Emerging contaminants in the indoor environment

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Toxicological Center, University of Antwerp
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
Why are we interested in the indoor environment?

Indoor environment

- Consumer products, building materials
  - Air
  - Dust

Release of chemicals

Exposure

Human exposure to chemicals
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 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

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- 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

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Mechanisms of accumulation of SVOCs in dust

1) Volatilisation
2) Abrasion
3) Direct contact
Analysis (air, dust, products)

Connections to WGs of NORMAN
GCxGC-ToFMS of an hexane extract of dust

Hilton et al., J. Chromatogr A, 2010
Routes of exposure
- Inhalation (gas phase vs particules)
- Ingestion (dust)
- Dermal exposure
- Food

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

BIOMONITORING

Toxicity!!

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Goals:
- Understanding exposure to indoor contaminants from *product* to *person*
- Linking exposure to possible adverse effects

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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

PentaBDE Congeners:

Polybrominated Diphenyl Ether (PBDE)

DecaBDE:

Polybrominated diphenyl ethers (PBDEs)

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

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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

<table>
<thead>
<tr>
<th>Short name</th>
<th>Chemical name</th>
<th>Technical name</th>
<th>Structure</th>
<th>Potential substitute for</th>
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<tbody>
<tr>
<td>TBB + TBPH</td>
<td>TBB: 2-ethylhexyl 2,3,4,5-tetrabromobenzoate</td>
<td>FR 550</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>Penta - BDE</td>
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<tr>
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<td>TBPH: (2-ethylhexyl) tetrabromophthalate</td>
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<td>BTBPE</td>
<td>1,2-bis(2,4,6-tribromophenoxy)ethane</td>
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<td><img src="image6.png" alt="Structure" /></td>
<td>HBCD</td>
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Organophosphorus flame retardants (PFRs)

- TiBP
- TBP
- TCEP
- TCPP
- TDCPP
- TBEP
- TPP
- EHDPP
- TEHP
- TCP
- DBPhP
- DPhBP
More... PFRs

- V6
- BDP
- RDP
- Trixylenyl Phosphate (TXP)
- Isodecyl diphenyl phosphate (iDPP)
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

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Chlorinated FRs

Polychlorinated paraffins (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_{10-13})
  - medium chain CPs (MCCPs, C_{14-17})
  - long chain CPs (LCCPs, C_{\geq 17})

Dechlorane Plus

Dechlorane 602

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PFRs in house dust

PFRs in house dust - profiles

<table>
<thead>
<tr>
<th>FRs</th>
<th>Air</th>
<th>Dust</th>
<th>Consumer products</th>
<th>Humans</th>
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- 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

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Diisononyl cyclohexane-1,2-dicarboxylate (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-Jörg Moriske
International Journal of Hygiene and Environmental Health 214 (2011) 26–35
**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 carboxyisooctyl ester (MCOCH)
- Monohydroxy cyclohexane MINCH
- Ring hydroxy MONCH
- Ring and side chain dihydroxy, MHNCH
- Ring hydroxyl MCOCH

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**Samples above LOQ:**
1999: 0%
2003: 0%
2006: 6.7%
2009: 43.3%
2012: 98.3%

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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
<table>
<thead>
<tr>
<th>Plasticizers</th>
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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
Bisphenol-A analogues

- Bisphenols (e.g. bisphenol-S, -F, -B)
  - Polyethersulfone (PES) – including baby bottles
  - 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 known about other bisphenols 😞
<table>
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<tr>
<th>Bisphenols</th>
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Perfluorinated compounds (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
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 thyroid cancer in rats.

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

<table>
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<th>PFCs</th>
<th>Air</th>
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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

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

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

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- 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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