Phthalates in Environment

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Modern Methods for Analyses of Organic Pollutants
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- whether or why is it important
- phthalates
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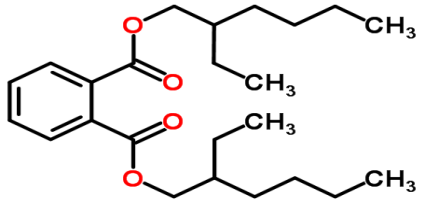
Introduction – Is It Important?

- ubiquitous, high-volume production
- plasticizers, non-odour solutions
- pseudopersistent compounds
- considered high priority pollutants
- reprotoxicity, cardiotoxicity, hepatotoxicity
- indoor pollutants – 95% of time actually indoor

→ It IS important to solve

Phthalates



DEHP – diethyl hexyl phthalate

- ortho-phthalic acid esthers
- lipophilic with ability to bioaccumulate, semivolatile (DMP* – volatile)
- since 20. of 20. century, industrially 80 years ago
- about 40 million tuns per year made
- not directly bonded to plastic, easily enter environment
- can constitute up to 40% of total mass in PVC

*DMP – dimethyl phthalate

Phthalates

- ubiquitous in environment, possible migration
- **metabolism** – *phase I* – hydrolysis – transformation from dialkyl-form to monoalkyl-form

  – *phase II* – conjugation – excretion in glucuronidated form in urine

Source	Matrix	Phthalates [ng/mL]
Ustun et al., 2014	Bottled mineral water	85,0-312,0
Del Carlo et al., 2008	Wine	138,0-385,0
Mortensen et al., 2005	Comercially available milk	0,6-9,1
Frederiksen et al., 2007	Human amniotic fluid	2,8-264,0
Černá et al., 2015	Human urine	3,3-98,4
Mortensen et al., 2005	Human milk	72,0-10 900,0

Phthalates - concentrations

➢comparison of concentration of phthalates in river water from years 1999 and 2014 [ng/mL]

Phthalate	Peňalver et al., 1999	Valton et al., 2014
DMP	<LOD	0.04
DEP	0.26–0.62	0.53
DBP	0.12–0.16	0.12
BzBP	<LOD	0.06
DEHP	0.70–2.12	0.98
LOD	0.0007–0.17	–
Method	SPE–GC–MS	GC–MS
Sampling site	Ebro, Spain	Orge, France

DMP – dimethyl phthalate, DEP – diethyl phthalate, DBP – dibutylphthalate, BzBP– benzylbutyl phthalate, DEHP – diethylhexyl phthalate, LOD – limit of detection

Occurence

Used as:	Already measured in:
plasticizers	air
solutions in cosmetics (personal care products – PCPs): deodorants, perfumes, hair sprays, nail polish	water
industrial products – paints, glues, building materials, house stuff, clothes	soils, sediments
	dust
	food packaging materials, food itself
	human blood/serum, milk, urine
	bottled drinks, beer, wine
	PCPs, wet wipes, diapers,…

Toxicological information

Plasticizer	REACH	Endocrine Disruptor	Toxicity	TDI [mg/kg of body weigh]	Banned in
DEHP	X	Cat. 1	Reproductive, causes alergies, asthma	0,05	Toys, products for children, cosmetics
DBP	X	Cat. 1	Reproductive, developmental	0,01	Toys, products for children, cosmetics
DIDP		Cat. 2	Hepatotoxicity	0,15	Toys for „chewing“
BzBP	X	Cat. 1	Reproductive, developmental	0,50	Toys, products for children, cosmetics
DINP		Cat. 2	Hepatotoxicity, causes alergies, asthma	0,15	Toys for „chewing“
DIBP	X	Cat. 2	Reproductive, developmental	Unknown	-
DNOP		-	Hepatotoxicity	-	Toys, products for children
DPP (dipentyl phthalate)	X	-	Reproductive, developmental	-	-

Exposure

- highest exposure – children (toys, playing on the foor in dust, eating everything, cosmetics, mainly private parts – diapers, wet wipes), breast milk
- women – higher exposure to phthalates used in PCPs than men (MEP, MBP, MiBP)
- interesting – high concentration of MEP in pregnant women (3rd trimester)
- phthalates in plastic products – not gender specific (MMP, MBzP, MEHHP)

MEP – monoethyl phthalate, MBP – monobutylphthalate, MiBP – monoisobutyl phthalate, MMP – monomethyl phthalate, MBzP– monobenzyl phthalate, MEHHP – monoethylhexyl hexyl phthalate

Lack of Data?

- plenty of data, but not in highest quality
- measurements in huge amount of matrices
- „standard“ environmental – air, water, soils, sediments
- human matrices – blood/serum, urine, milk
- beverages – non-alcoholic and alcoholic
- food wrapping materials, food itself
- PCPs, diapers, wet wipes, …
- toys
- mural paintings, fishing baits, pharmaceutic wrapping, glues, building materials, …

Instrumental Methods

- GC–ECD
- GC–MS, GC–MS/MS
- LC–UV/VIS
- LC–APCI–MS, LC–APCI–MS/MS
- LC–ESI–MS, LC–ESI–MS/MS

Suitable Aproach

- create high quality instrumental method respecting metabolism, monitor in urine
- measurement possible in many matrices, difficult to estimate exposure or main source
- some phthalates characterised well (toxicity), desirable to complete these information to all phthalates

Legislation

- 1999/815/ED – DEHP, DBP a BzBP in toys
- e.d. 1223/2009 – DEHP and BzBP in cosmetics
- decree. No. 38/2001 Coll., + 271/2008 Coll., – DEHP and DBP in food wrapping materials
- 2009/48/ED – DINP in toys (czech legislation – government regulation 86/2011 Coll.)
- decree. No. 284/2006 Coll. – DIDP and DNOP in toys and in children care products
- decree. No. 38/2001 Coll., + 54/2004 Coll. – DIDP in food wrapping materials
- usage of surrogates

DINP – diisononyl phthalate, DIDP – diisodecyl phtthalate, DNOP – di-n-octyl pthalate

Surrogates

- DEHP banned, substituted by DINP and DIDP, banned in 2005
- 2002 – DINCH introduced to the market (1,2-cyclohexane carboxylic acid) aka Hexamoll (instead of DINP)
- does not have influence on fertility up to 1000 mg/kg body weigh per day
- 1999, 2003 – DINCH not detected
- since 2006 concentration of DINCH increase

DINCH	2006	2009	2012
Increase in samples (from 2003)	7%	43%	98%

Surrogates - terephthalates

- in 80. of the last century – DEHT introduced, aka Kodaflex DOTP
- 50 thousand tuns per year
- no information about toxicity
- NOAEL (reproductive toxicity) = 800-1000 mg/kg body weigh per day
- NOEL (carcinogenity) = 666 mg/kg body weigh per day

DEHT – diethylhexyl terephthalate

Surrogates

- DEHT and DINCH abundantly used for production, mainly PVC

Comparison of boiling point (DINP, DINCH):	
DINP	DINCH
244–252 °C	240–250 °C

Comparison of boiling point (DEHP, DEHT):	
DEHP	DEHT
385 °C	400 °C

Gaps in knowledge

- toxicological information is not complete
- hard to quantitate exposure routes
- difficult to find surrogates with simmilar properties without creating the same problem
- not possible to ban phthalates and surrogates – necessary to plastic production
- (possible to reduce plastic products – e.g.using glass)

Conclusion

Until now

- plenty of data
- huge amount of matrices
- some toxicological information available
- few phthalates forbidden

Future plan

- higher quality of data
- more precise instrumental methods
- monitoring in urine (pregnant women, +children)
- combination with personal questionares
- being focused on surrogates now

Thank you for your kind Attention!