AARHUS UNIVERSITY

Identifying potential other contaminants

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AMAP Assessment Report on Contaminants of Emerging Concern in the Arctic

Chapter	Title
1	Introduction
2	Contaminants of emerging concern (CECs)
3	Biological and toxicological effects of CECs
4	Further contaminants of potential Arctic concern *
5	Policy options and recommendations
Appendix	

* Written by Derek Muir, Environment and Climate Change Canada

Environment and Climate Change Canada
Environnement et Changement climatique Canada

New contaminants of relevance for the environment of Greenland

„4.1.4 Stoffer med potentiale til at være arktiske kontaminanter"

Literature review of seven modelling studies identifying potential Arctic contaminants.

Chemosphere 111 (2014) 379–395

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Review

A review of new and current-use contaminants in the Arctic environment: Evidence of long-range transport and indications of bioaccumulation

Katrin Vorkamp [a,*], Frank F. Rigét [b]

Vorkamp & Rigét, 2013, Technical report no. 19; Vorkamp & Rigét, 2014, Chemosphere 111, 379.

Further contaminants of potential Arctic concern

More than 100 million compounds with CAS numbers.

150,000 substances registered for use in Europe.

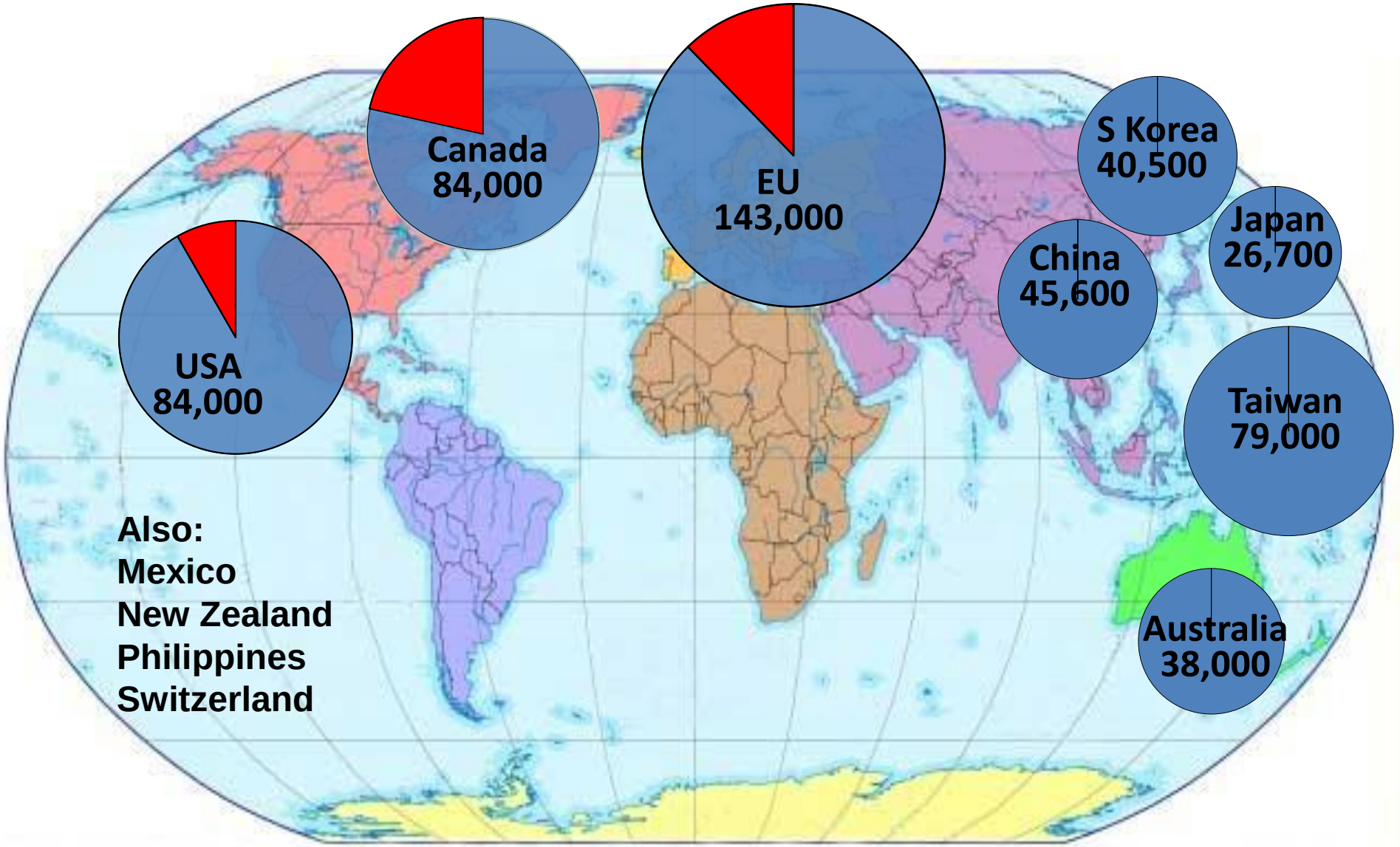
→ *In silico* screening of chemical inventories to predict persistent, bioaccumulative and toxic compounds (with long-range transport potential).

	POP (Stockholm Convention)	PBT (REACH)
Persistence	$t½_{water}$ > 2 months $t½_{soil/sediment}$ > 6 months	$t½_{mar.\ water}$ > 60 days $t½_{soil}$ > 120 days etc.
Bioaccumulation	BCF > 5000 $logK_{OW}$ > 5	BCF > 2000
Toxicity	Toxicity/ecotoxicity data	EC10 < 0.01 mg/L or other evidence
Long-range transport	$t½_{atmosphere}$ > 2 days	-

Lists and databases

Acronym	Name	Country
EINECS	European Inventory of Existing Commercial Chemical Substances	EU
ELINCS	European List of Notified Chemical Substances	EU
ECHA-REACH	ECHA list of pre-registered substances under REACH	EU
TSCA-IUR	Toxic Substances Control Act Inventory Update Rule	USA
DSL	Domestic Substance List	Canada
IECSC	Inventory of Existing Chemical Substances Produced or Imported in China	China
ENCS	Japanese Existing and New Chemical Substances Inventory	Japan
SMILECAS	Simplified molecular input line entry system (SMILE) and CAS number database with USE EPA EPISuite program	USA

Chemical inventory lists – global



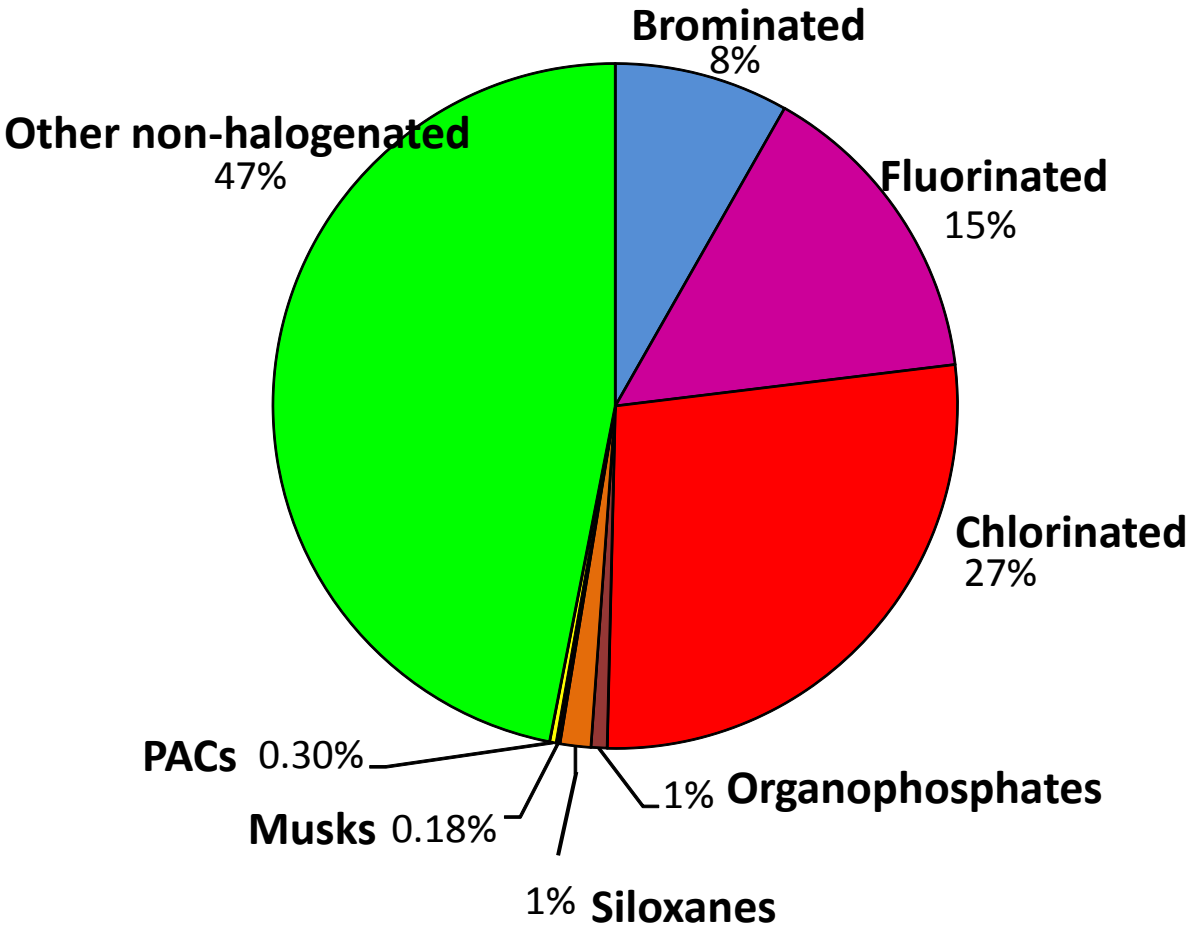
Graphics provided by Derek Muir

Recent *in silico* screening studies

List / Database	Chemicals screened	P + B	P + B + LRT	Reference
DSL	11,317	30	28	Muir & Howard, 2006
DSL, TSCA-IUR	22,263	610	105	Howard & Muir, 2010
EINECS and others	107,337	1,986	1,171	Rorije et al., 2011
EINECS, ELINCS, SMILECAS	127,281	1,202	-	Strempel et al., 2012
EINECS, SMILECAS	122,000	-	510	Scheringer et al., 2012
ECHA pre-registration	118,285	829	125	Öberg & Iqbal, 2012
Re-assessment of studies above	4,412	1,313	-	Gramatica et al., 2015
Total		**3,567**		

Muir & Howard, 2006, Environ. Sci. Technol. 40, 7157; Howard & Muir, 2010, Environ. Sci. Technol. 44, 2277; Rorije et al., 2011, RIVM report 601356001; Strempel et al., 2012, Environ. Sci. Technol. 46, 5680; Scheringer et al., 2012, Atmos. Pollut. Res. 3, 383; Öberg & Iqbal, 2012, Chemosphere 87, 975; Gramatica et al., 2015, Environ. Int. 77, 25.

P + B results by compound group



Graphics provided by Derek Muir

Howard and Muir (2010)

DSL (Canada) and TSCA-IUR (USA): 22,263 compounds

- K_{OW}
- Bioconcentration factor
- K_{OA}
- Vapour pressure
- Atmospheric oxidation half-life

P + B: 610 compounds

About 110 of these had been detected in the environment.

Top 10 brominated compounds:

Tetrabromobisphenol A (TBBPA)
Pentabromomonochlorocyclohexane (PBCC)
Tetrabromopyrene
Hexabromocyclododecane (HBCDD)
1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (TBECH / DBE-DBCH)
Tetrabromophthalic acid ester (BEH-TEBP)
Ethylene bis(tetrabromophthalimide) (EBTBP)
1,2-bis(2,4,6-tribromophenoxy)-ethane (BTBPE)
Decabromodiphenyl ethane (DBDPE)
Octabromo-1,1,3-trimethyl-3-phenylindan (OBIND)

Howard & Muir, 2010, Environ. Sci. Technol. 44, 2277

Howard and Muir (2010)

Top 10 chlorinated compounds:

Hexachlorocyclopentane (HCCP)	Taken off OSPAR's List of Chemicals for Priority Action
Bis-(4-chlorophenyl)sulfone (BCPS)	Used in polymer production, found in Baltic Sea biota (Norström et al., 2004)
Triclocarban	
Pentachlorothiophenol	Transformation product of HCB, also used in rubber industry. No data on bioaccumulation, but long-range transport potential.
3,5-dichloro-2,4,6-trifluoropyridine	Intermediate in herbicide production. $LogK_{OW}$ 2.69
Dibutyl chlorendate	
Dechlorane plus	Reactive flame retardant. No environmental data. $LogK_{OW}$ 7.25
Heptachlorocyclopentene	
Heptachlorocyclopentane	
Pentachloropyridine	

Top 10 fluorinated / siloxane / other compounds

Howard & Muir, 2010, Environ. Sci. Technol. 44, 2277; Vorkamp & Rigét, 2013, Technical report no. 19; Norström et al., 2004, Environ. Int. 30, 667.

Brown and Wania (2008)

Starting with 105,584 chemicals (SMILESCAS database)

Arctic contamination and bioaccumulation potential (based on partition properties)

Persistence (based on atmospheric oxidation half-life)

Structural resemblance to known Arctic contaminants (based on molecular size, halogenation and internal connectivity)

822 chemicals

Registered on one of five lists of chemicals

27 chemicals

Brown & Wania, 2008, Environ. Sci. Technol. 42, 5202; Vorkamp & Rigét, 2013, Technical report no. 19

Brown and Wania (2008)

	Bioaccumulation	Persistence	Structural resemblance	
50293	yes	yes	yes	p,p′-DDT
58899	yes	yes	yes	γ-HCH
68360	yes	yes	yes	1,4-bis(trichloromethyl)-benzene
82688	yes	yes	yes	pentachloronitrobenzene
87843	yes	yes	yes	1,2,3,4,5-pentabromo-6-chlorocyclohexane
95943	yes	yes	yes	1,2,4,5-tetrachlorobenzene
117088	yes	yes	yes	4,5,6,7-tetrachloro-1,3-isobenzofurandione
118741	yes	yes	yes	HCB
133493	yes	yes	yes	pentachlorobenzenethiol
626391	yes	yes	yes	1,3,5-tribromobenzene
632791	yes	yes	yes	4,5,6,7-tetrabromo-1,3-isobenzofurandione
634662	yes	yes	yes	1,2,3,4-tetrachlorobenzene
1134049	yes	yes	yes	2,3,4,5-tetrachloro-6-(trichloromethyl)-pyridine
1203867	yes	yes	yes	2,2-dichloro-1-(2,4,5-trichlorophenyl)-ethanone
1817136	yes	yes	yes	3,6-dichloro-2-(trichloromethyl)-pyridine
2176627	yes	yes	yes	pentachloropyridine
5216251	yes	yes	yes	1-chloro-4-(trichloromethyl)-benzene
17700093	yes	yes	yes	2,3,4-trichloronitrobenzene
29091096	yes	yes	yes	2,4-dichloro-1,3-dinitro-5-(trifluoromethyl)-benzene
30554724	yes	yes	yes	tetrabromodichlorocyclohexane (1,2,3,4-tetrabromo-5, 6-dichlorocyclohexane)[e]
62111471	yes	yes	yes	heptachlorocyclopentene (1,2,3,3,4,4,5-heptachloro-1-cyclopentene)[e]
68258902	yes	yes	yes	heptachlorocyclopentane (1,2,3,3,4,5,5-heptachlorocyclopentane)[e]
68258913	yes	yes	yes	hexachlorocyclopentane (1,2,2,3,4,4-hexachlorocyclopentane)[e]
69045836	yes	yes	yes	2,3-dichloro-5-trichloromethylpyridine
72030263	yes	yes	yes	hexachlorocyclopentene (1,2,3,4,5,5-hexachloro-1-cyclopentene)[e]
73588428	yes	yes	yes	1,3-dichloro-5-(1,3,3,3-tetrachloro-1-methylpropyl)-benzene
75147205	yes	yes	yes	2,2,3,4,4-pentachloro-3-butenoic acid, butyl ester

Brown & Wania, 2008, Environ. Sci. Technol. 42, 5202

Wiandt and Poremski (2002)

OSPAR/DYNAMEC:

Dynamic selection and prioritisation tool for hazardous substances in the marine environment

OSPAR COMMISSION
Protecting and conserving the North-East Atlantic and its resources

OSPAR:
Oslo-Paris Commission for the Protection of the North-East Atlantic

Inter-governmental organisation

Contracting parties:

Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, The Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, United Kingdom

Wiandt & Poremski, 2002, Ecotoxicol 11, 393

OSPAR's Hazardous Substances Strategy

- **Discharges, emissions and losses of hazardous substances cease within one generation (by 2020).**
- **Concentrations near background values for naturally occurring substances**
- **Concentrations of zero for man-made substances**

Table 1. OSPAR list of chemicals for priority action, OSPAR 1998

Polychlorinated dibenzodioxins (PCDDs)
Polychlorinated dibenzofurans (PCDFs)
Polychlorinated biphenyls (PCBs)
Polyaromatic hydrocarbons (PAHs)
Pentachlorophenol (PCP)
Short-chained chlorinated paraffins (SCCP)
Hexachlorocyclohexane isomers (HCH)
Mercury and organic mercury compounds
Cadmium
Lead and organic lead compounds
Organic tin compounds
Nonylphenol/ethoxylates (NP/NPEs) and related substances
Musk xylene
Brominated flame retardants
Certain phthalates—dibutylphthalate and diethylhexylphthalate

Initial selection

↓

Ranking

↓

Risk assessment

Wiandt & Poremski, 2002, Ecotoxicol 11, 393

OSPAR DYNAMEC

Initial screening

Wiandt & Poremski, 2002, Ecotoxicol 11, 393

Nordic Substance Database (18,000)
Danish EPA QSAR Database (166,000)
Netherland's BKH/Haskoning report (180,000)

- persistence: not readily biodegradable,
- bioconcentration: $\log K_{ow} \geq 4$ or $BCF \geq 500$,
- aquatic toxicity: acute $L(E)C_{50} \leq 1$ mg/l, long-term $NOEC \leq 0.1$ mg/l or mammalian toxicity: CMR or chronic toxicity.

Preliminary List of Substances of Possible Concern

Expert judgement (incl. additions) by contracting parties

List of Substances of Possible Concern

OSPAR DYNAMEC

Ranking

COMPPS: Combined monitoring-based and modelling-based priority setting procedure (Fraunhofer Institute)

- **Characterisation of production volume and use patterns**
- **Exposure score**
  Relative level of predicted or measured concentration in the environment. Here: Input loads to marine waters and sediments
- **Effect score**
  Relative toxicity (to aquatic organisms and to humans) and liability to bioaccumulation

Wiandt & Poremski, 2002, Ecotoxicol 11, 393

OSPAR DYNAMEC

Table 4. Twelve substances in groups A and B included in the OSPAR List of Chemicals for Priority Action by OSPAR 2000

CAS No	Name	IUPAC name
Group A		
732-26-3	Dodecyl phenol	Phenol, 2,4,6-tris(1,1-dimethylethyl)-
115-32-2	Dicofol	benzenemethanol, 4-choro-.alpha-(4-chlorophenyl)-.alpha.-(trichloromethyl)-
115-29-7	Endosulfan	6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-,3-oxide
72-43-5	Methoxychor	Benzene,1,1′-(2,2,2-trichloroethylidene)bis(4-methoxy
140-66-9	Octylphenol	Phenol, 4-(1,1,3,3,tetramethylbutyl)-
Group B		
107-46-0		Disiloxane, hexamethyl-
77-47-4		1,3-Cyclopentadiene, 1,2,3,4,5,5-hexachloro-
79-94-7	TBBA	Phenol, 4,4′-(1-methylethylidene)bis[2,6-dibromo-
120-82-1		Benzene, 1,2,4-trichloro-
87-61-6	Trichlorobenzene	Benzene, 1,2,3-trichloro-
108-70-3	1,3,5-Trichlorobenzene	Benzene, 1,3,5-trichloro-
98-51-1	4-tert-butyltoluene	Benzene, 1-(1,1-dimethylethyl)-4-methyl-

Wiandt & Poremski, 2002, Ecotoxicol 11, 393

Swedish air monitoring

- **Empirical data on occurrence in air**
- **Assessment of persistence and long-range transport**
- **Assessment of bioaccumulation**
- **Estimation of detection frequency**

→ **Combined score**
Pentabromophenol: 1
SCCPs: 9

Name	CAS no.
Short-chain chlorinated paraffins (C10–C13)	85535-84-8
Perfluorooctane sulfonate	2795-39-3
Octachlorostyrene	29082-74-4
1,2,5,6,9,10-Hexabromocyclododecane	3194-55-6
Hexachlorobenzene	118-74-1
Pentachloroanisole	1825-21-4
Decamethylcyclopentasiloxane	541-02-6
Octamethylcyclotetrasiloxane	556-67-2
Pentachlorobenzene	608-93-5
1,2,3,4-Tetrachlorobenzene	634-66-2
Hexachlorobutadiene	87-68-3
Dodecamethylcyclohexasiloxane	540-97-6
Perfluorodecane sulfonate	67906-42-7
1,2,4,5-Tetrachlorobenzene	95-94-3
Pentabromophenol	608-71-9

Cousins et al., 2012, Environ. Monit. Assess. 184, 4647.

Targeting POP candidates in Norway

- **Empirical data on occurrence in the Arctic or Antarctic**
- **Ranking according to persistency, bioaccumulation, long-range transport and toxicity**

TABLE 10: SELECTED CANDIDATS FOR THE STOCKHOLM CONVENTION

CATEGORY	COMPOUND	ABBREVIATION	CAS - NUMBER
Brominated flame retardants	Decabromodiphenyl ether	BDE-209	1163-19-5
	Hexabromobenzene	HBB	87-82-1
	Pentabromotoluene	PBT	87-83-2
Chlorobenzene	1,2,3,4-tetrachlorobenzene	1,2,3,4- TeCB	634-66-2
	1,3,5-trichlorobenzene	1,3,5-TCB	108-70-3
Organo-phosphate	Tris(2-chloro-1-methylethyl) phosphate	TCPP	13674-84-5
Perfluorated compound	Perfluorodecanoate acid	PFDA	335-76-2
	Perfluorodecane sulfonate	PFDS	335-77-3
	Perfluorononanoate acid	PFNA	375-95-1
Pesticide	Trifluralin		1582-09-8
	Pendimethalin		40487-42-1
	Methoxychlor		72-43-5
Siloxanes	Decamethylcyclopentasiloxane	D5	541-02-6
	Dodecamethylcyclohexasiloxane	D6	540-97-6
	Octamethylcyclotetrasiloxane	D4	556-67-2
By product of chlorinated compounds	Octachlorostyrene	OCS	29082-74-4
Pesticide metabolite	Pentachloroanisole		1825-21-4

Lambert et al., 2011, TA-2871/2011.

Some considerations about screening criteria

Atmospheric vs. ocean transport

- **PFOS and β-HCH are transported in ocean waters.**
- **Canadian DSL list (neutral organic chemicals): 38% of chemicals had a higher characteristic travel distance in water than in air (Zarfl et al., 2011)**

Microplastics

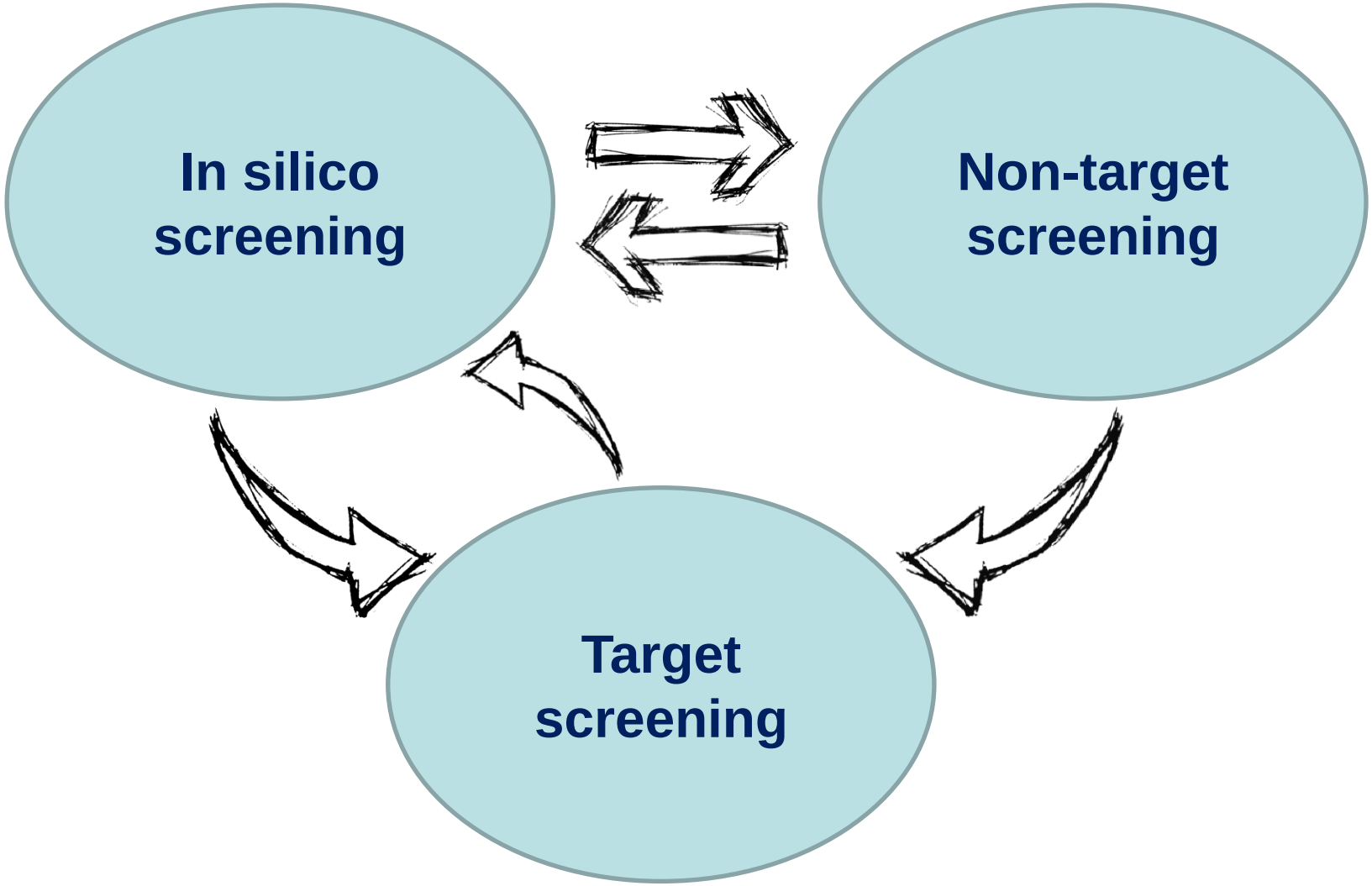
- **Sorption and transport of contaminants**
- **Release of additives that would not undergo long-range transport in water or air.**

Degradation products

- **Pentachlorophenol → Pentachloroanisole**
- **Fluorotelomer alcohols → Perfluorocarboxylates**

Zarfl et al., 2011, Environ. Sci. Technol. 45, 10075.

Combining different screening approaches



Conclusions

- ***In silico*** **screening studies combine lists and databases of chemicals with physical-chemical data to predict certain environmental behaviour (e.g. POP-like characteristics).**
- **Examples have been given of predictions in research, national monitoring programmes and in regional sea conventions (OSPAR).**
- **Most predictions are based on lists and databases of registered chemicals and atmospheric transport. Ocean-transported chemicals and degradation products might be overlooked.**