DUTCH SURVEY OF CHLORINATED PERSISTENT BIOACCUMULATING TOXIC COMPOUNDS IN INDUSTRIAL EFFLUENTS AND OTHER EMISSION SOURCES

Marja Lamoree[1], Bert van Hattum[1], Thomas Sanderson[2] and Henk Senhorst[3]

[1]Institute for Environmental Studies (IVM), Faculty of Earth and Life Sciences, De Boelelaan 1087, 1081 HV Amsterdam, The Netherlands
[2]Institute for Risk Assessment Studies (IRAS), PO Box 80176, 3508 TD Utrecht, The Netherlands
[3]Institute for Inland Water Management and Water Treatment (RIZA), PO Box 17, 8200 AA Lelystad, The Netherlands

Introduction

As a result of the Dutch national debate on chlorine in the 1990s, a study on the occurrence of unidentified chlorinated compounds in industrial effluents and other selected emission sources was designed in close cooperation with the government, industry, environmental NGOs and a number of research institutes. In this study, the following questions will be addressed: (1) does the problem of chlorinated microcontaminants in the environment (still) exist, and - if yes - to what extent, (2) which persistent, bioaccumulating and toxic compounds or group of compounds are emitted from the chlorine chain into the environment from point or non-point sources?

A four year study was initiated consisting of background literature studies and experimental screening studies, which include (industrial) effluents, atmospheric emissions and products that are marketed on an industrial scale. The present paper deals with 18 industrial effluents, a cooling water inlet and outlet, an effluent from a municipal wastewater treatment plant (MWTP), surface water from an area that is considered to be relatively unperturbed, and a blank. In agreement with all participants, the samples are processed using a code to guarantee anonimity. A bioassay-directed approach was followed for classification of the samples on toxicity, hydrophobicity and presence of chlorinated compounds. Samples that contain chlorinated compounds and show a response in the bioassays will be submitted to further biodegradation testing and bioassay-directed identification of toxicants.

Materials and methods

Sampling of the 16 industrial effluents and the 5 water samples from other sources was performed by only two persons based on a strict protocol, ensuring a high degree of comparability of the sampling conditions for all samples. Samples of industrial effluents reflect typical operating conditions and are taken from a flow where cooling water discharges are not mixed in yet, but after wastewater treatment.

Extraction of 8 L sample was done using liquid/liquid extraction with pentane at pH 2 and pH 10. Prior to further processing, extracts were pooled and transferred to 8 mL methanol. See fig. 1 for details on sample processing and testing.

Fractionation of the total extracts was carried out under isocratic conditions using methanol on a HPLC system equipped with a 250 x 4.6 mm, 5 µm C18 column. The eluent was collected in three fractions roughly indicating low, medium and high log K_{ow}. Purge and trap extracts will not be discussed.

Chemical analysis of the fractionated extracts was done with both GC-ECD and GC-MSD. The total ECD-respons was taken as an indication for chlorine content of the samples, while mass spectrometry enabled us to confirm the presence of chlorine atoms in a molecule by the obersvation of isotope patterns in the mass spectra.

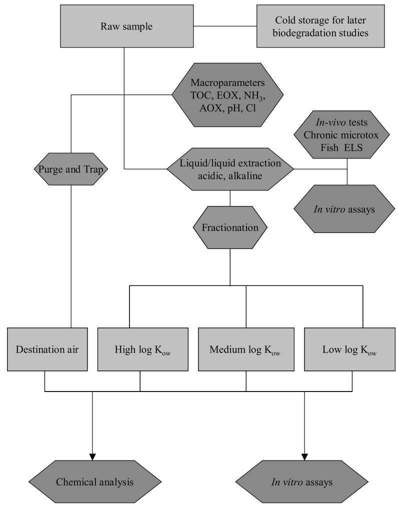

Figure 1. Schematic representation of the treatment of aquatic samples from industrial and other sources regarding extraction, fractionation, chemical analyses and in vitro assays.

In vivo bioassays that were used were zebrafish-early life stage mortality (ELS)[1] and semi-chronic microtox-test[2] (Vibrio Fischeri).

In vitro bioassays included DR-CALUX[3] and carp hepatocyte EROD induction[4] for screening on compounds with dioxin-like mode of action.

Results and discussion

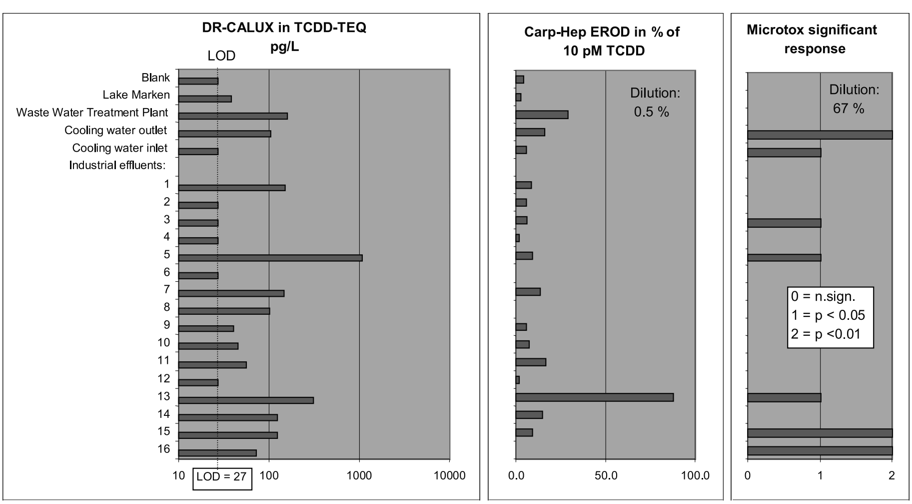

Figure 2. Results of the toxicicity screening. All assays carried out with total extracts.

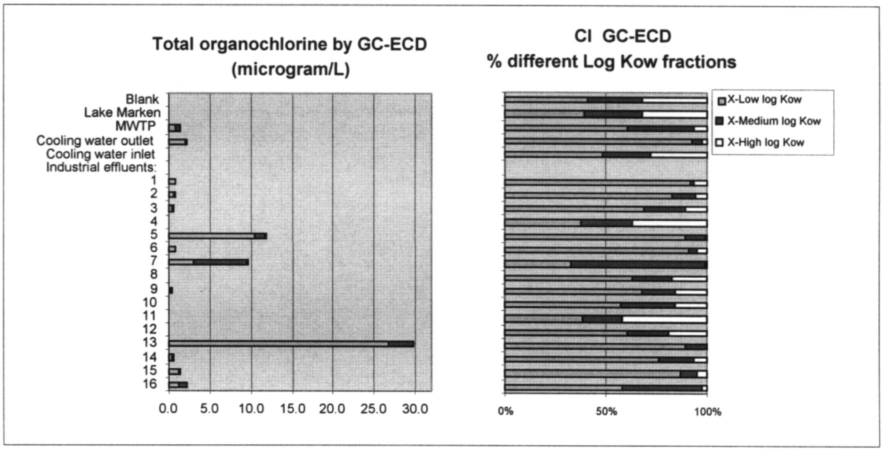

Figure 3. Results of the chemical screening of the fractions with low, medium and high log K_{ow} with GC-ECD

A multi-criteria approach was used for classification:

	in-vivo	*in-vitro*				Bioaccumulation potential	
	Micro-Tox	Carp-hep EROD	DR-CALUX concentration	DR-CALUX load	AOX load	Cl Medium log Kow load	Cl High log Kow load
Blank	+						
Lake Marken			+				
MWTP	++	++	++	+	++	+	+
Cooling water outlet	+	+	++		+		
Cooling water inlet							
Industrial effluents							
1		+	++	+	++		+
2	+				++	+	+
3	+				+++	+	+
4	+						
5	+	+	+++	+++	+++	+++	+
6					++		
7		+	++		++	+	
8			++	++	+++	++	++
9			+		+		
10			+		+		
11		+	+				
12					++		

13	+++	+++	+++		+		
14		+	++	+	+++	+	+
15	+	+	++	++	++	+	+
16	++		+	++			

DR-Calux, carp hepatocyte EROD and semi-chronic microtox tests were responsive in various samples. The zebra fish ELS test was not responsive for any of the samples.

Halogenated compounds were detected to varying extent in all fractions with different hydrophobicity. Based on these integrated results, responsive fractions have been selected for biodegradation studies and further bioassay-directed identification of chlorinated compounds.

References

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4. Burke M.D. and Mayer R.T. (1974) Drug Metab. Dispos. 2, 583.