

ANALYSIS OF NATURALLY PRODUCED ORGANOHALOGENS IN SURFACE WATER

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ABSTRACT

A survey of adsorbable organic halogen (AOX) in industrially unaffected surface waters in southern Sweden showed that the AOX concentrations varied between 13 and 185 ug Cl/l. In addition, two individual organochlorine compounds, 2,4,6-trichlorophenol (TrCP) and 2,4,6-trichloroanisole (TrCA), were detected in low concentrations. It is suggested that TrCP is formed by enzymatically mediated chlorination of humic substances and that TrCA is then formed by microbial methylation of TrCP.

INTRODUCTION

Until recently it has been a widespread conception that practically all organohalogen compounds in the environment are xenobiotic. Group parameters, such as AOX (adsorbable organic halogen), have been suggested as indicators of industrial pollution (Hoffman et al., 1988). During the past few years, however, the situation has gradually changed, and there are now several studies giving evidence of a substantial natural production of organohalogens (Asplund et al., 1989; Grön, 1989).

The present study focused on industrially unaffected surface waters in Sweden. Data on AOX levels and concentrations of 2,4,6-trichlorophenol (TrCP) and its methylated analogue 2,4,6-trichloroanisole (TrCA) are given. A pathway for the formation of these compounds is suggested.

EXPERIMENTAL

AOX analysis

The concentration of AOX was determined by adsorption on activated carbon in acid solution, removal of inorganic chloride, incineration at 1000°C and microcoulometric titration with silver ions (DIN, 1985) using a Euroglas AOX analyzer model 84/85. Milli-Q water (Millipore) was used to

determine blank values. Each sample was analysed twice.

Analysis of selected chlorinated compounds

Chlorophenols were analysed after derivatization with acetic anhydride and extraction with n-hexane (extractive acetylation). Gas chromatography (GC) with electron capture detection (ECD) was used for quantification, and mass spectrometry in the selected ion monitoring mode (GC-MS-SIM) was used to confirm the ECD results. The method was originally developed by Abrahamsson and Xie (1983). In the present study, the detection limit was lowered by including an XAD-8 adsorption step (Jonsson et al., 1990).

Chloroanisoles were enriched by nitrogen gas purging at a water temperature of 60°C, using an open stripping system and carbon disulphide/acetone (9:1) for extracting the carbon filter (Borén et al., 1985). GC-ECD and GC-MS-SIM were used for separation and detection.

Pentachlorobenzene was used as an internal standard.

Water samples

The AOX analyses were based on samples from 150 lakes in the county of Jönköping ("Jönköpings län") in southern Sweden. Sampling for the analysis of chlorophenols and chloroanisoles was done in 10 rivers and lakes in different parts of southern Sweden. All selected waters were located in forested areas not directly affected by human activities.

RESULTS AND DISCUSSION

The frequency distribution of AOX in the lake waters showed a maximum in the range of 20-60 ug Cl/l (Fig. 1). A great number of lakes, however, had remarkably high AOX concentrations (100-185 ug Cl/l). These concentrations are comparable to, or even higher than, the AOX concentrations in Swedish rivers exposed to effluents from pulp mills with chlorobleaching (Wigilius et al., 1988a). In a nationwide survey of AOX in river waters in Sweden, annual mean values between 10 and 80 ug Cl/l were reported (Enell et al., 1989).

By the use of size exclusion chromatography and ultrafiltration, it has previously been shown that the major part of AOX in natural waters is of high-molecular-weight (Grön, 1989; Wigilius et al., 1988b). Considerable amounts of AOX have also been found in humic matter isolated from surface water.

In search of individual organohalogen compounds in surface water, the analyses of chlorophenols and chloroanisoles gave the most interesting results. 2,4,6-Trichlorophenol and its methylated analogue, 2,4,6-trichloroanisole, were detected in practically all of the analysed samples (see Table

1). However, it should be noted that these identified compounds constitute only a very small fraction of the total amount of organohalogens measured as AOX.

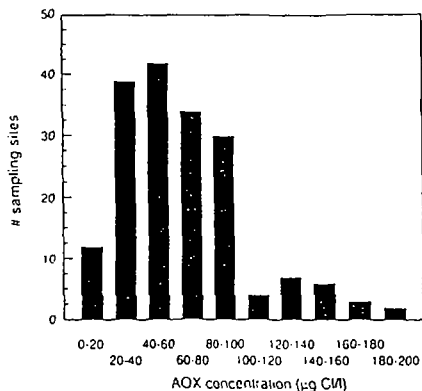


Figure 1. Frequency distribution of adsorbable organic halogen (AOX) in 150 lakes in the county of Jönköping, Sweden.

Table 1. Analysis of TrCP and TrCA in industrially unaffected surface waters.

Compound	Concentration range (ng/l)	Number of rivers/lakes
2,4,6-Trichlorophenol	0.3 - 10	5
2,4,6-Trichloroanisole	0.1 - 1.5	7

The data in this paper give further evidence of the existence of significant amounts of organohalogens in natural waters not directly influenced by human activities. We suggest a pathway for the production of organohalogens in the environment, where enzymatically mediated halogenation of humic substances in soil plays a key role. The enzyme chloroperoxidase, in the presence of inorganic chloride and hydrogen peroxide, has been shown to catalyze chlorination of organic matter, resulting in a significant increase of the AOX level and the formation of specific low molecular weight compounds, such as 2,4,6-trichlorophenol (Asplund et al., 1990; Hodin et al., 1990). The general occurrence of 2,4,6-trichloroanisole is most probably explained by fungal methylation of the corresponding phenol.

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