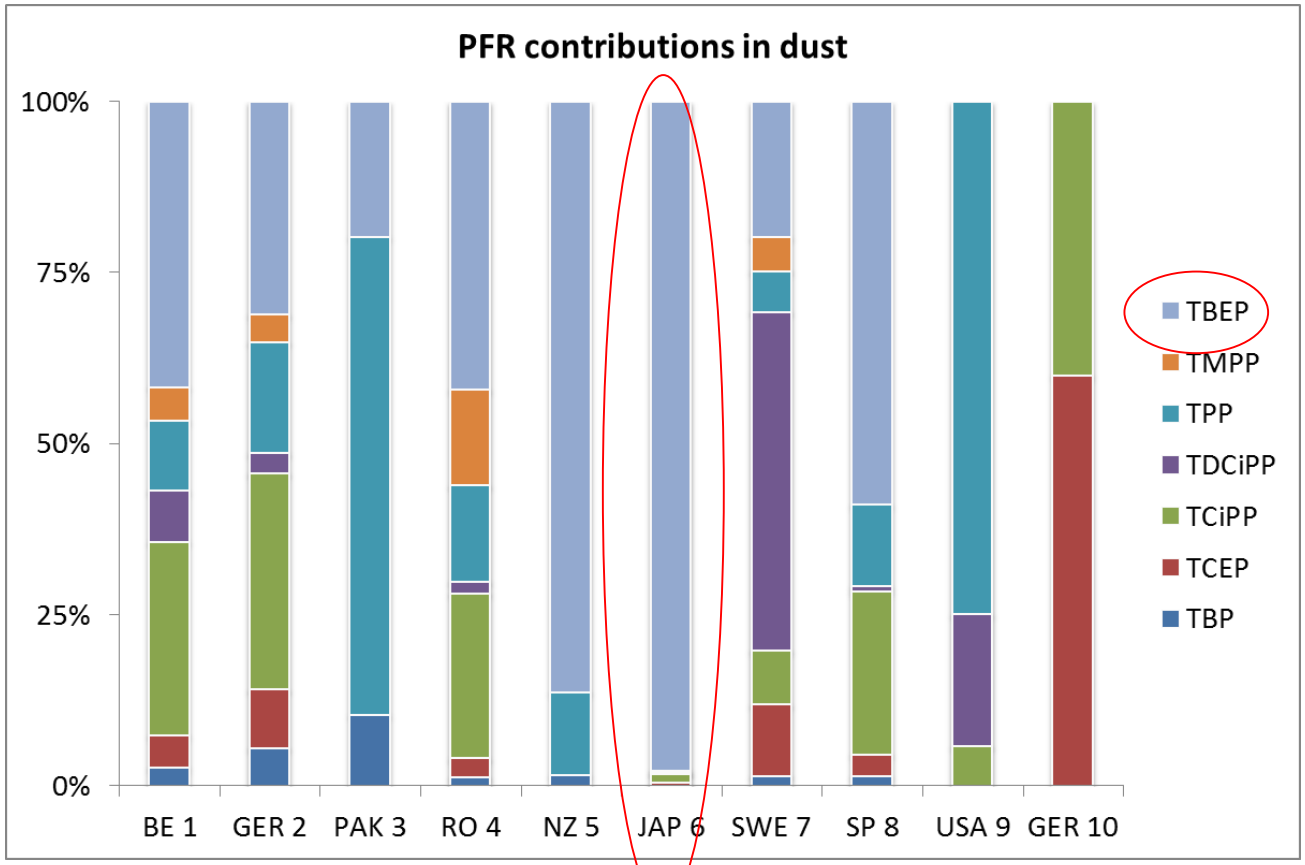


PFRs in house dust



BE1: Van den Eede et al. ENVINT 2011, GER2: Brommer et al. JEM 2012, PAK3: Ali et al. IA 2012, RO4: Dirtu et al. ENVINT 2012; NZ5: Ali et al. CHEM 2012; JAP6: Kanazawa et al. IA 2010, SWE7: Bergh et al. IA 2011, SP 8: García et al. ACA 2007, USA9: Stapleton et al. ES&T 2009; GER10: Ingerowski et al. IA 2001

PFRs in house dust - profiles



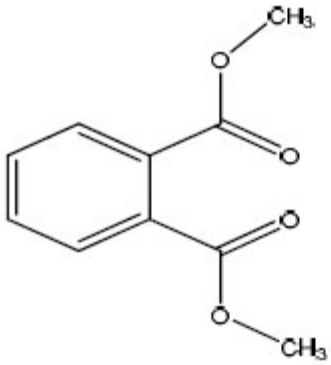
BE1: Van den Eede et al. ENVINT 2011, GER2: Brommer et al. JEM 2012, PAK3: Ali et al. IA 2012, RO4: Dirtu et al. ENVINT 2012; NZ5: Ali et al. CHEM 2012; JAP6: Kanazawa et al. IA 2010, SWE7: Bergh et al. IA 2011, SP 8: García et al. ACA 2007, USA9: Stapleton et al. ES&T 2009; GER10: Ingerowski et al. IA 2001

FRs	Air	Dust	Consumer products	Humans
PBDEs	+	++	+	++
HBCDs	+	+	+	+
TBBPA	(+)	+	(+)	(+)
NBFRs	(+)	(++)	(+)	(+)
Dechloranes	-	+	(+)	(+)
CPs	-	-	-	-
PFRs	+	+	+	(+)

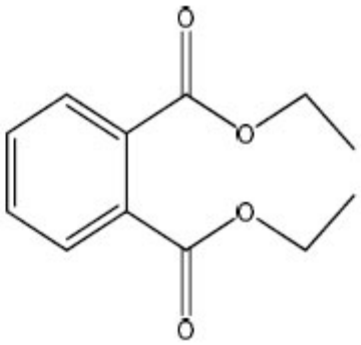
- Very little knowledge
+ some knowledge
++ more knowledge

Plasticizers

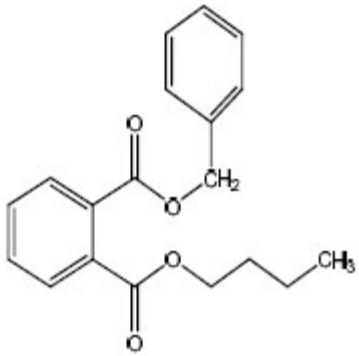
Phthalates



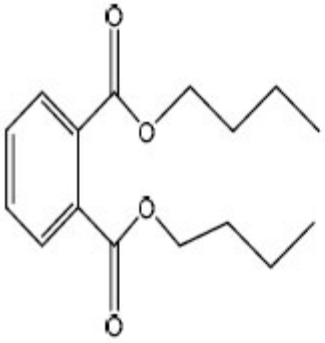
Dimethyl phthalate (DMP)



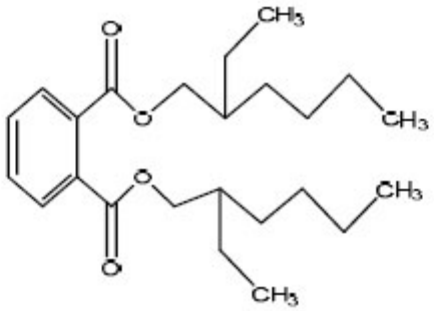
Diethyl phthalate (DEP)



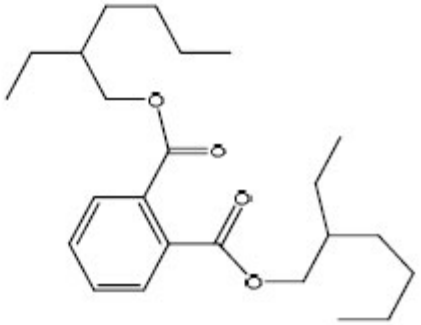
Butyl benzyl phthalate (BBP)



Dibutyl phthalate

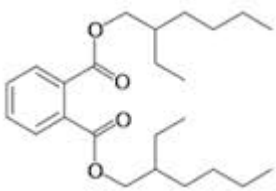


Di-(2-ethylhexyl) phthalate (DEHP)



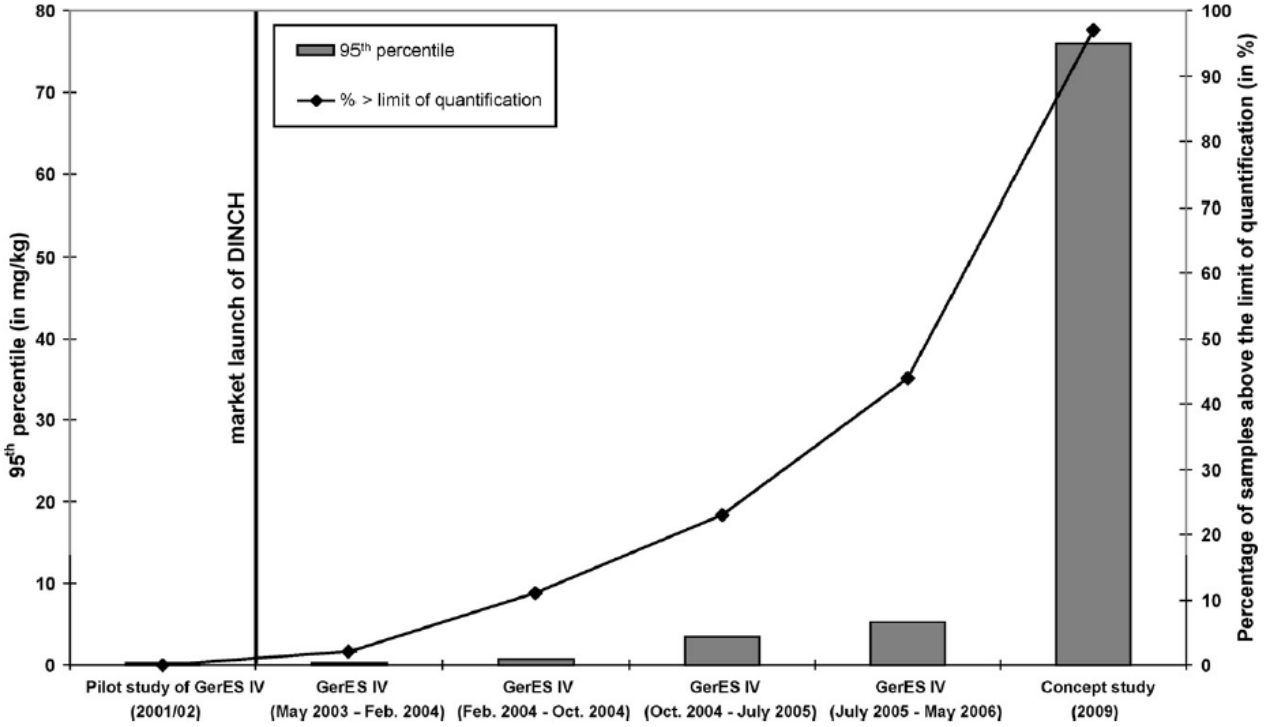
Dioctyl phthalate

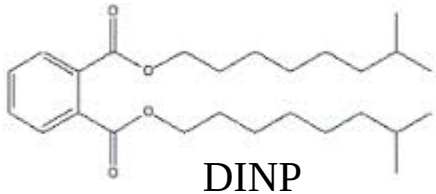
DINCH



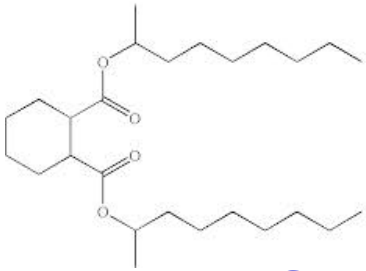
DEHP

- Diisononyl cyclohexane-1,2-dicarboxylate (DINCH)





DINP



(II)

DINCH

Diisononyl 1,2-cyclohexanedicarboxylic acid (DINCH) and Di(2-ethylhexyl) terephthalate (DEHT) in indoor dust samples: Concentration and analytical problems

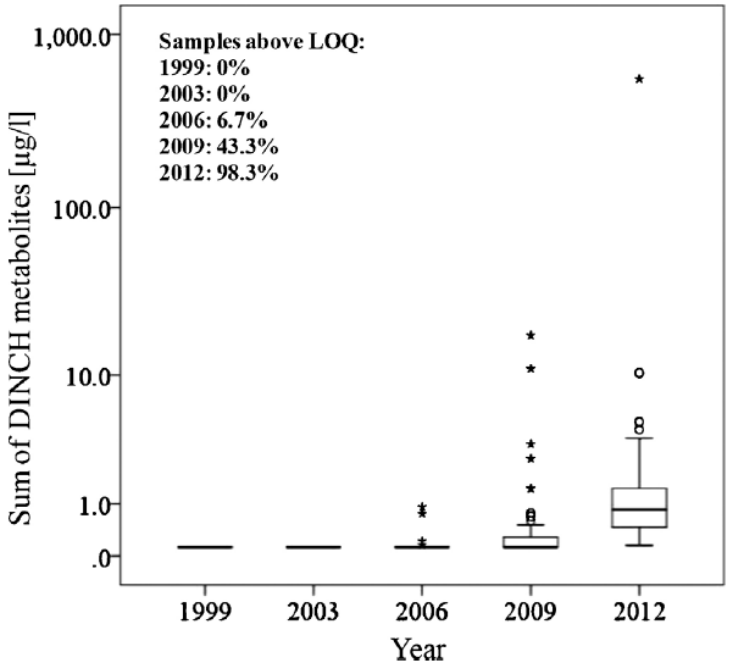
Regine Nagorka*, André Conrad, Christiane Scheller, Bettina Süßenbach, Heinz-Jörn Moriske

International Journal of Hygiene and Environmental Health 214 (2011) 26–35

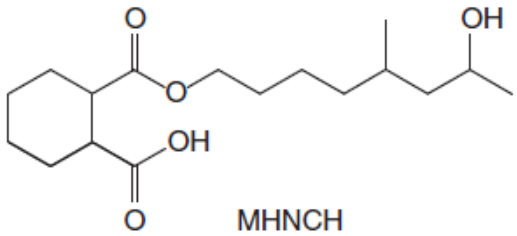
DINCH

urine

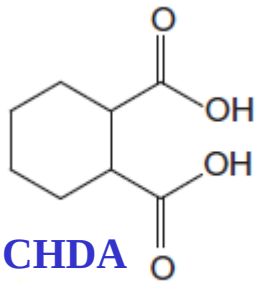
DINCH Metabolite	In vivo metabolism in rats
Cyclohexane-1,2-dicarboxylic acid (CHDA)	
Cyclohexane-1,2-dicarboxylic acid, mono carboxyethyl ester (MCECH)	
Cyclohexane-1,2-dicarboxylic acid, mono carboxypropyl ester (MCPrCH)	
Cyclohexane-1,2-dicarboxylic acid, mono carboxyisobutyl ester (MCBCH)	
Cyclohexane-1,2-dicarboxylic acid, mono carboxyisopentyl ester (MCPeCH)	
Cyclohexane-1,2-dicarboxylic acid, mono isononyl ester (MINCH)	
Cyclohexane-1,2-dicarboxylic acid, mono carboxyisohexyl ester (MCHxCH)	
Cyclohexane-1,2-dicarboxylic acid, mono oxoisononyl ester (MONCH)	
Cyclohexane-1,2-dicarboxylic acid, mono hydroxyisononyl ester (MHNCH)	
Cyclohexane-1,2-dicarboxylic acid, mono carboxyisoheptyl ester (MCHpCH)	
Cyclohexane-1,2-dicarboxylic acid, mono carboxyisooctyl ester (MCOCH)	
Monohydroxy cyclohexane MINCH	
Ring hydroxy MONCH	
Ring and side chain dihydroxy, MHNCH	
Ring hydroxyl MCOCH	



MINCH



MHNCH



CHDA

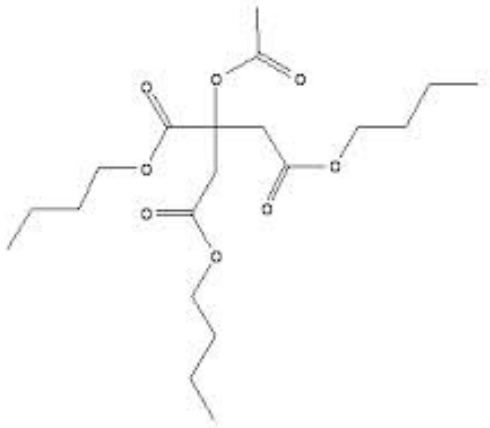
Schütze et al., Int J Health Environ Hyg, 2014

Acetyl tributyl citrate (ATBC)

Plasticizer for cellulose-based, vinyl-based and urethane polymers

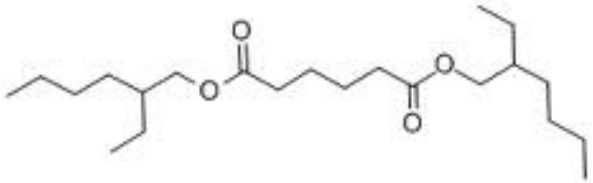
Applications:

- Medical plastics: Aqueous pharmaceutical coatings; extra-corporeal tubing
- Food contact products: Food wraps, films, and containers; aluminum foil coatings
- Children's toys; animal ear tags; ink formulations; adhesives; pesticide inerts



Diethylhexyl adipate (DEHA)

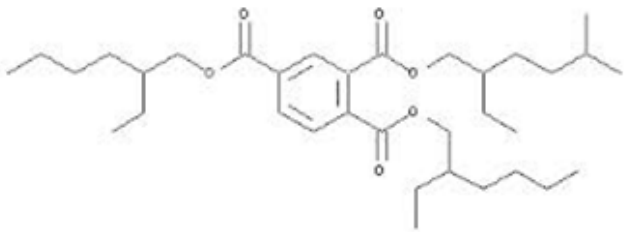
Food contact products: Food wraps, films, and containers



Tri-2-ethylhexyl trimellitate (TETM)

Used in

- Electrical cable insulation
- Medical devices (☹) – e.g. for dialysis

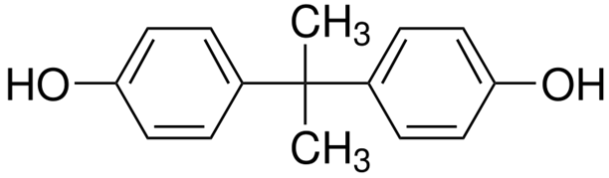


Plasticizers	Air	Dust	Consumer products	Humans
Phthalates	++	++	++	++
DINCH	-	(+)	-	(+)
ATBC	-	-	-	-
DEHA	-	-	(+)	-
TETM	-	-	-	-
others	-	-	-	-

- Very little knowledge
+ some knowledge
++ more knowledge

Bisphenols

Bisphenol-A (BPA)



High production volume chemical: > 4 million tons in 2009

Applications:

- As monomer
  - 65% in production of polycarbonate (PC)
  - 30% in production of epoxyresins (food can coatings or adhesives)
  - 1-2% in dental sealants/adhesives
- As additive
  - 1-2% in thermal paper

Geens et al. (2012) *Food Chem Toxicol*

Toxicity of BPA

In humans, BPA has been linked with

- Altered brain development and behavior

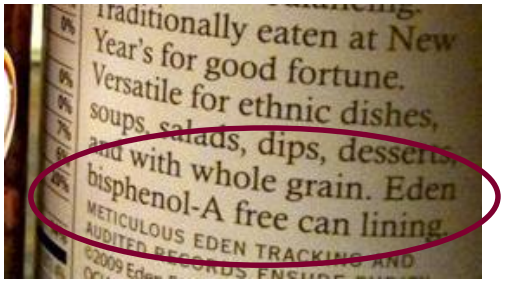
- Activity as estrogen
- Reproductive effects
- Altered mammary gland development
- Prostate cancer

- Thyroid hormone disruption
- Insuline resistance
- Obesity-promoting effects (acting as obesogen)

- Cardiovascular diseases

- Endocrine disruption

Epidemiological studies and *in vitro* experiments

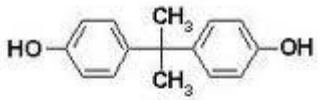


Chocolate mould

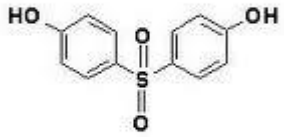
Universiteit Antwerpen

Bisphenol-A analogues

- Bisphenols (e.g. bisphenol-S, -F, -B)

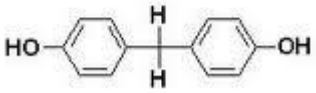


Bisphenol A (BPA)



Bisphenol S (BPS)

- Polyethersulfone (PES) – including baby bottles



Bisphenol F (BPF)

- Food can coating

Toxicity of BPS and other bisphenols

BPS is more stable to heat and light than BPA.

BPS has also endocrine disrupting properties (due to the presence of the alcohol group on the benzene ring) and shows similar *in vitro* estrogenic activity to BPA.

In rodent studies, BPS has shown influenced uterine growth which indicates activation of estradiol.

One study showed that exposure to low levels of BPS in cultured rat pituitary cells altered the estrogen estradiol signaling pathway to affect cell proliferation and apoptosis.

BPS has also been linked to changes in neurodevelopment, since BPS disrupted the timing of neurogenesis within the hypothalamus in embryonic zebrafish.

Much less is know about other bisphenols ☹

Bisphenols	Air	Dust	Consumer products	Humans
BPA	+	++	++	++
BPS	-	-	-	(+)
Other bisphenols	-	-	-	-

- Very little knowledge
+ some knowledge
++ more knowledge

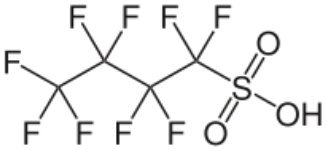
Perfluorinated compounds (PFCs)

PFCs

Classes of PFCs

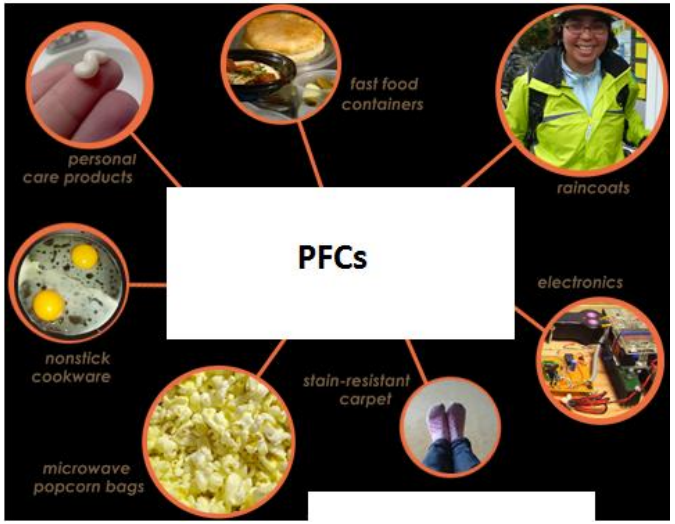
-Perfluorosulfonic acids
-Perfluorocarboxylic acids
-Perfluorinated alkyl and aryl halides
-Perfluoroalcohols
-Perfluorinated phosphates
-Perfluoroethers and epoxides
-Perfluoroamines
-Perfluoroketones
-Perfluoronitriles and isonitriles
-Perfluorinated aryl borates

Various lengths of the chain: C4-C14



PFBS

PFOS



PFCs

Properties

- Oil repellant
- Water repellant
- Widely used in the production of teflon and related fluorinated polymers
- Confer hydrophobic, stain-resisting properties to fabrics

Toxicity

- PFOA is a likely human carcinogen; it causes liver, pancreatic, testicular, and mammary gland tumors in laboratory animals.
- PFOS causes liver and thryoid cancer in rats.

PFCs cause a range of effects in laboratory animals, including liver and kidney damage, as well as reproductive problems.

PFCs

PFCs	Air	Dust	Consumer products	Humans
PFSAs	+	+	+	+
PFCAs	+	+	+	+
PFalcohols	(+)	-	(+)	-
PFphosphates	-	-	-	-
others	-	-	-	-

- Very little knowledge
+ some knowledge
++ more knowledge

Pesticides/biocides

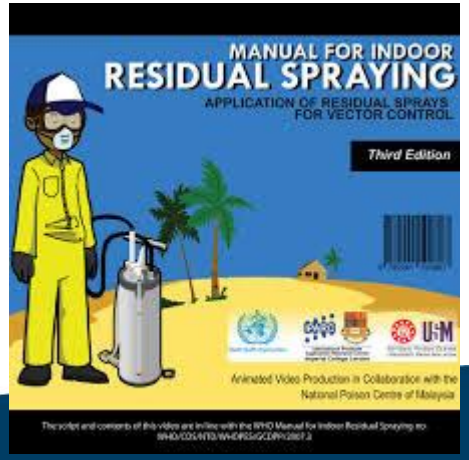
Pesticides/biocides

Most of exposure is outdoors (on crops/fruit/land), but they can be found also indoors:

- Tracked inside on shoes and clothing (farmers)
- Direct use indoors
- Use in products and material buildings

Very dynamic character
Some are more emerging than others
Specific uses

Toxicity



Pesticides/biocides

European Community Classification - *Biocidal Products Directive 98/8/EC (BPD)*

GROUP 1: **Disinfectants and general biocidal products**
Human hygiene, Private area and public health area disinfectants, Veterinary hygiene, Food and feed area disinfectants, Drinking water disinfectants

GROUP 2: **Preservatives**
In-can, Film, Wood, Fibre, leather, rubber and polymerised materials, Masonry, Preservatives for liquid-cooling and processing systems, Metalworking-fluid preservatives

GROUP 3: **Pest control (pesticides)**
Rodenticides, Avicides, Molluscicides, Piscicides, Insecticides, Acaricides and products to control other arthropods, Repellents and attractants

GROUP 4: **Other biocidal products**
Antifouling products, Embalming and taxidermist fluids

Personal care products + Others

Personal care products

- consumer products used in personal hygiene and for beautification

Very dynamic character
Some are more emerging than others

- Air freshners
- Deodorants (fragrances)
- Cleaning products
- Anti-microbials
- Others?

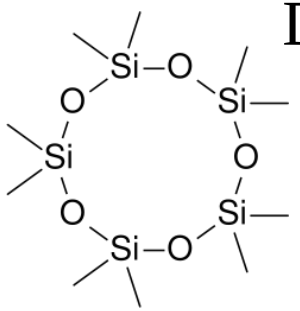
Toxicity
- dermal!!

Other emerging contaminants

- Perchlorate (ClO_4^-)
  - component of solid rocket fuel
  - perchlorates are used extensively within the pyrotechnics, in munitions and matches
  - has a negative influence on the thyroid gland

- Siloxanes
  - Linear vs cyclic
  - used in biomedical and cosmetic applications

D5

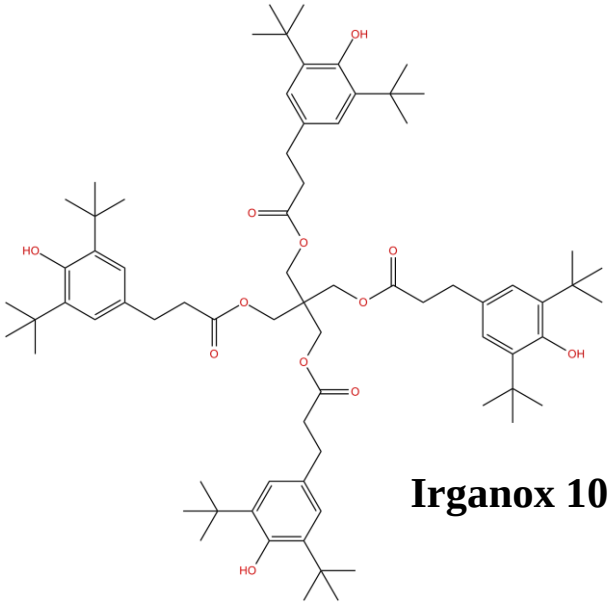


  - LD50 in rats of>50 g/kg, very low toxicity
  - Yet, D4 is toxic to some aquatic organisms
  - In mammals, D4 may impair fertility, damages the liver and has an estrogenic effect
  - Both D4 and D5 are bioaccumulative
  - In the EU, D4 and D5 have been deemed hazardous as per the REACH directive.

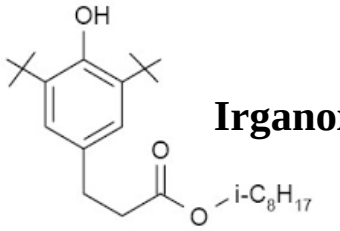
Other emerging contaminants

- Antioxidants
  - Stabilizers for polymers
  - Irganox, Irgafos
  - Can degrade in the environment

- Degradation/transformation products
  - PBDD/PBDFs
  - Tribromophenol
  - dehalogenation products
  - products from Irganox, etc



Irganox 1010



Irganox 1135

	Air	Dust	Consumer products	Humans
Biocides	+	+	+	(+)
PCPs	+	+	+	(+)
Perchlorate	(+)	(+)	-	-
Siloxanes	+	+	+	-
Antioxidants	-	-	(+)	-
Degradation products	-	-	-	-

- Very little knowledge
+ some knowledge
++ more knowledge

Quo Vadis?

- Make a correct inventory of the emerging contaminants present indoors
- Identify new chemicals (by non-targeted approaches)
- Standardized sampling of air, dust, and products
- Correctly “translate” concentrations into exposure by using appropriate metrics
- Prioritize chemicals

EMERGING CONTAMINANTS

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University of Birmingham, UK

Prof. Gang YU
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Tsinghua University, China

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