

CARBOXYLIC ORGANIC ACIDS (COA) IN OBERER SEEBACH BED SEDIMENTS

M. Rulik & P. Hekera

ABSTRACT

Sampling and analysis of interstitial water for qualitative and quantitative determination of carboxylic organic acids (COA) by analytical isotachopheresis is described. The replicated samples of interstitial water were collected with standpipe traps at five different sediment depth (0-50cm) during November 1994 and August 1995, preserved by toluene and kept cool while transported to the laboratory. After filtration through a paper filter, a pre-concentration of each sample was done by diethyl ether and sodium tetraborate. Dissolved CO₂ in a resulting extract was removed by hand vacuum pump with 850 mbar pressure during 2 min before injecting into an analyser. Capillary type isotachopheresis with a system of H₂S⁺Cl⁻ as leading electrolyte and 2-morpholinethansulfonic acid (MES) as terminal electrolyte was used for the determination of COA in the interstitial water samples. So far, two carboxylic organic acids were determined - lactic and acetic acids. The acetic acid concentrations determined from sodiumtetraborate extract vary between 41.73 µg.l⁻¹ and 78.05 µg.l⁻¹, the lactic concentrations between 39.9 µg.l⁻¹ and 60.67 µg.l⁻¹. Both acetic and lactic acid concentrations increase to a maximum in the depth layer of 20 to 30 cm. It is not yet clear how to explain the dominating presence of acetic and lactic acids during degradation of organic matter in the aerobic conditions of bed sediments of the Oberer Seebach.

Key words: carboxylic organic acids, dissolved organic matter, dissolved organic carbon, interstitial water, sampling, isotachophoretic analysis

INTRODUCTION

Several studies have been focused on the sources, fates, spatial and temporal variations of dissolved organic carbon (DOC) in fluvial ecosystems (see e.g. excellent reviews by Meyer 1990, Mulholland et al. 1990). Most of these studies examine DOC gradient and dynamics from upstream to downstream in the surface water (McDowell & Likens 1988, Ford et al. 1990, Sedell & Dahm 1990). Adjacent interstitial environments (hyporheic zone, bed sediments) participate strongly in stream functioning (e.g. Williams & Hynes 1974, Bretschko 1981 and many others) and exchanges between surface and subsurface water appear to be one important factor controlling stream metabolism (Grimm & Fisher 1984, Grimm 1987, Valett et al. 1990, Valett 1993). However, as has been pointed by Vervier & Naiman (1992) and Vervier et al. (1993), there is still a lack of knowledge about DOC dynamics in surface/subsurface exchange and its role in the interstitial hyporheic zone. DOC in surface waters originates from detrital and non-detrital sources (Miller 1987). This DOC appears to be an important source in the energy budget of bed sediment biofilms (Bärlocher & Murdoch 1989). Other potentially important sources of DOC to the interstitial DOC (IDOC) are both, the gradual decomposition of particulate organic matter (POM) buried in the stream sediments (Crocker & Meyer 1987, Meyer 1990, Smock 1990) and groundwater

seepage (Wallis 1981, Hynes 1983, Rutherford & Hynes 1987, Fiebig & Marxsen 1991, Fiebig 1995). The concentration of DOC in subsurface water is considered to be higher than in stream water (Wallis et al. 1981) or lower (Rutherford & Hynes 1987). Heterotrophic benthic bacteria associated with biofilms (Lock 1981, Hamilton 1987, Lock et al. 1984, Marshall 1984, Characklish & Wilderer 1989, Characklish & Marshall 1990) appear to be more important than suspended bacteria in the processing of dissolved organic matter (DOM) (Lock & Hynes 1976, Dahm 1981). In the sediments, their main function is the removal of dissolved substances from the water and their conversion into a particulate form (Mickleburgh et al. 1984).

The chemical nature of the DOC in aquatic ecosystems is still largely unknown, primarily because the heterogenous mixture composing DOM defies separation and identification (Dahm 1981). Larson (1978) classified only about 20 % of the DOM as lipids, carbohydrates, phenols, proteins, or amino acids. Carboxylic organic acids (COA) are the organic substances containing a carboxyl group -COOH in their molecule. COA belong to the main components of DOM in freshwaters. Thurman (1985) found that COA represents 7 % of DOM and belong to low molecular weight acids with about 0.5 percent of dissolved organic carbon (DOC). It is not yet clear to what extent these organic acids (OAs) in an aquatic system reflect their natural or

anthropogenic sources, what time scales are involved in their transformations, and what processes occurring in the aquatic environment affect their properties (Glaze et al. 1990). Carboxylic acids with only a few C atoms per molecule are significant products of chemical and biological degradation of organic matter. Because most of the simple acids are readily biodegradable, they occur in aquatic systems in fairly low steady-state concentrations (Frimmel 1990). Generally, there are two possible ways for organic matter to degrade: aerobic and anaerobic. According to a very simplified hypothesis based on COAs, it is possible to characterize the processes involved in this degradation. Both chromatographic method and distillation can be used for the measurement of organic acids and volatile fatty acids (Greenberg et al. 1992). Because the pre-treatment of the sample prior to chromatographic analysis is sometimes rather complicated, an isotachopheresis method (e.g. Arlinger 1974, Everaerts & Verheggen 1974) has been used successfully to determine some organic acids in silage extracts (Bocek et al. 1978). This project which aimed to analyze COAs in the interstitial waters of bed sediments from two different localities in Austria and Czech Republic and tried to characterize the decomposition processes of OM. Three objectives of our COA research are highlighted: 1) characterize the COAs composition and concentrations in the interstitial water of bed sediments, 2) studies examining vertical distribution of COAs and their relationship to the distribution of total DOC and POM in the bed sediments, and 3) characterization of microbial (decomposition) processes involved in COAs formation under aerobic and anaerobic conditions and resulting differences (structural quality, quantity) in the produced COAs.

This paper deals with the research on Oberer Seebach in Lunz am See, Austria and presents methods for sampling and analysis of interstitial water of bed sediments for the determination of COAs by the isotachopheresis methods. The results presented here are only preliminary and will be developed further.

MATERIALS AND METHODS

SAMPLE COLLECTION

Quantitative samples of interstitial water were collected within the Ritrodat-Lunz study area of the Oberer Seebach, a calcareous second order gravel stream in Lower Austria. In accordance with the area's high porosity, indicating large interstices (Leichtfried 1988), oxygen saturation of the bed sediments is generally very high, varying between 80 and 120 % near the sediment surface, and drops

with increasing sediment depth, but never below 60 % (Bretschko 1991a, 1991b). Further detailed descriptions of the research area are given by Bretschko (1991a, 1991b).

The samples were collected with standpipe traps (Bretschko & Klemens 1986). This method collects sediment water and the moving interstitial sediment. Groups of 12 traps are installed in a randomly stratified design at two locations - riffle and pool - in the research area (see Schmid-Araya 1993). The standpipe traps were made of plastic tubes (diameter 7 cm, overall length 177 cm); and a circle of catching holes (diameter 8 mm) was located near the bottom of each tube (Bretschko & Klemens 1986). Replicated samples were taken every two months at five different sediment depths (0-10, 10-20, 20-30, 30-40 and 40-50 cm) between November 1994 and August 1995. Usually, a half liter of interstitial water and sediment was collected from each depth layer. Samples of water were removed, placed in glass bottles, preserved by toluene (0.5 ml per 0.5 l of sample) and kept cool, while transported to the laboratory together with sediment samples.

SAMPLE ANALYSIS

Only clear water without sediment, filtrated through paper filter, was used for analysis. Preconcentration of water samples was done in several steps as shown in Fig. 1. Two modifications of this pattern were used: 1) after extraction by sodium tetraborate one sample was again acidified with 2M HCl (pH about 2) followed by a second extraction with diethyl ether. The resulting diethyl ether extract was evaporated in a fume cupboard and dissolved in 1 ml of distilled water. This solution is then used for analysis; 2) sodium tetraborate extract has been used directly for analysis (see Fig. 1), only about 5-6 ml per sample is obtained after the latter preconcentration procedure. Dissolved CO₂ in the resulting extract was removed by a hand vacuum pump with 850 mbar pressure during 2 min before being injected into an analyser. The determination of carboxylic organic acids was made with an isotachopheretic analyser ZKI-001 (made in ÚRVJT VVZ PJT Spišská Nová Ves, Slovak Republic). The capillary type isotachopheresis method is used with a system of two electrolytes: HIS⁺CT⁻ as leading electrolyte and 2-morpholinethansulfonic acid (MES) as terminal electrolyte. The evaluation of the separation process is carried out on a pen recorder TZ 4620 (made in Laboratorni pristroje Praha, Czech Republic). The samples of interstitial water extracts were injected with a microsyringe, the volumes injected being 20 µl. Aqueous solutions of lactic and acetic acids served as standard solutions. One analysis of a sample was complete in 25 min. For quantification, a calibration graph was advantageous for the direct comparison of the

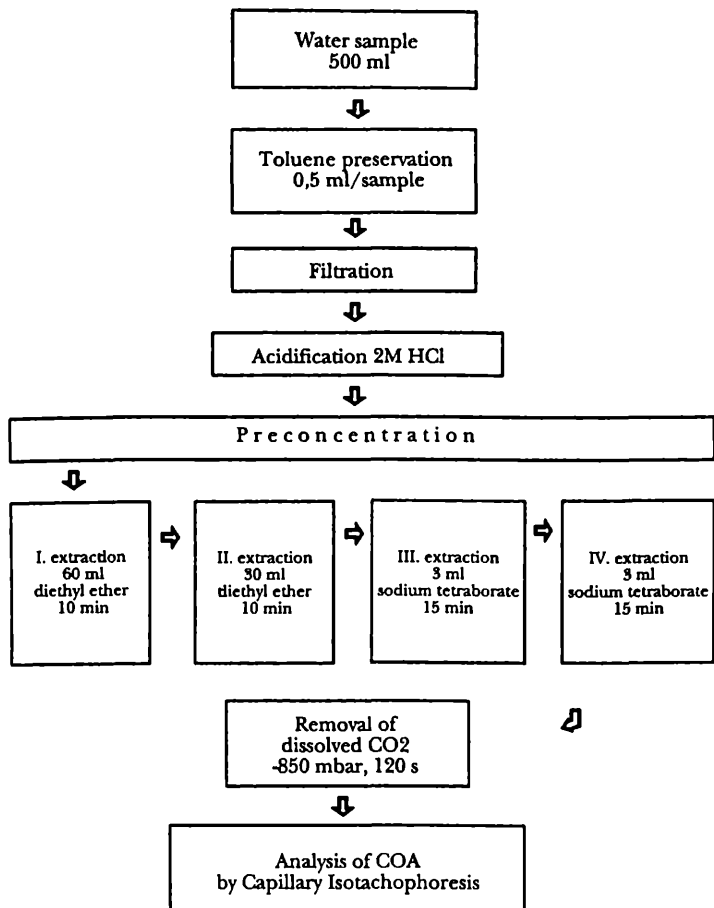


Fig. 1: Steps for analysis of COA

length of zones of a sample and those of a standard solution. This analysis described above is based on the work of Bocek et al. (1978) and on the improvement by Prof. Stránský and his coworkers at the Department of Organic and Analytical Chemistry, Palacky University, Olomouc, for standard use in agrochemical laboratories (Z. Stránský, personal comm.). Samples of interstitial sediments smaller than 8 mm (0.5 l) from each observed depth, were passed through paper filter, dried (105°C) and weighted.

PRELIMINARY RESULTS AND DISCUSSION

Average amounts of interstitial sediments vary vertically between 0.80 g.l⁻¹ and 6.53 g.l⁻¹ with the highest values in the deepest layers (Fig. 2). So far, we are positive of the presence of two carboxylic organic acids acetic and lactic acids (Fig. 3). The acetic acid concentrations determined from sodium tetraborate extracts (Fig. 1) vary between 41.73 µg.l⁻¹ and 78.05 µg.l⁻¹, the lactic acid concentrations between 39.9 µg.l⁻¹ and 60.67 µg.l⁻¹. Both, acetic and lactic acid concentrations increase to a maximum in the depth layer of 20 to 30 cm (Fig. 4). A ratio between acetic and lactic acids appears to be highest in the uppermost layers 10 to 20 cm and decreases slightly with depth (Fig. 4). In difference to the results of COA concentrations obtained by the analysis of sodium tetraborate extract, very low concentration of both, acetic and lactic acids were obtained when a diethyl ether solution with distilled water was used for analysis.

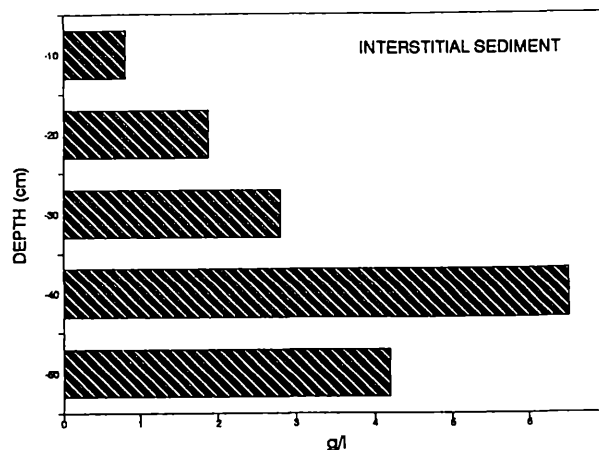


Fig. 2: Amount of interstitial sediments (g.l⁻¹) smaller than 8 mm in different horizons of the Oberer Seebach bed sediments.

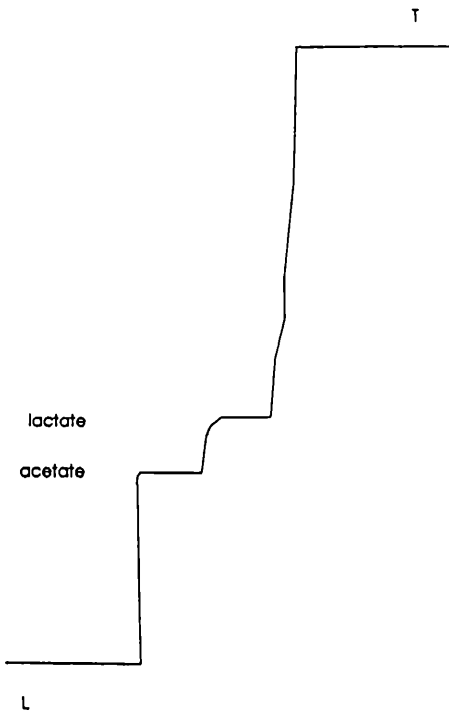


Fig. 3: Isotachophoregram of a sodium tetraborate extract.

The acetic acid concentrations vary between $2.94 \mu\text{g.l}^{-1}$ and $5.51 \mu\text{g.l}^{-1}$ and the lactic acid concentrations between $6.89 \mu\text{g.l}^{-1}$ and $18.69 \mu\text{g.l}^{-1}$. The vertical distribution patterns are similar to that of interstitial sediments, the highest values were found in deeper layers (Fig. 5). On the contrary to sodium tetraborate modification analysis the ratio acetic/lactic acid is always lower than one, indicating much higher concentration of lactic than acetic acid. The ratio values vary between 0.29 and 0.49 and tend to decrease with the depth, except in the layer 40 to 50 cm (Fig. 5).

The discordance in the concentrations between sodium tetraborate and diethyl ether extracts are probably due to the very volatile character of acetic acid because some of this acid is probably lost during evaporation in the fume cupboard. Moreover, a sodium tetraborate extract contains more of acids than a diethyl ether extract. Therefore, we would like to suggest to use for the next analysis only the preconcentration procedure resulting in sodium tetraborate extract as shown in Fig. 1. The vertical distribution pattern of interstitial sediments is similar to that reported by Leichtfried (1991, 1994). She found that fine sediments (grain size class smaller than 1 mm diameter) reach maximal values in the middle layers between 20 and 40 cm of

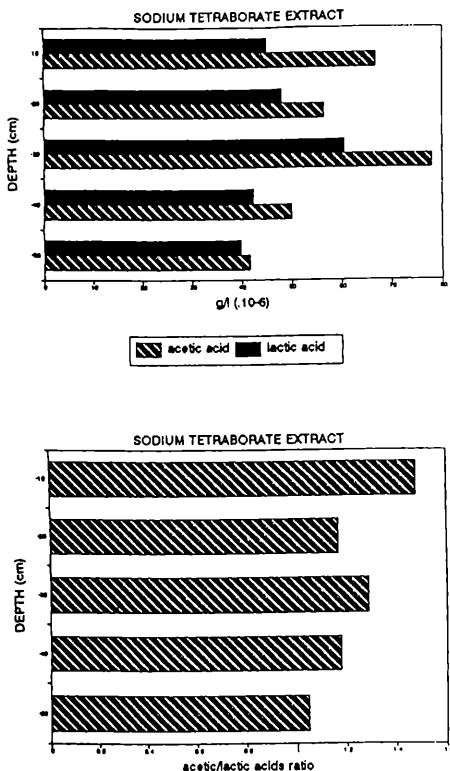


Fig. 4: Vertical distribution of COAs concentrations determined from sodium tetraborate extract.

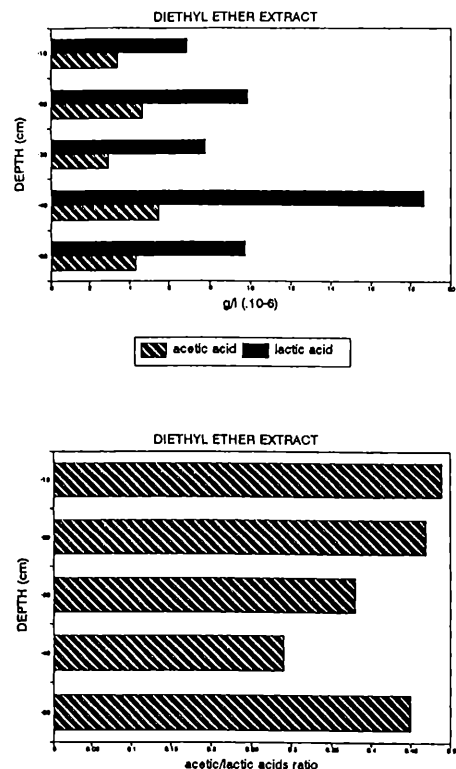


Fig. 5: Vertical distribution of COAs concentrations determined from diethyl ether extract.

sediment depth. Previous studies (Bretschko & Leichtfried 1988, Leichtfried 1985, 1988, 1991, 1994) showed that grain size fractions smaller than 1 mm contain by far most of the organic matter and that protein, TOC and TON content distributions reflect the distribution of the small grain size class (Leichtfried 1994). Vertical distributions of concentrations of COAs show a similar pattern. However, it is not yet clear if their concentrations (probably resulting of degradation of buried POM) are depending on the metabolic activity of biofilm (Marshall 1984 etc.) or if this pattern can be explained by groundwater and lateral bank seepage. Although the data presented here are only preliminary and have to be more developed, it is very interesting that both, acetic and lactic acids, are found in the bed sediments of Oberer Seebach. The Oberer Seebach's sediments have a very high porosity (Bretschko & Leichtfried 1988) and also the oxygen saturation is very high (Bretschko 1991a, Bretschko 1991b). Generally, in such good oxygen conditions aerobic processes of organic matter degradation should be expected. Carboxylic acids produced by such process are mainly acids involved in the tricarboxylic acid cycle or Krebs cycle (Conn & Stumpf 1976, Rheinheimer 1992). It is not possible to explain these results now. It seems to be obvious that COAs found in the interstitial water represent only very small amounts of carboxylic acids produced during organic matter degradation. We assume that concentrations of COAs in this water can be 100x less than at the sediment surface where the exoenzymatic activity of bacteria and biofilm is highest (Lock 1981, Lock et al. 1984, Hamilton 1987, and others). Therefore, both, analyses of sediments for COA determination and bacteria identification appears to be very important in future research.

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