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# Characterisation of suspended matter in river systems: River Sava in Slovenia case study

## Značilnosti suspendirane snovi v rečnih sistemih: primer reke Save v Sloveniji

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**Abstract**

$\delta^{13}C$ and $\delta^{15}N$ values in suspended matter were used to examine the seasonal (late summer 2004 and spring 2005) relationship with hydrological characteristics of the River Sava watershed in Slovenia. $\delta^{13}C$ values range from - 29.2 to - 23.0 ‰ and $\delta^{15}N$ values from 0.5 to 16.7 ‰ and indicate that the samples are a mixture of two end members: modern soils and plant litter. A simple mixing model was used to indicate that soil organic carbon prevails over plant litter and contributes more than 50 % of suspended material. The total suspended solid flux (TSS) is estimated to be $1.3 \times 10^{12}$ g/year. Anthropogenic impact was detected only in a tributary stream of the River Sava which is located in an agriculture-industrial area and is reflected in higher $\delta^{15}N$ values in suspended matter in the late summer season.

**Izvleček**

Vrednosti $\delta^{13}C$ in $\delta^{15}N$ v suspendirani snovi smo uporabili za proučitev sezonskih odvisnosti od hidroloških karakteristik v porečju reke Save v Sloveniji. $\delta^{13}C$ vrednosti se spreminjajo od - 29.2 do - 23.0 ‰ in $\delta^{15}N$ vrednosti od 0.5 do 16.7 ‰ in nakazujejo, da so vzorci mešanica dveh končnih členov: preperin oz. tal in rastlinskega materiala. Uporabili smo enostaven mešalni model, s pomočjo katerega smo izračunali, da preperinski organski ogljik prevladuje nad rastlinskim materialom in prispeva več kot 50 % suspendiranega materiala. Celotni snovni tok suspendirane snovi (TSS) je ocenjen na $1.3 \times 10^{12}$ g/leto. Antropogeni vpliv smo zasledili samo v pritoku reke Save, ki se nahaja na območju kmetijsko-industrijske površine in se odraža v višjih vrednostih $\delta^{15}N$ v suspendirani snovi samo v poletni sezoni.

## Introduction

Suspended organic matter is a complex mixture of molecules such as: carbohydrates, amino acids, fatty acids and phenols, particles from wastewater and industrial water, soil organic matter and biological material like phytoplankton and other plant parts (Hope et al., 1994). High carbon dioxide concentrations in rivers originate largely from *in situ* respiration of organic carbon, but little agreement exists about the sources or turnover times of this carbon (Tipping et al., 1997; Ankers et al., 2003). The relative contributions of $C_3$ and $C_4$ vegetation to an ecosystem can be reconstructed using the isotopic composition of particulate carbon ($\delta^{13}C_{POC}$), because of their different isotopic composition, which range from - 32.0 to - 20.0 ‰ for $C_3$ plants, and from - 15.0 ‰ to - 9.0 ‰ for $C_4$ plants (Deines, 1980). Suspended organic matter in rivers is mostly derived from soil and plant material, therefore the isotopic composition of suspended organic matter ($\delta^{13}C_{POC}$) in rivers has been used to ascertain the contribution of terrestrial vegetation and soil matter in the river ecosystems (Ittekot, 1988, Hedges, 1992). $\delta^{13}C_{POC}$ values are also used to indicate the distribution of vegetation in terrestrial ecosystem (Gibson et al., 1999; Lobbes et al., 2000; Weiguo et al., 2003).

In this study the characteristics of suspended matter in the River Sava, Slovenia were studied in detail, but it has to be mentioned that details on stream major and minor element geochemistry discharge and carbonate weathering fluxes for River Sava are presented elsewhere (Kanduč, 2006; Kanduč et al., 2007 a,b). Seasonal data in the River Sava watershed based on investigations of dissolved oxygen and silica concentrations showed that photosynthesis/respiration processes (in stream processes) are less pronounced in the River Sava. Based on carbon isotope mass balance calculations at the border with Croatia, it was also calculated that degradation of organic matter is more pronounced in the late summer season. Among the biogeochemical processes in the River Sava degradation of organic matter is the most important process after dissolution of carbonates, contributing to carbon isotope dissolved inorganic carbon values (KANDUČ et al., 2007A).

This work describes the first comprehensive investigation of suspended matter in river ecosystems in Slovenia. Investigation of suspended matter was performed in different sampling seasons according to the hydrological characteristics of the Sava basin. We also report data on $\delta^{15}N$ of suspended matter in river ecosystems, which happen to be scarce elsewhere in the literature. It was reported that in suspended matter $\delta^{15}N$ values in the Mississippi river basin ranged from - 15 to + 15 ‰ (KENDALL et al., 2001).

The aim of this study was to determine the quantity and quality composition of suspended matter in the upper, central and lower flows of the River Sava through: (1) $\delta^{13}C_{POC}$ and $\delta^{15}N$ of suspended matter in the Sava watershed in relation to different discharge regimes (spring and late summer sampling season); (2) annual fluxes of total suspended matter (TSM) and (3) determine anthropogenic impact on the River Sava in mining and industrial areas.

## Area description

The valley of the River Sava extends in a NW–SE direction and comprises almost half the Slovenian territory (Figure 1). The area is located in the temperate climate zone (latitude 46°03' N; longitude 14°30'E) with temperate to hot summers and cold winters, with average seasonal air temperatures (data for central flow of the River Sava): from – 1.3 to 0.8 °C in winter, from 5 to 13.2 °C in spring, from 16.5 to 18.4 °C in summer and from 3 to 14 °C in autumn (KANDUČ et al., 2007b).

The Sava originates in the Triassic carbonate hinterland at Zelenci (Figure 1, location 1) as the Sava Dolinka, and from the karst spring Savica (Figure 1, location 6) as the Sava Bohinjka. The confluence of these two sources is at Radovljica (location 9). From there on the river is named the Sava and finishes its course at Belgrade (Serbia), merging with the Danube. At the confluence of the Sava Bohinjka and Sava Dolinka it accumulates Pleistocene fluvioglacial sediments and formed terraces. From Radovljica (location 9) the watershed is composed of a mixture of Permo-Carbonian clastic sedimentary rocks, which alternate with Triassic carbonates in the central flow and pass over to Miocene sandstones, clays and gravels on the left bank of the river in the lower part of the flow. In the Krško–Brežice (location 37) area the watershed mainly consists of terrace Pleistocene sediments and from there the flow continues to Croatia. The watershed of the Sava's tributaries is composed of Triassic and Jurassic carbonates, Permo-Carbonian, Oligocene, Miocene clastic rocks and Pleistocene sediments (BUSER, 1989).

Discharge regimes along its flow are controlled by precipitation and the configuration of the landscape. Annual maxima are characteristic in spring and autumn, while minima occur in the summer and winter months. In years 1961 to 1990 annual precipitation ranged from 800 to 1800 mm. More precipitation occurs in the upper part of the flow (1200–1800 mm), from 1200 to 1600 mm in the central part of the flow and in the lower flow from 800 to 1000 mm (MESP, 1995). Up to this study the River Sava in Slovenia was dammed only at four locations: two in the upper and two in the lower flow.

Tributaries of the River Sava collect water mainly from forest areas. The prevailing forest communities in the River Sava watershed are different types of European beech (*Fagus sylvatica* L.) forests depending on climatic and edaphic conditions, altitude and relief (KANDUČ et al., 2007B).

Dense populated and larger agricultural areas are present at following areas of the River Sava watershed: Kranj (location 12), Ljubljana (location 15) and Krško–Brežice (location 37) (Fig. 1), where also alluvium aquifers with groundwater supply are located and its main tributaries: Krka (location 38), Savinja (location 33) and Ljubljanica (location 17) (Figure 1). However, in the larger part of the River Sava watershed the percentage of forests and seminatural areas still sums only from 54.1 to 70.5%, except in the upper part where there is 81.7 % and the most lower part, where there is only 37.1 % of forests and seminatural areas (JOGAN et al., 2004).

## Methodology

Discharge data were obtained from the Environmental Agency of the Republic of Slovenia (Table 1). Samples for characterization of suspended matter from each location (Figure 1) were collected using standard representative sampling techniques (SHUSTER & REDDY, 2001). From each location 4 l (1 l for SEM/EDXS – scanning electron microscope/energy dispersive X-ray spectroscopy microscopy (only at locations 1, 4 and 15), 1 l for $\delta^{13}C_{POC}$ determination and 1 l for $\delta^{15}N$ determination) of the sample were taken and then filtered through a Whatman GF/F (pore size 0.7 μm) glass fibre filter. According to the model of (DEVOL & HEDGES, 2001), suspended matter (particulate in continuation) may be divided into three fractions: coarse particulate organic material (CPOM, > 63 μm), fine particulate organic material (FPOM, 63–0.1 μm) and ultra filtered dissolved organic matter (UDOM < 0.1 μm and > 100 kDa). In our study a 0.7 μm pore size filter was used, which comprises coarse and fine particulate organic material. Filters were ignited before sampling at 480 °C with the aim of eliminating organic impurities and then weighed. Samples for carbon analysis were pre-treated with 1M HCl to remove carbonates. Filters coated with suspended matter were then washed with distilled water, dried at 60 °C and then weighed again to recalculate the mass of total suspended matter (TSM). Samples of suspended matter from the upper, central and lower flow (locations 1, 15 and 39) of the River

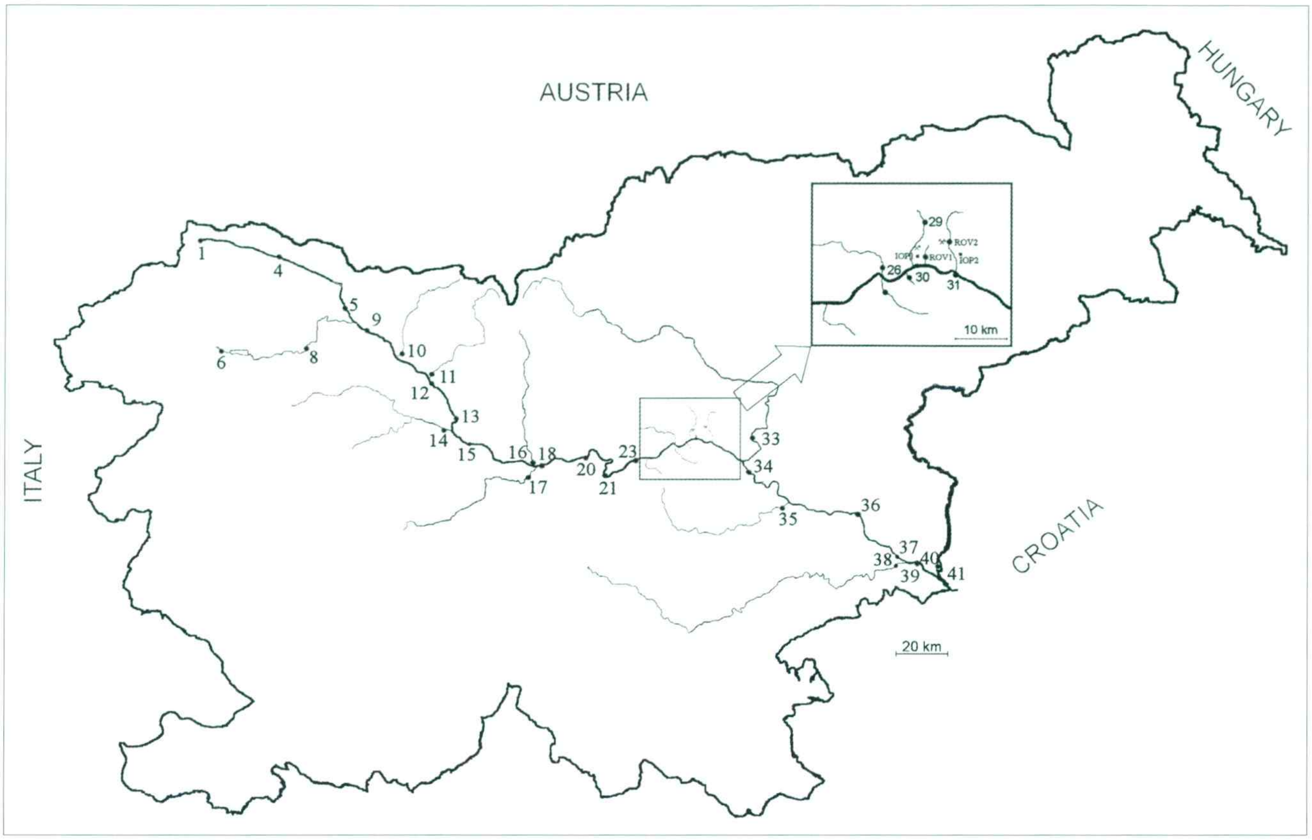


Figure 1. Sampling locations (numbers marked as in Table 1) in the River Sava watershed (Slovenia).

Sava watershed were examined to determine their qualitative and quantitative composition using a JEOL JSM 5800 with electron micro analyzer scanning electron microscope at the Department of Ceramics at the Jožef Stefan Institute.

Also coal mine wastewater (ROV1 and ROV2) and industrial wastewater (IOP1 and IOP2) were sampled in August 2004 (Figure 1) for suspended matter characterization.

The isotopic composition of carbon and nitrogen in suspended matter, plants and soils was determined using a Europa 20–20 continuous flow IRMS ANCA–SL preparation module. Approximately 1 mg was weighed in a tin capsule for carbon analysis and 10 mg of sample for nitrogen analysis. The isotopic composition of nitrogen and carbon was determined after combustion of the capsules in a hot furnace (temperature 1000 °C). Generated products were reduced in a Cu tube (600 °C), where excess $O_2$ was absorbed. $H_2O$ was trapped on a drying column composed of $MgClO_4$. Gases were separated on a chromatographic column and ionized. NBS 22 (oil) and IAEAN-1 (ammonium sulphate) reference materials were used to relate the analytical results to the VPDB and AIR standards. Sample reproducibility for carbon and nitrogen was ± 0.2 ‰.

## Results

The hydrological characteristics of the River Sava watershed from each location, as well as the results for the mass of total suspended matter ($m_{TSM}$), $\delta^{13}C$ and $\delta^{15}N$ of suspended matter during different sampling seasons (late summer 2004 and spring 2005) are presented in Table 1.

Results of SEM/EDXS microscopy of filters from different locations (upper (1), central (15) and lower flow (39)) showed that the inorganic component prevailed over the organic component (Figure 2). The results of qualitative composition of grains (spectrum of grains represented in belonging graphs) obtained from SEM/EDXS microscopy (Figures 2 A, 2 B, 2 C) indicate that the inorganic component in the River Sava watershed is composed of terrigenic components like silica, alumosilicate minerals (clay minerals), Fe and Al oxides, hydroxides and carbonates (dolomite and calcite with magnesium) as remnants of weathering products. SEM microscopy of filters was performed during the late summer season when only minor precipitation fall on the surface and therefore weathering processes and leaching from the surface were less significant than during the wet season, when the discharge is generally higher, and also more suspended material is determined (Table 1).

The mass of total suspended matter in the River Sava watershed varied from 0.4 to 18.4 mg/l in late summer 2004, and according to (Meybeck, 1981) classification falls in the lower classes (1. class from 0 to 15 mg/l, and 2. class from 15 to 50 mg/l). The mass of suspended matter is related to slope denudation processes and rises during the rainy season (Summerfield, 1991) in areas with less vegetation, higher soil thickness and steeper slopes in the watershed composed of clastic rocks (lower flow of the River Sava). The mass of suspended matter in the River Sava watershed increased in

Table 1. Discharge data, total mass of suspended matter ($m_{TSM}$), $\delta^{13}C_{POC}$ and $\delta^{15}N$ of suspended matter River Sava basin (Slovenia) in different sampling seasons (late summer, 2004, spring 2005) as well as $\delta^{13}C_{POC}$, $\delta^{15}N$ of suspended matter of industrial (IOP2) and mining wastewaters (ROV1, ROV2).

| | | | | | late summer, 2004 | | | | | spring, 2005 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Number of locations | Location | Height above see level (m) | Distance from the source (km) | Catchment area (km²) | Q ($m^3/s$) | $m_{TSM}$ (mg/l) | $\delta^{13}C_{POC}$ (‰) | $\delta^{15}N$ (‰) | $NO_3^-$ (mg/l) | Q ($m^3/s$) | $m_{TSM}$ (mg/l) | $\delta^{13}C_{POC}$ (‰) | $\delta^{15}N$ (‰) | $NO_3^-$ (mg/l) |
| 1 | Zelenci | 830 | 0 | | | 0.9 | - 25.7 | | 2.1 | | 2.0 | - 25.1 | | 2.1 |
| 4 | Dovje | 704 | 18 | 44.9 | 11.4 | 2.8 | - 27.4 | | 3.5 | 10.2 | 2.0 | - 27.3 | | 2.1 |
| 5 | Šobec | 459 | 39.8 | 505.4 | 28.6 | 5.0 | - 26.0 | 6.4 | 3.7 | 27.3 | 2.0 | - 26.6 | 4.3 | 2.5 |
| 6 | Savica | 700 | 42.6 | 66.7 | | | | | 1.8 | 0.5 | 0.5 | - 26.1 | | 2.2 |
| 8 | Nomenj | 509 | 42.6 | 354.5 | 10.5 | 0.4 | - 23.6 | | 2.8 | 18.0 | 1.0 | - 26.9 | 4.2 | 2.6 |
| 9 | Otoče | 415 | 51.7 | 895.3 | 39.9 | 2.2 | - 26.8 | | 2.9 | 44.8 | 3.0 | - 26.6 | 2.8 | |
| 10 | Tržiška Bistrica (tributary) | 422 | 56.8 | 121 | 2.4 | 5.7 | - 25.6 | 6.3 | 2.5 | 3.7 | 5.0 | - 26.7 | 3.6 | 2.6 |
| 11 | Kokra (tributary) | 407 | 65.7 | 220.2 | 4.2 | 1.6 | - 27.0 | 2.7 | 3.0 | 3.5 | 1.5 | - 28.3 | 0.5 | 2.5 |
| 12 | Kranj | 350 | 65.7 | 1201 | 31.9 | 5.5 | - 27.0 | 4.9 | 6.0 | | | | | 2.9 |
| 13 | Smlednik | 336 | 76.3 | 2191 | 67.2 | | | | 3.7 | 21.3 | 9.5 | - 27.0 | 5.2 | 4.0 |
| 14 | Sora (tributary) | 313 | 79.9 | 566.3 | 4.3 | 4.9 | - 27.6 | 3.9 | 9.0 | 10.2 | 1.5 | - 27.2 | 2.8 | 2.6 |
| 15 | Tacen | 280 | 84.5 | | | 1.4 | - 23.0 | | 4.5 | 97.5 | 3.0 | - 26.1 | 3.7 | 4.6 |
| 16 | Kamniška Bistrica (tributary) | 260 | 100.4 | 207.8 | 0.7 | 1.6 | - 26.5 | 16.7 | 42.6 | 8.3 | 27.5 | - 27.4 | 9.0 | 5.3 |
| 17 | Ljubljanica (tributary) | 267 | 100.6 | 1762.5 | 7.2 | 1.0 | - 27.0 | 8.2 | 6.5 | 168.0 | 12.5 | - 29.2 | 5.7 | 13.0 |
| 18 | Dolsko | 265 | 103.9 | | | 3.1 | - 26.7 | 6.6 | 7.6 | | 22.7 | - 27.6 | 6.6 | 6.1 |
| 20 | Kresnice | 235 | 119.9 | | | 2.7 | - 26.7 | | 6.3 | | | | | 5.7 |
| 21 | Litija | 230 | 123.5 | 4821 | 105.0 | 6.5 | - 26.7 | 7.2 | 7.5 | 225.0 | 25.0 | - 28.4 | 6.0 | 7.2 |
| 23 | Log | 230 | 130.1 | | | 3.0 | - 26.1 | 6.2 | 5.9 | | | | | 5.8 |
| 26 | Zagorje | 225 | 139.6 | | | | - 27.4 | 6.8 | 6.0 | | | | | 6.2 |
| 29 | Trboveljščica (tributary) | 230 | 143.8 | | | 2.3 | - 28.0 | 9.1 | 3.7 | | | | | 5.0 |
| 30 | Trbovlje | 220 | 143.8 | | | 2.4 | - 27.8 | 7.8 | 6.7 | | | | | 6.4 |
| 31 | Hrastnik | 210 | 148.4 | 5176 | 92.2 | 11.3 | - 27.0 | 7.8 | 10.3 | 344.0 | 64.0 | - 27.8 | 4.9 | 6.1 |
| 33 | Savinja (tributary) | 200 | 156.4 | 1842 | 25.0 | 6.9 | - 25.8 | 7.7 | 7.6 | 103.0 | 80.5 | - 27.8 | 5.4 | 9.2 |
| 34 | Radeče | 193 | 159.1 | | | 0.4 | - 27.2 | 7.9 | 6.2 | | 52.5 | - 28.2 | 5.7 | 5.9 |
| 35 | Mirna (tributary) | 191 | 173.3 | 270 | 1.9 | 0.9 | - 27.7 | 5.0 | 3.3 | 42.2 | 103.0 | - 28.0 | 4.0 | 7.4 |
| 36 | Brestanica | 150 | 187.8 | | | | - 26.6 | 7.9 | 6.7 | | | | | 6.2 |
| 37 | Brežice | 145 | 202.9 | | | 0.4 | - 26.9 | 8.8 | 6.8 | | 160.9 | - 28.0 | 5.2 | 6.0 |
| 38 | Krka (tributary) | 140 | 203.7 | 2238 | 26.9 | 0.8 | - 28.8 | 8.5 | 7.3 | 188.0 | 78.5 | - 28.6 | 5.8 | 3.1 |
| 39 | Mostec | 140 | 205.9 | 10186 | 120.0 | 4.1 | - 27.5 | 7.2 | 6.3 | 720.0 | 111.7 | | | 6.2 |
| 40 | Sotla (tributary) | 140 | 212.6 | 557.7 | 1.8 | 1.2 | - 26.3 | 10.6 | 8.3 | 59.6 | 313.0 | - 26.8 | 5.1 | 5.3 |
| 41 | Bregana | 135 | 213.2 | 10881 | 144.0 | 18.4 | - 27.3 | 6.1 | 6.5 | 725.0 | 108.0 | - 28.5 | 6.0 | 5.3 |
| ROV1 | Sava shaft | | 144.6 | | | 65.1 | - 27.6 | - 1.0 | 0.7 | | | | | |
| ROV2 | Cave Hrastnik | | 148.4 | | | 13.2 | - 34.5 | 1.9 | 2.1 | | | | | |
| IOP2 | Glasshouse Hrastnik | | 148.4 | | | 51.2 | - 23.8 | 2.6 | 2.9 | | | | | |

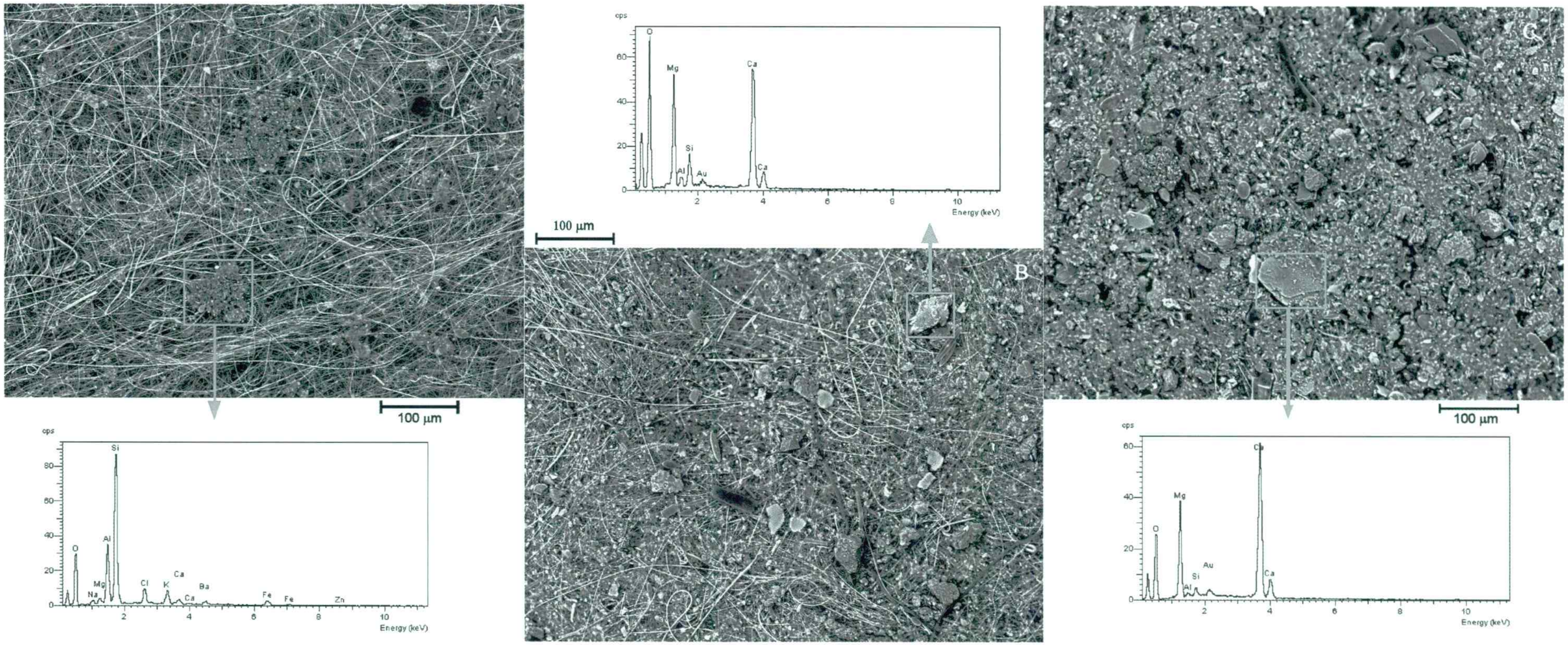


Figure 2. **A** – SEM/EDXS microscopy of suspended matter in the River Sava watershed from location 1 (Zelenci), marked grain represents a qualitative spectrum (belonging graph) of the terrigenous component composed of alumo-silicates, low content of suspended matter is observed, filter fibres represent the uncovered area of the filter, **B** – SEM/EDXS microscopy of suspended matter in the River Sava watershed from location 15 (Tacen), marked grain (belonging graph) indicate that terrigenic grains of pure dolomite and silicates prevail on filter, filter is coated with of skeleton in comparison to other locations, **C** – SEM/EDXS microscopy of suspended matter in the River Sava watershed from location 39 (Mostec): area of filter is completely covered with terrigenic grains composed of carbonates and silicates, qualitative composition of spectrum shows that marked grain (belonging graph) is composed of carbonate.

the spring season and varied from 0.4 to 313 mg/l (Table 1). According to the classification of (MEYBECK, 1982), this belongs to the fourth Class (from 150 to 500 mg/l). The highest class according to (MEYBECK, 1982) is the ninth, with a mass of suspended matter of 50.000 mg/l.

Results of $\delta^{13}C$ and $\delta^{15}N$ values of suspended matter from two different sampling seasons (late summer 2004 and spring 2005) are shown in Table 1. Concentrations of particulate organic carbon (POC) in suspended matter in the River Sava watershed varied from 2.4 to 31.9 % in late summer 2004 and from 2.9 to 38.1 % in spring 2005 (Table 1). $\delta^{13}C_{POC}$ values ranged from - 27.8 to - 3.0 ‰ in the River Sava and from - 28.8 to - 23.6 ‰ in its tributaries in late summer season, while $\delta^{13}C_{POC}$ values ranged from - 28.5 to - 25.1 ‰ in the River Sava and from - 29.2 to - 26.1 ‰ in its tributaries in spring season. $\delta^{15}N$ values ranged from 4.9 to 8.8 ‰ in the River Sava and from 2.7 to 16.7 ‰ in its tributaries in late summer season, while $\delta^{15}N$ values ranged from 2.8 to 6.6 ‰ in the River Sava and from 0.5 to 9.0 ‰ in its tributaries for spring 2004 sampling season (Table 1).

C/N ratios of plants varied from 8.6 to 36.3 (KANDUČ et al., 2007b). The stable isotope composition of plant litter ($\delta^{13}C_{plant}$) varied from of - 34.8 to - 29.2 ‰, with an average of - 31.6 ‰ ± 1.5 ‰ (n = 23), except *Z. mays* (a C4 plant) has a $\delta^{13}C$ value of - 13.6 ‰ (KANDUČ et al., 2007B). Values of $\delta^{13}C$ of C3 plants in the River Sava watershed deviate from average carbon isotopic values for C3 plants ($\delta^{13}C$ = - 27.0 ‰) (CERLING, 1991), while values for *Z. mays* are in good agreement with data from literature (- 13.6 ‰). The isotopic composition of soil ($\delta^{13}C_{soil}$) varies from - 26.4 to - 25.7 ‰ (- 26.2 ± 0.4, n = 3). Flood sediment (from sampling location 30 (Figure 1), central River Sava flow) has a $\delta^{13}C$ value of - 26.0 ‰ and a value of $\delta^{15}N$ 4.0 ‰ similar to soil from the River Sava watershed. The soils analyzed from the River Sava watershed are enriched with heavier carbon and nitrogen isotopes comparing to plants.

Coalmine wastewater contained a high concentration of total suspended matter ranging from 13.2 to 65.1 mg/l. The sample of industrial wastewater (IOP2) contained a high concentration of suspended matter (51.2 mg/l) with $\delta^{13}C_{POC}$ and $\delta^{15}N$ values of - 23.8 ‰ and 2.6 ‰, respectively, while the sample from location IOP1 was without any suspended matter. Values of $\delta^{13}C_{POC}$ coal mine waste water (ROV1 and ROV2) ranged from - 34.5 to - 27.6 ‰, while $\delta^{15}N$ of suspended matter ranged from - 1.0 to 1.9 ‰ (Table 1).

## Discussion

### Composition of suspended matter in River Sava

Allochtonic sources of suspended matter in river ecosystems, besides plant and soil contributions also contain anthropogenic inputs as a consequence of municipal wastewaters, industrial and agricultural sewage (MIDDELBURG & NIEUWENHUIZE, 1998). Autochthonic parts of suspended matter could be produced due to phytoplankton production, microphytobentos and higher plants (ARTEMEYEV, 1996). In the Sava channel stream bed the variety of macrophytic species is insignificant since the velocity of the water flow and the unsuitable substratum make it difficult for them to root. Therefore their primary production is insignificant (URBANC & BERČIČ, 1999).

Suspended material in rivers is a mixture of plant litter and soil material; therefore both components contribute to $\delta^{13}C_{POC}$ values (ITTEKKOT, 1988). In some rivers also phytoplankton could represent another source of POC (particulate organic carbon). The estimated $\delta^{13}C$ values of phytoplankton calculated from the $\delta^{13}C$ of dissolved inorganic carbon (MAYORGA et al., 2005) fall in the River Sava in the range between - 28.2 ‰ and - 35.1 ‰ (KANDUČ, 2006). Phytoplankton binds $CO_2$ from dissolved inorganic carbon in water leading to $^{13}C$ fractionation around - 20 ‰, producing biomass with $\delta^{13}C_{POC}$ values from - 8.0 in temperate to - 45.0 ‰ in tropic rivers (KRUSCHE et al., 2002). In our study an average $\delta^{13}C_{POC}$ value is - 26.7 ‰ ± 1.2, therefore phytoplankton could not represent the possible source of POC in River Sava.

The C/N ratio as well as $\delta^{13}C_{POC}$ values can be used to distinguish sources of suspended matter because of the different C/N ratios between soil and plants (KANDUČ et al., 2007b). According to a simple mixing model, at some sampling points in the River Sava the input of soil and plant material was estimated. The proportion of soil and its $\delta^{13}C$ values in suspended material can be found using a simple model as follows (WEIGUO et al., 2003):

$$(C/N)_{sus} = D \cdot (C/N)_{plant} + (1-D) \cdot (C/N)_{soil} \quad (1)$$

$$\delta^{13}C_{POC} = D \cdot \delta^{13}C_{plant.} + (1-D) \cdot \delta^{13}C_{soil} \quad (2)$$

From equations (1) and (2) the C/N ratio of soil material in the River Sava watershed can be further estimated:

$$(C/N)_{soil} = \frac{(C/N)_{sus.} - D \cdot (C/N)_{plant}}{(1-D)} \quad (3)$$

Where,

D – Proportion of plant material in suspended matter, [%]

(1 - D) – Proportion of soil material in suspended matter, [%]

$(C/N)_{sus.}$ – Weight ratio concentration of carbon and nitrogen in suspended matter

$(C/N)_{plant}$ – Weight ratio concentration of carbon and nitrogen in plant litter

$(C/N)_{soil}$ – Weight ratio concentration of carbon and nitrogen in soil matter

$\delta^{13}C_{POC}$ – Isotopic composition of carbon in suspended matter, [‰]

$\delta^{13}C_{plant}$ – Isotopic composition of carbon in plant litter, [‰]

$\delta^{13}C_{soil}$ – Isotopic composition of carbon in soil matter, [‰]

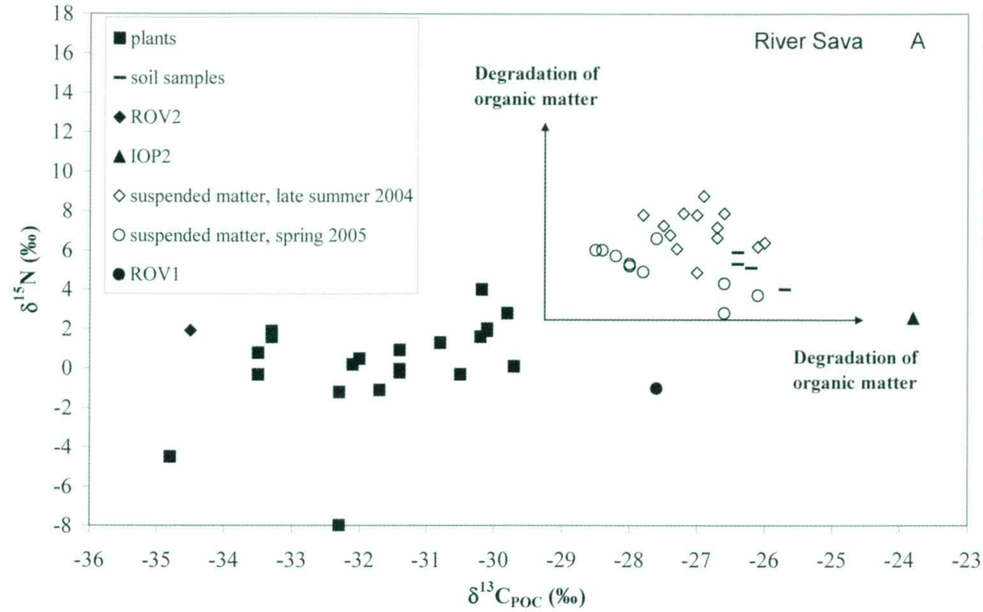



Figure 3. $\delta^{15}N$ versus $\delta^{13}C_{POC}$ of suspended matter, plant and soil material in the River Sava (A) and tributaries of the River Sava (B). Arrows indicate degradation of organic (Fig. 3 A) material leading to enrichment with $^{13}C$ and $^{15}N$ values. $\delta^{13}C$ and $\delta^{15}N$ of plant and soil material was determined in KANDUČ et al., 2006.

In equation (2) an average value of - 31.6 ‰ of $\delta^{13}C_{plant}$ (KANDUČ, 2006) was used (average for $C_3$ plants) and an average isotopic composition of soil material ($\delta^{13}C_{soil}$) - 26.0 ‰ (KANDUČ, 2006) (n = 4) was assumed. According to equation (2) the proportion of soil organic material (D) in suspended matter prevails and ranges from 50 to 100 % in late summer 2004 and from 43 to 98 % in spring 2005. Calculations of the proportion of organic soil material at locations (1, 8, 10, 15 and 33) were performed, where $\delta^{13}C_{POC}$ in suspended matter is higher than - 26.0 ‰. Higher $\delta^{13}C_{POC}$ values can be attributed to anthropogenic sources and wastewaters (MUNSON & COREY, 2006; ŠLEJKOVEC & KANDUČ, 2005) and/or more highly decomposed organic material (Figure 3). For a better estimate more soil profiles from different geological compositions in the River Sava watershed would provide a more reliable figure since in our case $\delta^{13}C_{soil}$ was measured only in 4 soil samples. According to equation (3) assuming soil (1 - D) and plant ratios (D) calculated according by equation (2) and taking into an account the average C/N ratio of plant litter of 20.3 (KANDUČ, 2006), then the calculated $(C/N)_{soil}$ ratio in the River Sava watershed would range from 0.6 to 13.3, which is in a higher range than measured C/N values of suspended organic matter (KANDUČ, 2006), probably due to more variable $(C/N)_{soil}$ ratios in the terrestrial ecosystem. This should be the subject of further investigation.

To obtain TSS flux at location Bregana (41) mass of suspended matter was multiplied with discharge data. Calculated annual fluxes at the sampling location of Bregana (41) at the border with Croatia are estimated as follows: (1) POC (particulate organic carbon) flux $5.2 \times 10^{10}$ g C/year (KANDUČ et al., 2007a), (2) PN (particulate nitrogen) flux $8.5 \times 10^9$ g N/year (KANDUČ et al., 2007b) and (3) TSS (total suspended solid) flux is estimated to be $1.3 \times 10^{12}$ g/year. According to the drainage area of the River Sava, the calculated annual fluxes are estimated to be: (1) POC flux $4.7 \times 10^6$ g C/ (year·km$^2$) (2) PN flux $7.8 \times 10^5$ g C/ (year·km$^2$) (3) TSS flux $7.9 \times 10^9$ g/ (year km$^2$). The most common literature estimations of the magnitude of global river carbon fluxes are 0.4 Pg C/year for total organic carbon (evenly divided between particulate and dissolved organic phases), and 0.4 Pg C/year for dissolved inorganic carbon. While these bulk fluxes are small components of the global carbon cycle, they are significant compared to the net oceanic uptake of anthropogenic $CO_2$ (STALLARD, 1998). Modern reservoirs have had a tremendous impact on the hydrological cycle. The exact magnitudes of global fluxes of suspended and dissolved carbon species in river ecosystems still remain uncertain. It was calculated that the POC flux in the River Sava in Slovenia represents 10.4 % (KANDUČ, 2006) of other measured or calculated carbon contributions (1.6 % $pCO_2$, 82 % DIC and 6 % DOC).

### Tracing anthropogenic impact using $\delta^{13}C$ and $\delta^{15}N$ values of suspended matter

Figure 3 shows $\delta^{15}N$ versus $\delta^{13}C$ of different sources in terrestrial ecosystem: (1) $C_3$ plants and soils, which represent terrestrial input to the river and (2) anthropogenic input (coal mine ROV and industrial IOP waste waters) into the river. Decomposition of organic matter is reflected in more positive $\delta^{13}C$ and $\delta^{15}N$ values in suspended organic matter in comparison with plant litter and is dependent upon the degradation of organic matter due to biological processes in terrestrial and/or river ecosystems. Industrial waste water (IOP2) has more positive $\delta^{13}C$ values (ADER et al., 1988), while coalmine wastewater has values of $\delta^{13}C$ and $\delta^{15}N$ similar to low rank coal from the Trbovlje basin (ŠLEJKOVEC & KANDUČ, 2005) and expresses no impact on $\delta^{13}C$ and $\delta^{15}N$ values in suspended matter in the River Sava.

$\delta^{15}N$ of bulk organic matter in sediments depends on $\delta^{15}N$ of atmospheric nitrogen, the source of the organic matter and on biogeochemical processes such as ammonification, nitrification and denitrification. However, the fate of organic nitrogen and the denitrogenation process during early digenesis is still poorly understood (CLARK & FRITZ, 1997). Higher $\delta^{15}N$ values of suspended matter during the late summer season are probably related to lower discharge conditions, higher microbial activity and local agriculture activity. Higher $\delta^{15}N$ values (Figure 3) at location 16 (Kamniška Bistrica tributary) are related to higher nitrate concentrations (up to 42.6 mg/l, Table 1) due to leaching of fertilizers in the late summer sampling season, while the nitrate concentration observed in the spring sampling season is lower (13 mg/l) (KANDUČ et al., 2007b). It is known that nitrogen originating directly from liquid manure has $\delta^{15}N$ value of 28 ‰ (KENDALL, 1998). This is reflected in $\delta^{15}N$ of suspended matter only in late summer season at location 16, when discharge conditions are lower (Figure 3). Higher values of $\delta^{15}N$ in nitrates are therefore locally expected in agricultural regions in the River Sava watershed (LI et al., 1997), where also higher concentrations of nitrates in groundwater are observed (KANDUČ, 2006). Higher concentrations of nitrate were also determined in open aquifers located in agriculture areas and in areas with explosive test facilities elsewhere (LI et al., 1997; BELLER et al., 2004).

## Conclusions

This investigation shows that $\delta^{13}C$ and $\delta^{15}N$ in suspended matter in the River Sava watershed vary seasonally according to discharge conditions in the basin. Higher $\delta^{13}C$ and $\delta^{15}N$ values are observed in the late summer season, which is probably due to lower discharge conditions and more intensive biological degradation. According to the SEM microscopy results, it can be concluded that suspended matter is mainly composed of mechanically degraded material, which includes alumosilicates and carbonates that prevail over organic material. In the Sava watershed C3 plants as well as soil material represent the most important contribution of organic matter to suspended matter in the river. The mass of total suspended solids is higher in mining and industrial areas but is diluted in the River Sava, causing no impact. The mass of suspended matter increases through the River Sava flow (in Slovenia) with increasing drainage area, and represents annually a total mass suspended flux of $1.3 \times 10^{12}$ g/year, according to the Sava drainage area of $7.9 \times 10^{9}$ g/(year·km$^2$) at the border with Croatia. Suspended matter is composed mainly (more than 50 %) of soil organic material. Anthropogenic impact due to higher $\delta^{15}N$ values was traced during the late summer season, especially at the sampling point on the tributary of the Sava, which is located in an agricultural-industrial area. Generally, the Sava has a good self-cleaning capacity; anthropogenic pollution is expressed only locally.

These first results on suspended matter in the River Sava watershed represent a data base, which will help in evaluation of total suspended matter and particulate organic matter fluxes and in estimating anthropogenic impact, especially in relation to future impacts due to hydroelectric power plant construction in upper, central and downstream locations along the River Sava. This study also represents a useful data base for long term planning for ecological management (e.g. deforestation, agriculture, industry).

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## References


Ader, M., Boudou, J. P, Javoy, M., Goffe, B. & Daniels, E. 1988: Isotope study on organic nitrogen of Western Middle field of Pennsylvania (U. S. A.) and from the Bramsche Massif (Germany) Org. Geochem., 29: 315–323.

Ankers, C., Walling, D. E. & Smith, R. P. 2003: The influence of catchment characteristics on suspended sediment properties, Hydrobiologia, 1: 16–24.

Artemyev, V. E. 1996: Geochemistry of organic matter in river – sea systems. Kluwer Academic Publishers Dodrecht, Amsterdam: 190 p.

Beller, H. R., Madrid, V., Hudson, G. B., Mcnab, W. W. & Carlsen, T. 2004: Biogeochemistry and natural attenuation of nitrate in groundwater at an explosives test facility. Appl. Geochem., 19: 1483–1494.

Buser, S. 1989: Geological map of Slovenia. In: M. Javornik (Ed.): Encyclopaedia of Slovenia, Mladinska knjiga (Ljubljana) (in Slovene), 3: 194–203.

Cerling, T. E. 1991: Carbon dioxide in the atmosphere: evidence from Cenozoic and Mesozoic paleosols. Am. J. Sci., 291: 377–400.

Clark, I. & Fritz, P. 1997 (Eds.): Environmental Isotopes in Hydrogeology, Lewis Publishers, New York: 326 p.

Deines, P. 1980: The isotopic composition of reduce organic carbon. In: P. Fritz, J. Ch. Fontes, (Eds.): Handbook of Environmental Isotopic geochemistry, Elsevier, Amsterdam, 1: 329–406.

Devol, A. H. & Hedges, J. I. 2001: Organic matter nutrients in the mainstem Amazon River. In: McClain, M. E., Victoria, R. L. &. Richey, J. E (Eds.): The biogeochemistry of the Amazon Basin, Oxford University Press, Oxford: 275–306.

Gibson, J. A. E., Trull, T., Nichols, P. D., Summons, R. E. & McMinn, A. 1999: Sedimentation of $^{13}$C-rich organic matter from Antartic Sea – ice algae: a potential indicator of past sea – ice extent. Geology, 27: 331–334.

Hedges, J. I. 1992: Global biogeochemical cycle: progress and problem. Mar. Chem., 39: 67–93.

Hope, D., Billet, M. F. & Cresser, M. S. 1994: A review of the export of carbon in river water: fluxes and processes. Environ. Poll., 84: 301–304.

Ittekkot, V. 1988. Global trends in the nature of organic matter in the river suspensions. Nature, 332: 436–438.

Jogan N., Kotarac, M. & Lešnik, A. 2004: Identification of sites containing non-forest natural habitat types of Community importance by using ranges of characteristic plant species. Centre for Cartography of Fauna and Flora, Miklavž na Dravskem polju, Ljubljana (in Slovene): 961 p.

Kanduč, T. 2006: Hydrogeochemical characteristics and carbon cycling in the River Sava watershed in Slovenia. Ph. D. Thesis, University of Ljubljana (in Slovene): 141 p.

Kanduč, T., Szramek, K., Ogrinc, N. & Walter, L. M. 2007a: Origin and cycling of riverine inorganic carbon in the Sava River watershed (Slovenia) inferred from major solutes and stable carbon isotopes. Biogeochemistry, 86: 137–154, doi: 10.1007/s10533-007-9149-4.

Kanduč, T., Ogrinc, N. & Mrak, T. 2007b: Characteristics of suspended matter in the River Sava watershed, Slovenia, Isotopes in Environmental and Health Studies, 43: 369–385.

Kendall, C. 1998: Tracing nitrogen sources and cycling in catchments. In: C. Kendall and J. J. McDonnell (Eds.): Isotope Tracers in catchment Hydrology, Elsevier, Amsterdam: 519–576.

Kendall, C., Silva, S. R. & Kelly, V. J. 2001: Carbon and nitrogen isotopic composition of particulate organic matter in four large river systems across the United States. Hydrol. Proc., 15: 1301–1346.

Krusche, A. V., Martinelli, L. A., Victoria, R. L., Bernardes, M., Camargo, P. B., Ballester, M. V. & Trumbore, S. E. 2002: Composition of particulate and dissolved organic matter in a disturbed watershed of southeast Brazil (Piracicaba River basin). Water Research, 36: 2743–2752, doi:10.1016/S0043-1354(01)00495-X.

Li, H., Hirata, T., Matsuo, H., Nishikawa, M. & Tase, N. 1997: Surface water chemistry, particularly concentrations of $NO_3^-$ and DO and $\delta^{15}$N values, near a tea plantation in Kyushu, Japan. J. Hydrol.; 202: 341–352.

Lobbes, J. M., Fitznar, H. P. & Kattner, G. 2000: Biogeochemical characteristics of dissolved and particulate organic matter in Russsian rivers entering the Arctic Ocean. Geochim. Cosmochim. Acta, 64: 2973–2983, doi:10.1016/S0016-7037(00)00409-9.

Mayorga, E., Aufdenkampe, A. K., Masiello, C. A., Krusche, A. V., Hedges, J. I., Quay, P. D., Richey, J. E. & Brown, T. A. 2005. Young organic matter as a source of carbon dioxide outgassing from Amazonian rivers, Nature, 436: 538–541, doi:10.1038/nature03880.

Meybeck, M. 1981: River transport of organic carbon to the ocean. In: Likens, G. E., Mackenzie, F. T., Richey, J. E., Sedell, J. R. & Turekian, K. K. (Eds.): Flux of organic carbon to the Oceans, 219–269, U. S. D. O. E. CONF – 8009140.

Meybeck, M. 1982: Carbon, nitrogen and phosphorous transport by world rivers. Am. J. Sci., 282: 401–425.

Middelburg, J. E. & Nieuwenhuize, J. 1998: Carbon and nitrogen stable isotopes in suspended matter and sediments from Schelde Estuary. Mar. Chem., 60: 217–225.

MESP Ministry of Environment and Spatial Planning (Ed) 1995: Climatography of Slovenia 1961–1990 precipitation, Plantprint, Ljubljana: 366 p.

Munson, S. A. & Carey, E. 2004: Organic matter and transport in an agriculturally dominated temperate watershed. App. Geochem., 19: 1111–1121, doi:10.1016/j.apgeochem.2004.01.010.

Schuster, P. F. & Reddy, M. M. 2001: Particulate Carbon (PC) and Particulate Nitrogen (PN).

In: Water and Sediment Quality in the Yukon River Basin, Alaska, During Water Year 2001, Open-File Report 03–427, National Research Program, USGS, available online: http://pubs.usgs.gov/of/2003/ofr03427/.

Stallard, R. F. 1998: Terrestrial sedimentation and the carbon cycle: coupling weathering and erosion to carbon burial. Glob. Biochem. Cycles, 12: 231–257.

Summerfield, M. A. (Ed) 1991: Global Geomorfology, An introduction to the study of landforms, Longman Scientific & Technical, New York: 537 p.

Šlejkovec, Z. & Kanduč, T. 2005: Unexpected arsenic compounds in low rank coal. Environ. Sci. Technol., 39: 3450–3454.

Tipping, E., Marker, A. F. H., Butterwick, C., Collettt, G. D., Cranwell, P. A., Ingram, J. G. K., Leach, D. V., Lishman, J. P., Pinder, A. C., Rigg, E. & Simon, B. M. 1997: Organic carbon in the Humber rivers. Sci. Total Environ., 195: 345–355.

Urbanc, J. & Berčič, O. 1999: Aquatic macrophytes in the rivers Sava, Kolpa and Krka. *Ichthyos*, 1: 23–34.

Weiguo, L., Zisheng, A., Weijian, Z., Head, M. J. & Delin, C. 2003: Carbon isotope and C/N ratios of suspended matter in rivers: as indicator of seasonal change in $C_4/C_3$ vegetation. App. Geochem., 18: 1241–1249, doi:10.1016/S0883-2927(02)00249-4.