  

Draft Risk Profile for ***methoxychlor***

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POPRC-16 Online pre-meeting, 1-3 December 2020

environment

Documents

- UNEP/POPS/POPRC.16/3
  - ➔ **Draft Risk profile: methoxychlor**
- Document 2
  - ➔ **Updated draft risk profile: Methoxychlor (pre-meeting document)**

Way to the Draft Risk Profile

POPRC-15 meeting (October 2019): The European Union submitted a proposal (UNEP/POPS/POPRC.15/4) for listing Methoxychlor in Annexes A, B and/or C

October 2019: The POPs Review Committee evaluated the proposal regarding methoxychlor and reached in **Decision POPRC-15/3** the conclusion that methoxychlor fulfilled the screening criteria specified in Annex D

4 October 2019: The Committee established an intersessional working group to prepare a draft risk profile for methoxychlor in accordance with Annex E

POPRC-16 meeting (January 2020): Draft Risk Profile for methoxychlor (POPRC-16/3) to be discussed for potential adoption

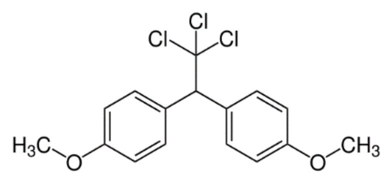
Substance identity

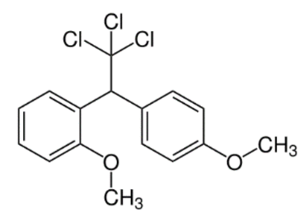
Methoxychlor – Organochlorine insecticide (OCP)

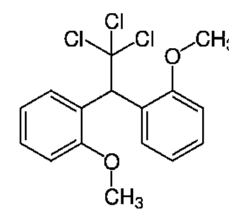
Chemical formula, mass and structure examples:

$C_{16}H_{15}Cl_3O_2$

345.65 g/mol







IUPAC name	1,1'-(2,2,2-trichloroethane-1,1-diyl)bis(4-methoxybenzene) 1-methoxy-2-[2,2,2-trichloro-1-(4-methoxyphenyl)ethyl]benzene 1,1'-(2,2,2-trichloroethane-1,1-diyl)bis(2-methoxybenzene)
CAS No *(non exhaustive list)*	72-43-5; 30667-99-3; 76733-77-2; 255065-25-9; 255065-26-0; 59424-81-6; 1348358-72-4
EC No	200-779-9

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Physico-chemical properties

Property	Value	References
Physical state at 20°C and 101.3 kPa	Solid (pale-yellow powder)	ATSDR, 2002
Melting/freezing point (MP)	87°C *(experimental)* 129.34°C *(estimated)*	Lide, 2007 US EPA, 2012
Boiling point (BP)	346°C *(experimental)* 377.87°C *(estimated)*	US EPA, 2012 US EPA, 2012
Vapour pressure	5.56×10^{-3} Pa at 25°C *(estimated)*	US EPA, 2012
Henry's Law constant	2.03×10^{-7} atm.m^3/mol at 25°C (or 2.06×10^{-2} Pa.m^3/mol) *(experimental)* 9.75×10^{-8} atm.m^3/mol (or 9.88×10^{-3} Pa.m^3/mol) *(estimated)*	Altschuh *et al.,* 1999 US EPA, 2012
Water solubility	0.040 mg/L at 24°C *(experimental, 99% purity)* 0.10 mg/L at 25–45°C *(experimental, shake flask-UV)* 0.12 mg/L at 25°C *(experimental)* 0.302 mg/L at 25°C *(estimated)*	Verschueren, 1996 Richardson and Miller, 1960 Zepp *et al.,* 1976 US EPA, 2012
Organic carbon normalized adsorption coefficient (log K_{oc})	4.9 (experimental) 4.43 *(estimated)*	Schüürmann *et al.,* 2006 US EPA, 2012
Octanol/water partition coefficient (log K_{ow})	5.08 *(experimental)* 5.67 *(estimated)*	Karickhoff *et al.,* 1979 US EPA, 2012
Octanol/air partition coefficient (log K_{oa})	10.48 *(experimental, GC retention time method)* 10.161 *(estimated)*	Odabasi and Cetin, 2012 US EPA, 2012
Air/water partition coefficient (log K_{aw})	-5.081 *(estimated)*	US EPA, 2012

Low vapour pressure

Low water soluble

Highly adsorptive
indicates chemical partitioning to solids (sediment, soils, particulate matter)

Strongly hydrophobic

High sorption onto aerosols

Information on production and uses

- **Uses**

→ Used as an **insecticide and as a biocide** (replacement for DDT) in both agricultural (crops and livestock, in animal feed, barns and grain storage bins) and veterinary practices (ectoparasiticide)

→ Applied as a spray or as dust. The use is seasonal (spring and summer)

- **Annex E Information**

→ It has been restricted/banned in several countries for more than 15 years

→ No information on the current production or use of methoxychlor at a global scale is publicly available

Releases to the environment

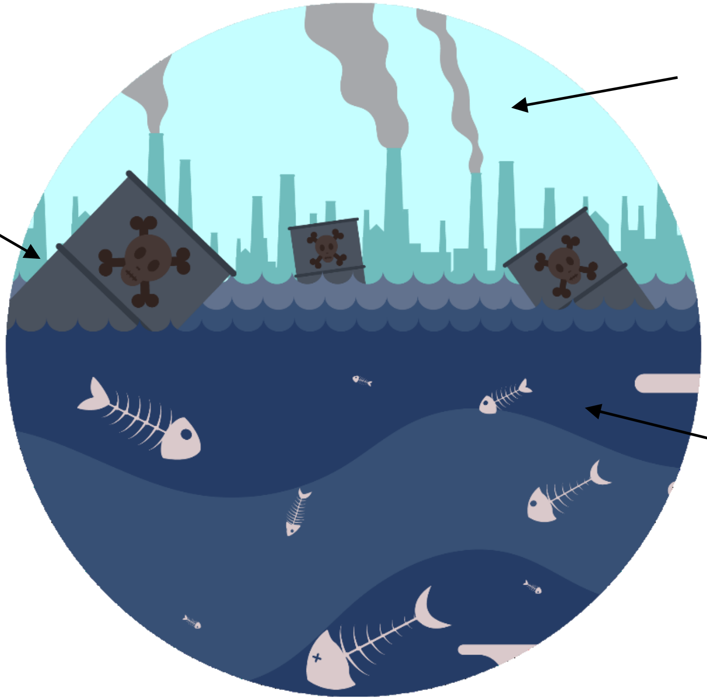
- **Mainly as a result of its application to crops and livestock as a pesticide**
  - ➔ Higher amount released during periods of insect control (spring and summer)

- **Smaller amounts may be released to the environment during:**
  - ➔ production, formulation, storage, shipment and disposal

Compartments of release:

Soil

(Use as insecticide; through leakage at storage and waste sites)



Air

(Use as pesticide; production/formulation and disposal)

Water

(Use as pesticide released to surface water on farms; runoff and leaching from soil; from industrial effluents; from leakage at storage and waste sites)

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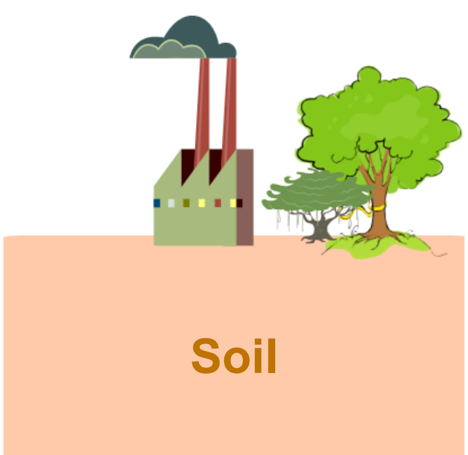
Persistence

- **Modelling data**
  - ➔ Modelling data (BIOWIN 2, 3, 6; *U.S. EPA, 2012*) indicate that methoxychlor is not expected to biodegrade fast

- **Abiotic degradation**
  - ➔ DT_{50} in air = 2.4 hours (AOPWIN v 1.92; *U.S. EPA, 2012*) *(underestimation)*
  - ➔ Hydrolysis expected to be negligible (half-life of 367 days at 27° C at pH 3-7; *Wolf et al., 1977*)
  - ➔ Possible indirect photolysis in water but only in the top layer of the water column
  - ➔ Photodegradation is likely to occur in soil but only at the very surface

- **Biotic degradation and monitoring data**



➔ Soil lab studies reported DT50s in the range of 7-210 days (reliability unknown*; Chen, 2014; Wauchope et al., 1992 and Guth et al., 1976)*

➔ Detected in soil samples from Italy several years after it was banned in the EU *(Thiombane et al., 2018)*

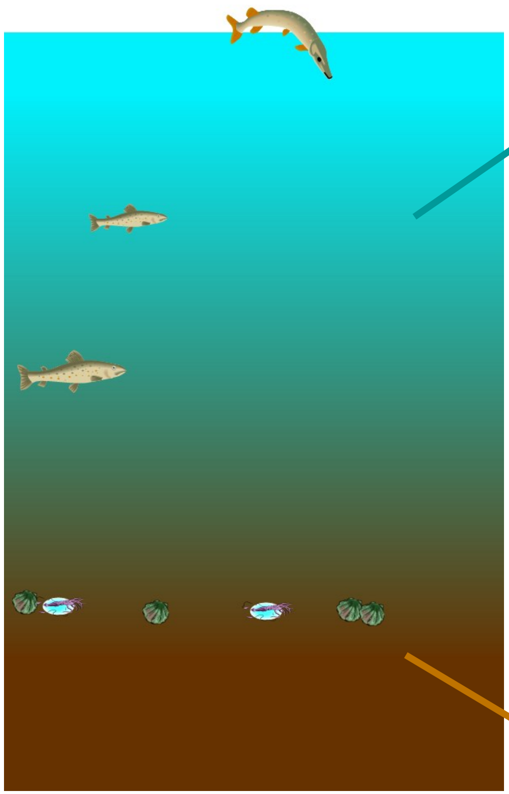
⬇

May be persistent in some aerobic soils *(WoE approach)*

Persistence

- **Biotic degradation and monitoring data**

Water



Sediment

- Continued to be detected in EU and Canadian surface waterbodies (and in French groundwaters) for years after it was phased out *(WFD factsheet; Naiade database and Annex E, 2019 information from Canada)*
- Detected in an Arctic lake water (in 1994) and in the Arctic Ocean (in 2016-2017) *(Muir et al., 1995 and Gao et al., 2019)*

⬇

May be persistent in water

- DT50 of methoxychlor in one of two aerobic sediments is **> 180 days** (116 days for pond and 206 days for lake) and <28 days anaerobically for both pond and lake *(Muir and Yarechewski, 1984)*
- Detected in sediment samples from Portugal, Australia and Canada several years after it was banned *(Pinto et al., 2016; Duodu et al., 2017 and Annex E, 2019 information from Canada)*

⬇

Persistent in aerobic sediments and may be persistent in some anaerobic sediments *(WoE approach)*

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Bioaccumulation

- BCFs vary largely between different fish species (**113 – 8,300**)
  - BCF_{aqua} = 8,300 in fathead minnows *(Pimephales promelas) (Veith et al., 1979)*
  - $BCF_{dietary}$ = 2,941 – 6,991 in rainbow trout *(Oncorhynchus mykiss) (growth-corrected and lipid normalised; OECD, 2012a and 2013; Environment Agency, 2014)*
  - $BCF_{dietary}$ = 667 – 1,867 in carp *(Cyprinus carpio) (growth-corrected and lipid normalised; OECD, 2012a and 2013; Environment Agency, 2014)*
  - $BCF_{aqua\ steady\text{-}state}$= 810 – 1,040 in carp *(Cyprinus carpio)* (lipid normalised; *Inoue et al., 2012)*
  - BCF_{aqua} = 113 in sheepshead minnow *(Cyprinodon variegatus)* (*Parrish et al., 1977)*
- BCF = 8,020 – 12,000 in mussels *(Renberg et al., 1985)*
- BCF = 5,000 – 8,570 in snails *(Physa integra) (Anderson and DeFoe, 1980)*
- Concentrations in biota (remote areas) were in the range of n.d. to 86 ng/g lw
- Concentration = 1.79±0.32 ng/g lw in the milk of elephant seals *(Miranda Filho et al., 2009)* and found in human breast milk *(Damgaard et al., 2006)*
- Log K_{OW} = 5.08 (experimental) *(Karickhoff et al., 1979)*
- MW = 345.65 $g.mol^{-1}$

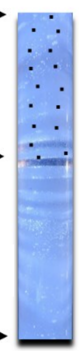
➡ **Methoxychlor has a bioaccumulation potential in some aquatic organisms (BCFs > 5000 and log K_{OW} >5)**

Potential for long-range environmental transport

Detected in various media in the Arctic:

- **In air**:
    - Concentrations = 0.12 – 0.41 pg/m^3 (annual mean; sum filter and plugs) between 1992 – 1995 at two Canadian and one Russian Arctic sites *(Hung et al., 2005)*
    - Concentrations = 0.02 – 0.42 ng/m^3 between 2016 and 2017 in the North Pacific to the Arctic Ocean *(Gao et al., 2019)*

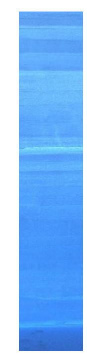
- **In ice core/caps**:



Austfonna ice cap on Svalbard

Increased concentrations from the early 1950s with a peak concentration in the early 1980s *(Hermanson et al., 2005)*

Indication of LRTP



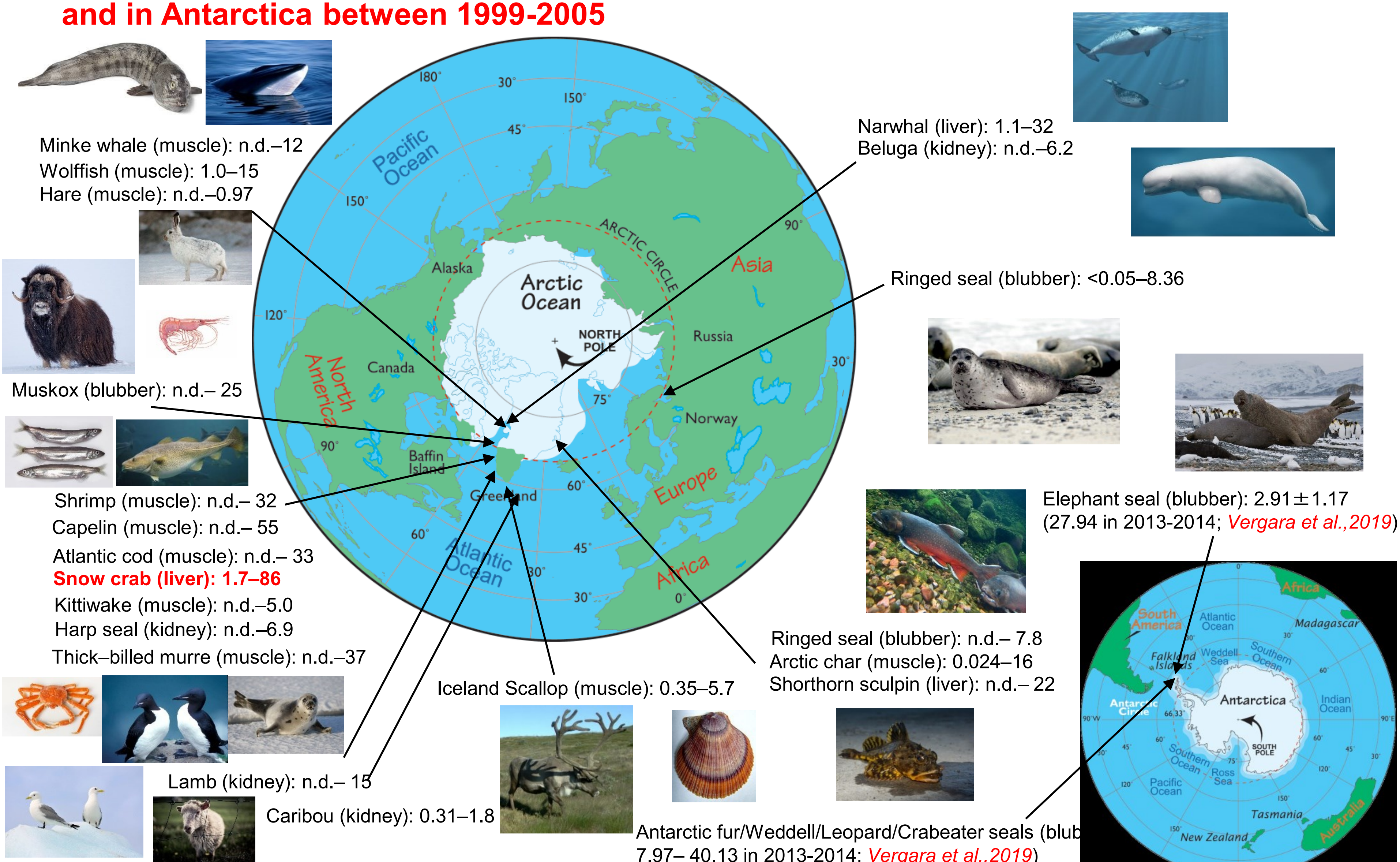
ice core on Holtedahlfonna on Svalbard
(Ruggirello et al., 2010)

- **In snow from the Canadian Arctic:**
    - Concentration = 0.234 ng/L in brown snow (melted snow and associated filtered particles) in May 1988 *(Welch et al., 1991)*

- **In lake water/surface seawater:**
    - Concentration < 0.01 – 0.022 ng/L in an Arctic lake water in July 1994 *(Muir et al., 1995)*
    - Concentration < MDL – 0.38 ng/L in the Arctic Ocean and Chukchi Sea in 2016 – 2017 *(Gao et al., 2019)*

Potential for long-range environmental transport

Concentrations (ng.g^{-1} lw) in terrestrial, avian and marine biota samples in the Arctic and in Antarctica between 1999-2005



References:Vorkamp et al., 2004; Savinov et al., 2011; Miranda Filho et al., 2009

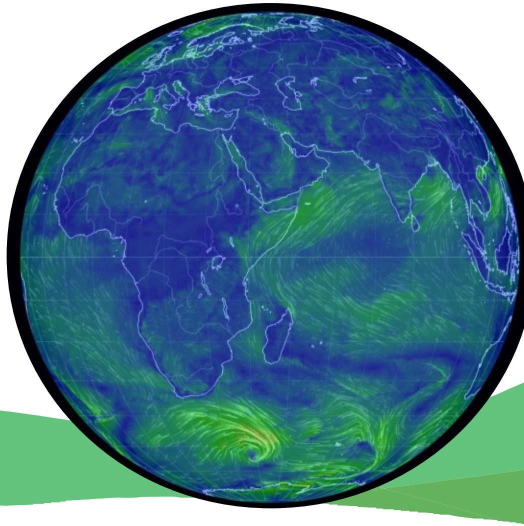
Potential for long-range environmental transport

- **OECD Pov & LRTP Screening Tool**
  - → Pov of **303 days** (>195 days Pov of α-HCH)
  - → CTD of 498 km (< 5097 km CTD of PCB-28)
  - → TE of 0.02 % (< 2.248% TE of PCB-28)

  } Reliable?
  (Uncertainties with the input parameters)

- **Measured levels of methoxychlor in remote high latitude regions indicate that LRT is possible via air**

- **LRTP via aqueous environment is possible considering its potential persistence in water and the measured levels in surface seawater in the Arctic Ocean**



➡ **LRTP to pristine regions via air and water is possible**

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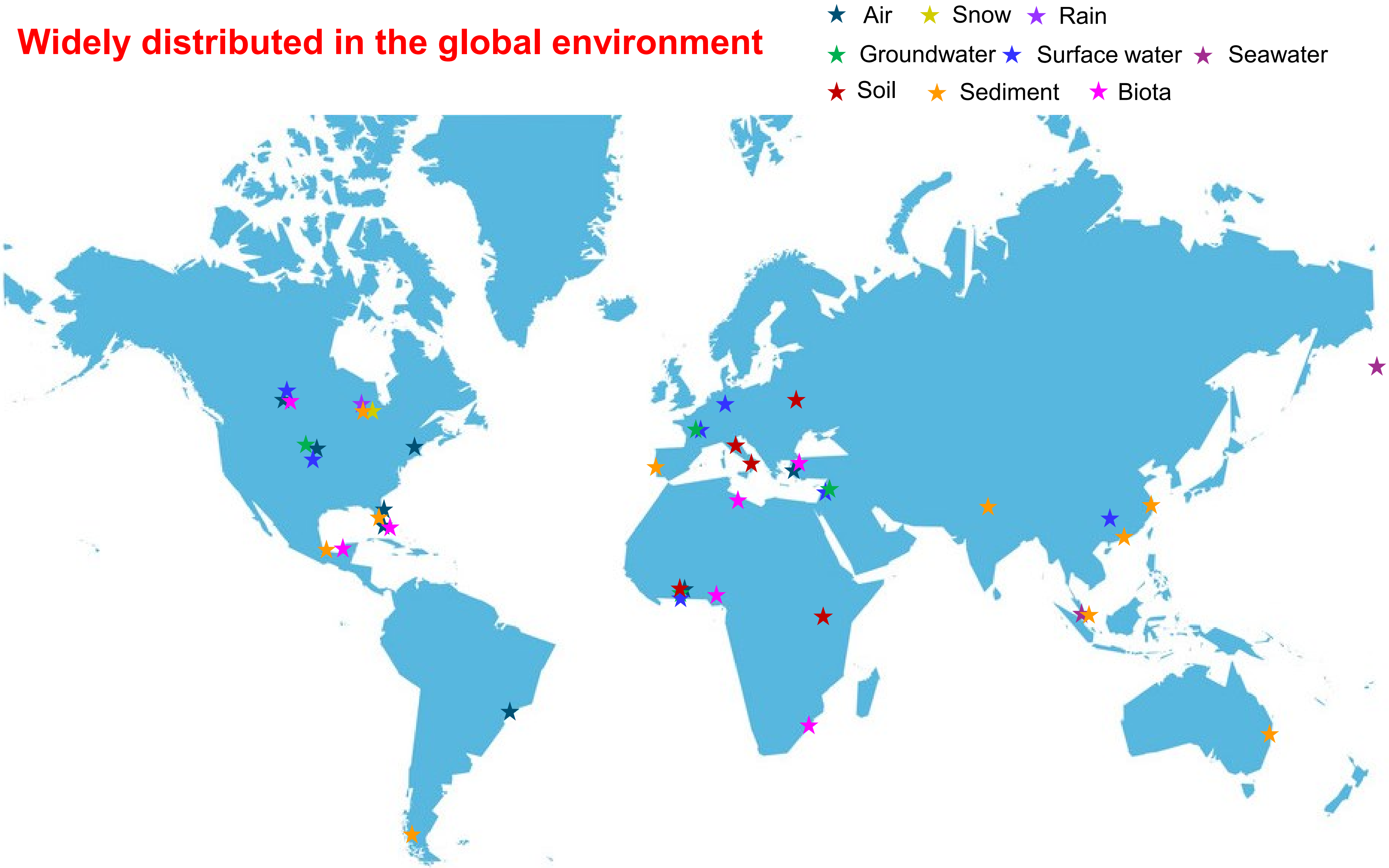
Environmental monitoring data

Widely distributed in the global environment



Monitoring data available between 1976 – 2018 with measured values ≥LOD (data in remote areas are not reported)

Human exposure

- The most probable route of exposure would be from **inhalation** or **dermal contact** by workers *(US EPA, 2000)*

- The general population can be exposed by **inhaling dusts and aerosols** in air surrounding areas where methoxychlor is used or by **consuming contaminated food**

- **(Bio-)monitoring data**
  - → Detected in drinking water and food
  - → Detected in human serum, adipose tissues, umbilical cord blood and human breast milk
  - → Detected in children adipose tissues

Adverse effects – Environmental effects

- Invertebrates are the most sensitive species (HC_5= 0.37 µg/L for freshwater arthropods; *Maltby et al., 2005)*

- Methoxychlor presents the following adverse effects:
  - Endocrine disruptive effects in fish, amphibian, and sea urchin fertility, growth, and development *(ATSDR, 2002)*
  - Cause neurological injury at high doses *(ATSDR, 2002)*
  - Cause effects on the reproductive system (interference with the normal actions of estrogen or androgen; *ATSDR, 2002)*
  - Potential to promote the epigenetic transgenerational inheritance of disease and associated sperm epimutations in rats (*Manikkam et al., 2014)*

➡ Methoxychlor meets the criterion on adverse effects

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Adverse effects – Human health effects

- Not possible to draw definitive conclusion as to whether methoxychlor is carcinogenic to animals or humans

- Genotoxic potential of methoxychlor appears to be negligible

- Animal and *in vitro* data strongly suggest that methoxychlor may **adversely affect the development, histopathology, and function of the human reproductive system (likely through an estrogenic mode of action). Reproductive effects** are indicative of interference with the normal actions of estrogen or androgen

- **Induce behavioral changes in primates**

- In certain defined cases, the simultaneous exposure of methoxychlor with other environmental chemicals has resulted in **additive effects**

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Overall conclusion on POP characteristics

Criterion	Meets the criteria (Yes/No)	Comments
Persistence	Yes	Persistent in sediment (aerobic conditions; half-life > 6 months; and may be persistent in some anaerobic sediments) Evidence of persistence in water May be persistent in some aerobic soils
Bioaccumulation	Yes	BCF or BAF > 5000 Log Kow > 5 Monitoring data in biota indicate a bioaccumulation potential
Potential for long-range transport (LRTP)	Yes	Detection in environmental and biota samples in locations distant from the sources
Adverse effects	Yes	Evidence of adverse effects to human health (reprotoxic, endocrine disrupter) and to the environment (toxicity to fish and aquatic invertebrates; and endocrine disrupter)

Reasons for concern

Due to its harmful POP properties and risks related to its possible continuing production, use and releases to the environment, measures taken nationally or regionally are not sufficient to safeguard a high level of protection of the environment and human health, and therefore **wider international action is necessary**

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Updated version of the Risk Profile

- UNEP/POPS/POPRC.16/3
  - ➔ **Draft Risk profile: methoxychlor**

- Document 2
  - ➔ **Updated draft risk profile: Methoxychlor (pre-meeting document)**
    - The risk profile has been updated after June 2020 as new information and new comments have been received
    - Most of the changes have been added to the Appendix due to the page limitations but key information has been reflected in the Risk Profile

ONLY ONE EARTH

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