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Atmospheric Hydrocarbon Concentrations in the Baltic Sea Area[†]

V. KARLSSON and A. KULMALA

Finnish Meteorological Institute, Sahaajankatu 22E, SF-00810 Helsinki, Finland

and

e. Häsänen

Technical Research Centre of Finland, Reactor Laboratory, Otakaari 3A, SF-02150 Espoo, Finland

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During a marine research expedition in 1983 in the Baltic Sea area air samples were collected for the analysis of several organic and inorganic pollutants. The aim of the expedition was to obtain information on the airborne load in the sea as well as to measure the concentrations of the pollutants far away from source areas. In this paper the background concentrations of the primarily traffic originated aromatic hydrocarbons benzene, toluene and xylenes will be presented.

The concentrations of benzene were from 0.2 to $2 \mu g/m^3$, of toluene between 0.4– $3 \mu g/m^3$, of *m*-xylene 0.02–0.60 $\mu g/m^3$ while the concentrations of *o*-xylene were 0.01–0.1 $\mu g/m^3$. The concentrations did not depend too much on the origin (continental/sea type) of the air masses. A weak minimum in the concentrations of the measured hydrocarbons was noticed in the central Baltic Sea area. When comparing lead concentrations in fine particles (<2.5 μ m) with those of benzene, toluene and *m*-xylene some coincidence between them could be observed.

KEY WORDS: Concentration, aromatic hydrocarbons, Baltic Sea area.

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1. INTRODUCTION

It is estimated that about 13 million $t C_6-C_8$ aromatic hydrocarbons enter annually the environment, mostly from the oil industry and from automobile exhaust, toluene and xylenes come also in considerable amounts from solvent losses.¹ On the global scale the main source of benzene, toluene, m- and o-xylenes is traffic. For example, traffic emissions of benzene are 80-90% of the total emissions.²

Air contains some micrograms of benzene, toluene and xylenes per cubic meter in remote rural areas remaining often $< 5 \,\mu g/m^3$. In streets the immission loads are of the order of $40-100 \,\mu\text{g/m}^3$ benzene, about $50-200 \,\mu\text{g/m}^3$ toluene and from $20-150 \,\mu\text{g/m}^3$ xylenes.² According to a Finnish research study exhaust gases contain from 100 to 350 mg/m^3 benzene, toluene, *m*- and *o*-xylene.³

In the atmosphere the photochemical reactivity of these aromatic compounds decreases in the order: m-xylene > o-xylene > p-xylene > toluene > benzene. According to Singh et $al.^4$ the residence times in the atmosphere (assuming 12h sunlight per day) are 8.3 days for benzene, 1.9 days for toluene, 0.5, 0.9 and 0.8 days for m-, p- and o-xylenes, respectively.

Benzene is the most volatile, most water soluble and most toxic of the aromatic one- or two-ring hydrocarbons. Toluene and xylenes have a medium volatility, a medium water solubility, they are relatively rapidly decomposed, and are not very toxic. It seems that C₆-C₈ aromatics evaporate or stay rather in the atmosphere and are transformed or degraded there. Neither do they seem to have a tendency of accumulating in the environment.¹

2. EXPERIMENTAL

2.1. Sampling

The route of the expedition is given in Figure 1. The route covers in a fairly representative way the northern, central and southern parts of the Baltic Proper.

Volatile aromatic hydrocarbons (benzene, toluene and xylenes) were absorbed on Tenax GC (2,6-diphenyl-p-phenyleneoxide) filled cartridges. The particles were filtered off by means of a Millipore prefilter. The sampling flow-rate used was between 0.03 and



FIGURE 1 Sampling route in the Baltic Sea in April-May 1983.

 $0.15 \,\mathrm{dm^3/min}$. The sampling periods were 12 or 24 hours. The sampling devices were located on the radar deck of the research vessel about 12 m above sea level. The samples were automatically protected against contamination from the vessel by a device which stopped the sampling when the wind blew from the stack. The sampling sector was 180° ahead.

2.2. Analytical results

The concentrations of benzene, toluene and xylene were analyzed using a Hewlett Packard 5830A gas chromatograph and a FID detector. The column was composed of 5.0% FFAP and was 4.5 m in length. The compounds were released from the sorbent material by thermal desorption as follows: thermal desorption at 180° C, condensation under liquid nitrogen in a steel spiral, heating at 180° C and leading of the vapourized samples to the gas chromatograph.

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3. RESULTS AND DISCUSSION

The measured benzene, toluene and m-xylene concentrations in the Baltic Sea area are shown in Figures 2, 3 and 4. In the Figures the areas of the circles are proportional to the concentrations of the compounds and the centers correspond to the sampling area.



FIGURE 2 Benzene concentrations in the Baltic Sea area.

The origin and the life history of the sampled air masses were studied by means of trajectories. Follow-up of the life history of air trajectories provides a chance of roughly classifying the samples. The samples taken from air masses which had flowed only for a few hours over the sea were classified as the continental type and the samples taken from air masses which had flowed for at least 12 hours over the Baltic Sea before reaching the sampling devices were classified as the sea type.

The concentrations did not greatly depend on the origin (continental/sea type) of the air masses (Figure 5). The fact that the stack gases of the vessels contain considerable amount of benzene and toluene and that there constantly is a busy traffic in the Baltic may



FIGURE 3 Toluene concentrations in the Baltic Sea area.



FIGURE 4 *m*-xylene concentrations in the Baltic Sea area.



FIGURE 5 Effect of the air masses origin on the hydrocarbon concentrations.



FIGURE 6 Pb concentrations in fine ($<2.5 \,\mu$ m) particles.

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cover the effect which the origin of air masses may have on the concentrations.

However, a weak minimum in the concentrations of the measured aromatic hydrocarbons can be observed in the central Baltic Sea area. This can be accounted for by the fact that in the central Baltic Sea gaseous hydrocarbon emissions caused by traffic (the main global scale source) are already well diluted, whereas in other parts of the sea emission sources lie closer to the sampling location.

When comparing lead concentrations (Figure 6) in fine particles $(<2.5 \,\mu\text{m})$ with those of benzene, toluene and *m*-xylene some coincidence between them can be noticed in different parts of the Baltic. The reason for correlation might be that the main source of both compounds is traffic and that the spreading of fine particles may resemble to some extent the spreading of gaseous compounds.

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