

Presence and weekly concentrations of Q1, bromoanisoles, and 2,4,6-tribromophenol in comparison to HCH isomers in air from Southern Norway (2003)

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Introduction

In the past years, the heptachlorobipyrrole Q1 as well as bromoanisoles and bromophenols (**Figure 1**) have been identified as marine halogenated natural products^{1,2}.

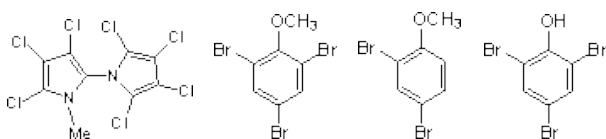


Figure 1: Structures of 2,3,3',4,4',5,5'-heptachloro-1'-methyl-1,2'-bipyrrole - Q1 (left), 2,4,6-tribromoanisole – 246-TBA (center, left), 2,4-dibromoanisole – 24-DBA (center, right), and 2,4,6-tribromophenol – 246-TBP (right)

Previously, bromoanisoles and Q1 have been detected in both Antarctic air^{3,4} and air from Lista (Southern Norway)⁴. In air from Lista (May 1999), 246-TBA was on the same level as *a*-HCH and lindane (25-35 pg/m³)⁴. Several of the ~20 additional brominated compounds in air samples from Lista were suspected to be bromoanisoles as well⁴. Recently, we have detected 246-TBP in sponges and seal blubber from the Antarctic⁵. In the present study we examined air samples weekly taken at Lista for trends in the concentrations of 24-DBA, 246-TBA, and Q1 in air. The results were compared with concentrations of anthropogenic hexachlorocyclohexane isomers. We expected differences in the peak profile of natural and anthropogenic organohalogen compounds.

Material and Methods

Samples and clean-up. Ambient air samples from Southern Norway were taken weekly throughout the year 2003 at Lista (58°06'N, 6°34'E, 14 m a.s.l.), a rural coastal site, located at the southernmost tip of Norway. Portions of ~550 m³ were collected at a rate of 20 m³/h with the help of a high volume sampling system⁶. Isotope dilution technique (¹³C₆-HCHs and ¹³C₁₂-PCBs) yielded recoveries >50% for nearly all samples. Sample blanks (whole clean-up w/o outdoor air) were analyzed for quality assurance.

GC/MS parameters. Analyses were run on an HP 6890/5973 GC/MS system operated in the GC/ECNI-MS-SIM mode. Next to the masses of the internal standards, m/z 79 and 81 (bromoanisoles), m/z 346 for 246-TBA, m/z 172/174 (monobromophenols), m/z 250/252 (dibromophenols), m/z 330/332 (tribromo-phenols), and m/z 386/388 (Q1) were recorded in the several time windows. Helium and methane were used as carrier and CI moderating gasses, respectively. The samples (1 µL) were injected in the splitless mode (split opened after 2 min) at 260 °C (injector temperature) using a 7683 auto injector. An Ultra-2 capillary column (25 m length, 0.2 mm i.d., 0.11 µm d_f) was installed in the GC oven.

Results and Discussion

Annual cycles of 246-TBA and 24-DBA are shown in **Figure 2a**. In most samples, 24-DBA was higher concentrated than 246-TBA. Both compounds showed comparable concentrations in the first half year but from September to December the abundance of 24-DBA was much higher (**Figure 2a**). As anticipated, the lowest air concentrations

were found in the beginning of the year (winter time). All in a sudden, the concentrations of 24-DBA and 246-TBA increased significantly in May. The increasing trend continued until August, and then slightly declined for 246-TBA but remained on the same high level in the case of 24-DBA, until the end of the year. Actually, the highest concentration of 24-DBA was found in December. For comparisons, we also determined the annual cycle of anthropogenic HCH isomers (**Figure 2b**). Concentrations of HCHs also increased during the warmer period (starting in May). However, the increase in abundance occurred with a delay of three weeks (week 19 vs. week 22) and the top concentrations were shifted by two weeks. For instance the ratio of 246-TBA / lindane of week #30 (climax of lindane) and #32 (climax of 246-TBA) was 0.50 and 2.3 respectively. This indicates two different sources which both showed some dependence of the air annual temperature profile. In addition, the HCH concentrations decreased starting from October which was not found for 24-DBA and only a lower decline in the case of 246-TBA. This agrees with our expectations since the bulk of HCH isomers were suspected to originate from terrestrial evaporation whereas 246-TBA was thought to be derived from the sea. Although there are known anthropogenic sources for 246-TBA, the bulk of 246-TBA in the air samples arises from sources of natural production³. Both, 24-DBA and 246-TBA were more abundant in air from Lista than the HCH isomers.

The concentration profile of Q1 was completely different to that of the HCH isomers (**Figure 2c**). It is noteworthy that concentration of Q1 only reached < 1% of 246-TBA. From February to August, only very low concentrations were determined, and in many samples the concentration was below the limit of quantification. Samples of weeks #30 and #32 which contained highest concentrations of 246-TBA and HCH isomers was not among the 10 samples with highest Q1 concentration. By contrast, the Q1 concentrations increased in September yielding a climax in October. Moreover, several elevated Q1 concentrations were determined in December and even in January. This concentration profile is different from any known anthropogenic compound detected at Lista. This is a further indication of the natural origin of Q1. However, due to the low concentrations, it became evident that a high rate natural production of Q1 is not occurring in proximity to Lista. Concentrations of bromophenols were ambiguous. 19 of the samples contained 246-TBP (S/N > 3) and several also 24- and 26-DBP. Note that the phenolic compounds were not validated, yet. Nevertheless, relatively high concentrations of 246-TBP in some samples indicated that occurrence of this compound in outdoor/marine air samples should be studied more in detail.

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References

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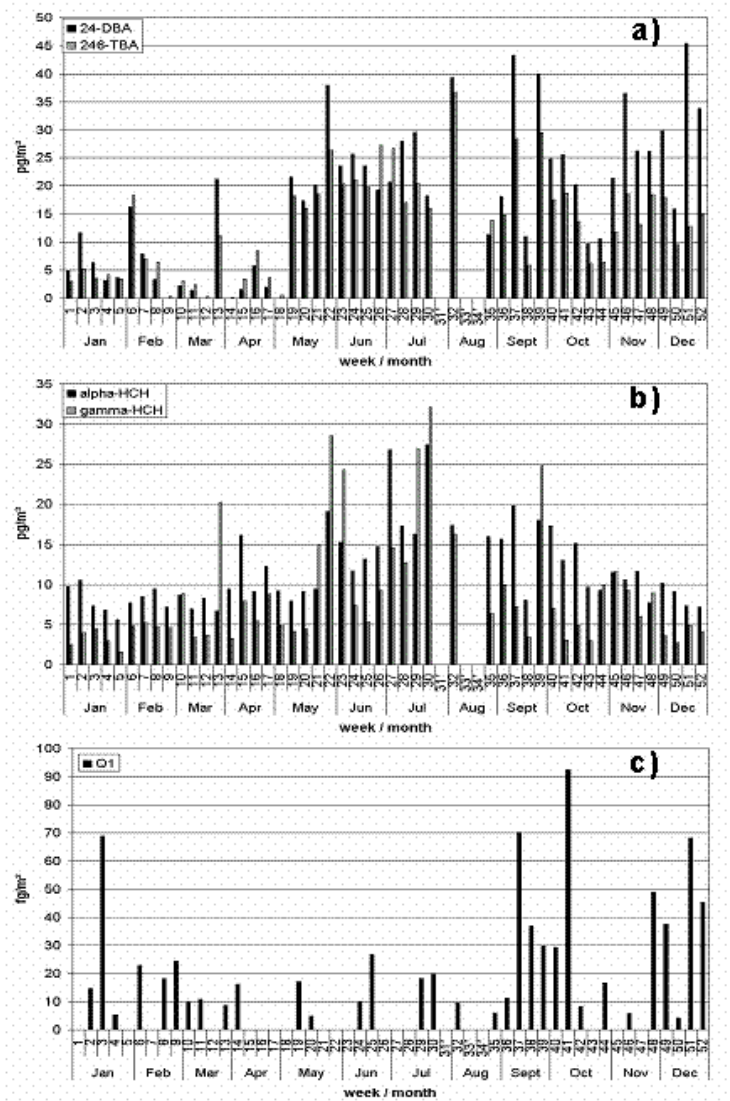


Figure 2: annual concentrations (pg or fg/m³) of (a) 246-TBA and 24-DBA, (b) lindane and α -HCH, as well as (c) Q1 air from Lista, Southern Norway (2003). Note that there were no samples available from week #31, #33 & #34