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HYDROCARBONS, ALCOHOLS AND STEROLS IN THE DISSOLVED + COLLOIDAL AND PARTICULATE PHASES OF THE WATERS FROM A DYSTROPHIC LAKE, SKJERVATJERN LAKE (NORWAY)

LOURDES BERDIÉ[1], JOAN O. GRIMALT[1]* and EGIL T. GJESSING[2]

[1]Department of Environmental Chemistry (C.I.D.-C.S.I.C.), Jordi Girona 18, 08034-Barcelona, Catalonia, Spain and [2]Norwegian Institute for Water Research, Brekkeveien 19, P.O. Box 173 Kjelsas, N-0411 Oslo, Norway

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Abstract—The composition of solvent extractable aliphatic, olephinic and aromatic hydrocarbons, alcohols and sterols, in the dissolved + colloidal and particulate water phases of a dystrophic lake are described. Contributions from terrestrial vegetation, particularly *Sphagnum* moss, appear to dominate the distribution of *n*-alkanes, *n*-alkan-1-ols and sterols in the two water fractions. Pyrolytic contributions representing long-range transported polycyclic aromatic hydrocarbons (PAH) over the Scandinavian Peninsula are also observed. All biogenic compounds exhibit, in general, similar distribution coefficients between the two water phases (lg K_D: 4.9–5.7) which is in agreement with their common combination with organic materials of analogous hydrophobic/hydrophilic properties. PAH constitute the only group of compounds with phase distribution coefficients (lg K_D: 4.4–5.2) lower than the general interval. Finally, both in the case of the biogenic and the pyrolytic compounds, incorporation into the water column seems to be preferentially mediated by transport through the particulate phase.

Key words—particulate organic matter, dissolved organic matter, aliphatic hydrocarbons, hopanoids, terpenoids, polycyclic aromatic hydrocarbons, alkan-1-ols, sterols, humic lake environments, *Sphagnum* moss.

INTRODUCTION

The high potential of sedimentary neutral lipids for the recognition of organic matter sources and diagenetic processes in lacustrine environments is limited by the poor knowledge on the dynamics of these compounds in the water column, namely their distribution between dissolved + colloidal and particulate phases.

Hydrocarbons in the water column have been studied in a number of cases. However, these have usually concerned coastal environments or open sea areas (e.g. Schultz and Quinn, 1977; Goutx and Saliot, 1980; Burns and Villeneuve, 1983; Tronczynski *et al.*, 1986; Gomez-Belinchon *et al.*, 1988; Saliot *et al.*, 1990; Yunker *et al.*, 1991; 1993; Grimalt and Olive, 1993). Other lipid fractions, such as the sterols, have received more limited attention and the studies have also concentrated on coastal environments (e.g. Grimalt and Olive, 1993; Laureillard and Saliot, 1993; Sicre *et al.*, 1993; 1994).

Lacustrine environments have only been considered in a few cases (e.g. Meyers *et al.*, 1984; Grimalt *et al.*, 1991) and these only concern the particulate phase. However, different dissolved + colloidal/particulate distribution processes are expected to occur in these freshwater systems since both the qualitative and quantitative organic matter composition in the dissolved + colloidal phase is remarkably different from seawater (Hedges *et al.*, 1993). The present study contributes to the knowledge of the dynamics of the major neutral lipids between these two water phases in lacustrine systems.

The lake selected for study, Skjervatjern Lake (Norway, *ca* 62°N, surface 2.4 ha, mean depth 4 m, water volume 67,000 m^3, catchment 9 ha), is dystrophic. The waters of these lakes are characterized by their low conductivity, high water colour and dissolved organic carbon, mostly originating from the influx of terrestrial compounds from the catchment area (Salonen *et al.*, 1983). As described in Gjessing (1994), since fall of 1988 Skjervatjern Lake was divided by a thick plastic curtain extending from floats on the surface to the underlying sediments where it is pressed with sandbags. The curtain was installed from the middle of the natural outlet to the opposite shore and defined two sections, A and B, encompassing 0.9 and 1.5 ha of the lake surface, respectively. The outflow waters of the two sides were canalized through large diameter pipes which collected surface and subsurface water leaving the lake

*Author to whom all correspondence should be addressed.

after average retention time of 1.6 and 4.5 months in A and B sections, respectively.

The lake has no stream inlets and most of the water enter through discrete passageways in the sediment (hydrolytic vents). This specific water entrance way and the high turnover rate involves a high exchange of organic and inorganic materials in the water column. Thus, no vertical gradient of total organic matter or sulphate is observed even in summer stratification (Gjessing, 1994). The outflowing A and B waters are therefore good representative samples of the average water lake composition in each side. In the present study, the solvent extractable aliphatic, olephinic and aromatic hydrocarbons, alcohols and sterols, in the dissolved + colloidal and particulate phases of these outflow waters are described. Their composition is discussed in terms of input sources and phase partitioning effects.

EXPERIMENTAL

Materials

Residue-analysis dichloromethane, methanol, *n*-hexane, *iso*-octane, analytical reagent-grade hydrochloric acid (25%), neutral silica gel (Kieselgel 40, 70–230 mesh) and alumina (aluminum oxide 90% active, 70–230 mesh) were from Merck (Darmstadt, Germany). Potassium hydroxide and bis(trimethylsilyl)trifluoroacetamide were purchased from Fluka Chemie (Buchs, Switzerland).

The potassium hydroxide was cleaned by sonication in *n*-hexane. The purity of the solvents was checked by concentrating, under vacuum, 100 ml of solvent to 50 μl for gas chromatographic (GC) analysis. Blank requirements were as follows: splitless injection of 2.5 μl should result in chromatograms with no unresolved GC envelope and with very few peaks, representing up to 0.1 ng in terms of their flame ionization detector response.

Sampling

Samples (*ca* 90 l) were collected and kept in glass bottles in which bacterial growth was avoided by $HgCl_2$ addition. All samples were analyzed individually. In two preliminary samples, taken in April 1991, the bulk water material was concentrated. In the samples collected in September 1991 and February 1993, the dissolved and particulate fractions were separated following the guidelines of previous studies (Grimalt *et al.*, 1990). After removal of particulates, the aqueous solution was evaporated at $<30°C$ under reduced pressure by rotary evaporation to an approximate volume of 500 ml. This was then dried by freeze-drying. The particulate fractions were also freeze-dried.

Sample handling

Aliquots (*ca* 0.5 g) of the freeze-dried dissolved and particulate material were extracted by sonication with (2:1, v/v) dichloromethane:methanol (4 × 40 ml). The extract was vacuum evaporated to 2 ml, hydrolyzed overnight with 6% KOH in methanol (50 ml) and further extracted with *n*-hexane (3 × 40 ml) to separate the neutral fraction. The latter extracts were vacuum evaporated to 1 ml and separated chromatographically using a column (25 cm × 1 cm i.d.) filled with 8 g of 5% water deactivated alumina (top) and silica (bottom). The fractions regularly collected with this method were as follows: F1) 20 ml of *n*-hexane, F2) 20 ml of (90:10) *n*-hexane/dichloromethane, F3) 40 ml of (80:20) *n*-hexane/dichloromethane, F4) 20 ml of (75:25) dichloromethane/*n*-hexane, F5) 40 ml of (5:95) methanol/dichloromethane and F6) 40 ml of (10:90) methanol/dichloromethane. The fractions eluted from the column were evaporated to dryness and redissolved in *iso*-octane for instrumental analysis. F5 and F6 fractions were also derivatized with bis(trimethylsilyl)trifluoroacetamide (100 μl, 80°C, 30 min) to obtain the trimethylsilyl ethers of alcohols, sterols and other hydroxyl substituted compounds.

Instrumental analysis

Gas chromatographic analysis was performed with a Carlo Erba Model HRGC5300 instrument equipped with a flame ionization detector and a splitless injector. A column of 30 m × 0.25 mm i.d. coated with DB-5 was used (film thickness 0.25 μm). Hydrogen was the carrier gas (50 cm/s). The temperature was programmed from 60 to 310°C at 6°C/min, maintaining the final temperature for 20 min. Both injector and detector temperature were 300°C. The injector was in the splitless mode (solvent, *iso*-octane, hot needle technique) keeping the split valve closed for 35 s. Data were acquired by means of a Perkin Elmer Nelson 900 interphase connected to a PS/2 computer programmed with the Nelson data treatment software. This software was used for quantitation with reference to external standards of *n*-tetradecane, *n*-dodecane, *n*-dotriacontane, *n*-hexatriacontane (aliphatic hydrocarbons), anthracene, fluoranthene, chrysene, benzo[*a*]pyrene, benzo[*ghi*]perylene (polycyclic aromatic hydrocarbons), coprostanol and 5α(H)-cholestan-3β-ol (alcohols and sterols). Samples and standards were repeatedly injected until less than 5% dispersion was observed in the integrated areas.

Gas chromatographic-mass spectrometric analysis was performed with a Hewlett-Packard HP-5890 chromatograph coupled to a Finnigan INCOS-XL mass spectrometer. The chromatograph was equipped with the same DB-5 column described above and helium was used as carrier gas (30 cm/s). The oven temperature was programmed from 60 to 150°C at 8°C/min and then from 150 to 310°C at 4°C/min, holding the final temperature for 15 min. Injection conditions (300°C) were the same as described above. The mass spectrometer was operated in the electron impact mode (70 eV). Transfer line and ion source temperatures were 300 and 180°C, respectively. Mass spectra were acquired by scanning m/z 50-600 with 1 s per decade and stored by a Compaq Deskpro 286N computer.

RESULTS AND DISCUSSION

Bulk composition

The major neutral lipid groups of Skjervatjern Lake waters are aliphatic hydrocarbons and *n*-alkan-1-ols and sterols. The total concentrations of these lipids in the dissolved + colloidal and particulate fractions of the samples analyzed are reported in Table 1.

No major differences in hydrocarbon content (*n*-alkanes) are observed between the two phases (0.14–0.33 and *ca* 0.21 μg/l, in the dissolved + colloidal and particulate fractions, respectively). The concentrations in the dissolved + colloidal fraction were higher than in some river waters (e.g. 5–86 ng/l in the Ebre River, Gomez-Belinchon *et al.*, 1988a), similar to others (e.g. 0.01–0.62 and 0.15–0.98 in the Chang Jiang and Huanghe Rivers, respectively, Saliot *et al.*, 1990) and lower than others (e.g. 0.35–16 μg/l in the Loire River, Tronczynski *et al.*, 1986). Similarly, coastal areas with dissolved + colloidal *n*-alkane values lower than Skjervatjern Lake have been reported (e.g. *ca* 120 ng/l off the coast of Monaco, Burns and Villeneuve, 1983, and 0.31–8 ng/l on the Beauford Sea shelf, Yunker *et al.*, 1991) as well as