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Hydrogeochemical and isotopic characterization of Pesnica River, Slovenia

Hidrogeokemične in izotopske značilnosti reke Pesnice

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Ključne besede: reka Pesnica, hidrogeokemijska sestava, stabilni izotopi, ogljik, biogeokemijski procesi

Abstract

The surface water geochemistry and carbon cycling studied here depend mainly on geological composition of the river catchment. The investigated surface waters in the river Pesnica catchment that are heavily hydromorphologicaly altered (reservoirs, channelization, land melioration systems) represent waters influenced by chemical weathering of carbonates and of mostly clastic rocks (claystone, sandstones, marlstones and siltstones). The objectives of our study were to analyze hydrogeochemical and isotopic composition of dissolved ($\delta^{13}C_{DIC}$) and particulate carbon ($\delta^{13}C_{POC}$) with characterization of suspended matter and evaluate biogeochemical processes in Pesnica River in Slovenia before and after the retention. Surface waters are generally close to saturation regarding calcite and dolomite, dissolved CO_2 is 49 to 1000 times oversaturated relative to atmosphere. $\delta^{13}C_{DIC}$ was in the range from -14.8 to -4.2 ‰ and shows following biogeochemical processes in river system: degradation of organic matter, dissolution of carbonates and biological activity, which was confirmed with SEM microscopy and EDXS microanalysis. Results of SEM/EDXS showed that suspended matter is composed of K, Mg and Ca from locations Pesnica 1 and Pesnica 2 (above retention Perniško lake). Sample from Pesnica 3 (below retention) shows higher biological activity, while sample from Pesnica 4 (tributary of Pesnica, drainage channel Biš) contains a lot of particles of microporous structure and fiber structure, which are probably of anthropogenic origin. $\delta^{13}C_{POC}$ is changing from -29.5 to-27.6‰ and showed different stages of degraded terrestrial material. More negative $\delta^{13}C_{POC}$ are shown at location at drainage channel Biš and show higher terrestrial input in river system as locations 1, 2 and 3 Pesnica, which have higher $\delta^{13}C_{POC}$ values. This first results about suspended matter in Pesnica watershed serve for evaluation of anthropogenic influences specially in relation with further influences and longer time planning of sustainable river water management.

Izvleček

Geokemija površinskih voda in kroženje ogljika v naši študiji v glavnem zavisita od geološke podlage v porečju. Raziskane površinske vode v porečju Pesnice, ki je hidromorfološko močno preoblikovano (vodni zadrževalniki, urejanje struge, melioracije), predstavljajo vode, na katere vpliva kemijsko preperevanje karbonatov in v glavnem klastičnih kamnin (glinavcev, peščenjakov, laporovcev in meljevcev). Namen naše raziskave je bil analizirati hidrogeokemično in izotopsko sestavo raztopljenega in partikulatnega ogljika skupaj s karakterizacijo suspendirane snovi in oceno biogeokemijskih procesov v porečju Pesnice v Sloveniji pred zadrževalnikom in za njim. Površinske vode so večinoma blizu nasičenja glede na kalcit in dolomit, raztopljen CO_2 je od 49 do 1000 krat prenasičen relativno na atmosfero. $\delta^{13}C_{DIC}$ je bil v razponu od -14.8 do -4.2 ‰ in kaže na sledeče biogeokemijske procese v rečnem sistemu: razgradnja organske snovi, raztapljanje karbonatov in biološka aktivnost, kar je bilo potrjeno s SEM mikroskopijo in EDXS mikroanalizo. Rezultati SEM/EDXS so pokazali, da je suspendirana snov iz Pesnice 1 in Pesnice 2 (nad zadrževalnikom Perniško jezero) sestavljena iz alumosilikatov s K, Mg in Ca. Vzorec iz Pesnice 3 (pod zadrževalnikom) kaže na veliko biološko aktivnost (diatomeje), medtem ko vzorec iz Pesnice 4 (pritok Pesnice, drenažni kanal Biš) vsebuje veliko delcev mikroporozne strukture in vlaknatih struktur, ki so po vsej verjetnosti antropogenega izvora. $\delta^{13}C_{POC}$ se spreminja od -29.5 do -27.6 ‰ in kaže na različne stopnje razgrajenega terestričnega materiala. Bolj negativne vrednosti $\delta^{13}C_{POC}$ opazimo na lokaciji v drenažnem kanalu Biš in kažejo na večji terestrični vnos v rečni sistem kot lokacije Pesnice 1, 2 in 3, ki imajo višje vrednosti $\delta^{13}C_{POC}$. Ti prvi rezultati o suspendirani snovi v porečju Pesnice služijo za evalvacijo antropogenih vplivov, posebno v povezavi s prihodnjimi vplivi in dolgoročnim načtrovanjem trajnostnega upravljanja s porečjem.

Introduction

It is well known that rivers reflect the biogeochemical processes occurring in their catchment areas (Meybeck, 1981; Meybeck, 1987; Popescu et al., 2015; Li et al., 2016). Understanding the organic and inorganic carbon cycles in river systems is important because it helps to understand the biogeochemical processes in a river and its catchment basin (Karim & Veizer, 2000; Barth et al., 2003; Sameer et al., 2016). Several studies evaluating biogeochemical processes in Slovenian rivers have been carried out in the past ten years, contributing substantially to a general understanding of their interactions with their catchments (Kanduč & Ogrinc, 2007; Kanduč et al., 2008; Zavadlav et al., 2013; Kanduč et al., 2013).

Suspended organic matter is known to be complex mixture of molecules such as carbohydrates, amino acids, fatty acids and phenols, particles from wastewaters and industrial water, soil organic matter and biological material like phytoplankton and plant parts (Hope et al., 1994). Suspended matter in rivers is derived mostly from soil and plant material, so suspended organic matter ($\delta^{13}C_{POC}$) in rivers can be used to determine the contribution of terrestrial vegetation and soil matter in the river ecosystem (Hedges, 1992).

Pesnica is a river that was extensively regulated in the 60's when it was channeled and when multipurpose retention basins were built to mitigate floods (Leitinger, 2012). Nowadays, droughts in combination with severe loads of nutrients and other pollutants from households and agriculture adversely affect the flora and fauna in the area (Markoli, 2012).

The main objective of our study was to understand the hydrogeochemical characteristics and prevailing biogeochemical processes in the Pesnica catchment waters using geochemical and stable carbon isotopes analysis, respectively.

Geological and geomorphological setting

River Pesnica is located in northeastern Slovenia (Fig. 1). It is a left tributary of River Drava, and is the main watercourse in Slovenske gorice. The river originates above Pesnica (in Austria) at an altitude of 300 m; at town Ormož (altitude 190 m) it flows out to the Drava River (Fig. 1). Its length is 69 km, of which 65 km being in Slovenia (Statistical Office of Republic of Slovenia, 2002). Its catchment area comprises 539 km^2. Its mean average discharge between 1926 and 1965 was 6.72 m^3/s. It has a mixed snow/rain river regime with high water levels in March and November and low in August and September. In Pesnica catchment area, 3 gauging stations are monitored by the Slovenian Environmental Agency (SEA): Ranca, Gočova, Zamušani I Kobold, 2012).

Land cover in Pesnica catchment is dominated by agriculture areas (~75 %), followed by forests and semi-natural areas (~23 %) and with less than 2% of artificial surfaces (CLC, 2012).

Since Pesnica flows through a lower bushy environment, it has a low specific runoff (10.6 l/s/km^2; gauging station Zamušani) and a runoff coefficient of 32.2 % (gauging station Zamušani).

In past years it was found, that mainly in summer, the discharge of Pesnica is mostly below 0.5 m^3/s (Urbanek, 1994). Since it flows through an intensively agricultural area, it contains large amount of atrazine and steroid organic substances, together with a high concentration of nitrates in past decade. Pollution with sewage sludge was moderate, and in recent years the river's ecological status has improved (Urbanek, 1994).

Pesnica River is heavily hydromorphologically altered (from Zgornja Kungota to outflow). For the purposes of flood prevention, several reservoirs have been constructed to retain the water: Pernica and tributaries were artificial lakes were constructed for water retention.

Drainage channel at settlement Biš-the municipality Trnovska vas, is a right hand tributary of Pesnica River (P4 in Fig. 1).

Geologically, Pesnica catchment area belongs to the Panonian basin and is of Tertiary and Quaternary ages. The catchment is composed of Miocene and Pliocene sediments (siltstones, marlstones, claystones, dolomite/calcite) and quaternary sediments. The area of the Panonian basin was split into more tectonic units with the Slovenske gorice as the largest tectonic unit. In the Pesnica catchment more faults were found in different directions, belonging to the category of tectonic faults. The most important are: Globovnica, Pesnica, Dravinja faults (named after the tributaries that flow through them). Surface water creates channels, in which the rocks are the most fractured (Mioč & Žnidarčič, 1989; Perko et al., 2001). Following Miocene and Quaternary sediments are present in the River Pesnica watershed:

Miocene sediments (M21) that outcrop up in the northeastern part of the catchment are composed of conglomerate, sandstone and marl.

M_2^2 – Miocene sediments are composed of gravel, sand, marl, limestone and sandstone.

M_3^1 – In the lower part of the catchment sandy marl sediments prevail and within them are mica, sandstone, claystones and marlstones. Gravels are composed of siliciclastic and other metamorphic and magmatic rocks.

M_3^2- Miocene sediments are located in the eastern part of Pesnica catchment and are composed of sandy clays, sandy clay marls, sands and sandy gravels.

Pliocene sediments are located in the southern part of the River Pesnica catchment (Pliocene) and are composed of clay, sand, conglomerate and clayey marl (Mioč & Žnidarčič, 1989).

Quaternary sediments are located along surface water flow in the valley and are composed of clastic material (gravels, sands, marls, clays).

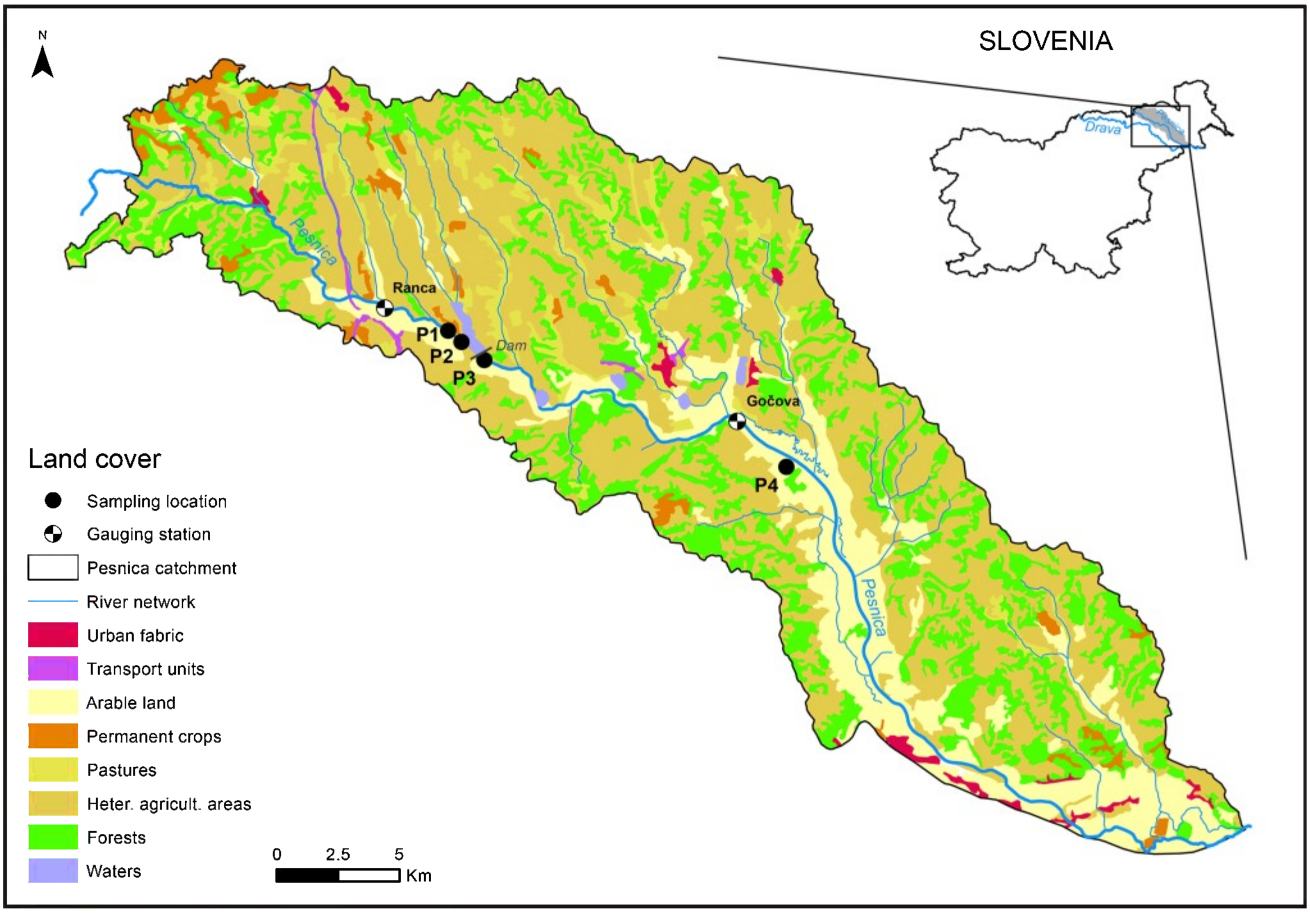

Fig. 1. Land use map of River Pesnica catchment area (Corine Land Cover 2012)

Materials and Methods

In order to determine how artificial reservoirs influence biogeochemical processes in the river system, water was sampled at the inflow and outflow of one of the accumulation lakes (Perniško jezero) during the crop growing season. In addition, a small drainage channel nearby Biš village was chosen to investigate how an area dominated by intensive agriculture contributes to the biogeochemical processes of Pesnica River.

Discharge data (Miha Supek, personal communication) were obtained from the Environmental Agency of the Republic of Slovenia (Tab. 1). Samples were collected four times in each month from February to September (except July) 2016 at four gauging stations: 1 (before dam), 2 (before dam), 3 (after dam), 4 (drainage channel Biš). Temperature and dissolved oxygen (DO) of surface waters were measured with a WTW Multi 340, CellOx 325. pH was measured with a Seven Compact pH/ion Metler Toledo and electroconductivity with an Ultrameter II MYRON L COMPANY 6 PFCE, serial 6218180, both in the laboratory after sampling.

Sample aliquots collected for cation, anion and alkalinity analyses were passed through a 0.20 µm nylon filter into HDPE bottles (30 ml) and kept refrigerated until analyzed. Samples for $\delta^{13}C_{DIC}$ analysis were passed through a 0.45 µm nylon filter and stored in glass serum bottles filled with no headspace and sealed with septa caps.

Alkalinity was measured using Gran titrations (Clesceri et al., 1998). Cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and anions (SO_4^{2-}, Cl^-, and NO_3^-) were measured by ion chromatography (Metrohm, 761 Compact IC).

The stable isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) was determined with a Europa Scientific 20-20 continuous flow IRMS (isotope ratio mass spectrometer) with an ANCA-TG preparation module. Phosphoric acid (100 %) was added (100-200 µl) to a septum-sealed vial which was then purged with pure He. The water sample (5 ml) was injected into the septum tube and headspace CO_2 was measured (modified after Kanduč, 2006). In order to determine the optimal extraction procedure for surface water samples, a standard solution of Na_2CO_3 (Carlo Erba) with a known $\delta^{13}C_{DIC}$ of -10.8±0.2 ‰ was prepared with a concentration of 0.66 g/l.

Samples for characterization of suspended matter from each location (Fig. 1) were collected (September 2016 sampling) using standard representative sampling techniques (Schuster & Reddy, 2001) in HDPE bottles. From each location, 3 l of surface water were sampled for microscopic (SEM/EDXS-scanning electron microscopy/energy - dispersive X-ray spectroscopy) analyses (suspended matter characterization) and for isotopic composition of carbon in suspended matter ($\delta^{13}C_{POC}$). Surface water samples were filtered through a Whatman GF/F (pore size 0.7 µm) glass fiber filter. The isotopic composition of carbon in suspended matter was determined using a Europa 20-20 continuous flow IRMS-SL preparation module. The filter was treated with 1M HCl to dissolve any carbonate present. Approximately 1 mg of sample was scrapped from the GF/F filter and dried at 60 °C. The isotopic composition of carbon was determined after combustion of the capsules in a hot furnace at 1000 °C. IAEA CH3 and IAEA CH6 standards were used to relate the analytical results to the VPDB. Sample reproducibility for carbon was ±0.2 ‰.

All stable isotope results for carbon are expressed in the conventional delta (δ) notation, defined as per mil (‰) deviation from the reference standard VPDB. Precision of working standards was ±0.2 ‰ for $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$.

Samples of suspended matter from Pesnica catchment area from September sampling were examined to study the morphology of particles and their element composition, using a field-emission-gun scanning electron microscope (FEGSEM) JEOL JSM 7600-F equipped with Oxford Instruments INCA energy – dispersive X-ray spectroscopy (EDXS) with 20-mm² silicon-drift detector (SDD). SEM/EDXS analyses were performed at 20kV accelerating voltage, 15 mm working distance and 100 s acquisition time. The internal INCA EDS standard database was used for the analyses.

Thermodynamic modeling was used to evaluate pCO_2 (partial pressure) and the saturation state of calcite ($SI_{calcite}$) and dolomite ($SI_{dolomite}$) using pH, alkalinity and temperature as inputs to the PHREEQC speciation program (Parkhurst & Appelo, 1999). Version 2.16.03 Phreeqc for Windows was used to calculate $SI_{calcite}$, $SI_{dolomite}$ and pCO_2.

Results and discussion

Theoretical background of dissolution of minerals

Dissolved Ca^{2+} and Mg^{2+} are largely supplied by the weathering of carbonates, with smaller contributions from silicate weathering, as indicated by the relatively high HCO_3^- and low Si concentrations. Most of the water samples in our study deviate from a 2:1 molar ratio of HCO_3^- (Fig. 2A) and are the consequence of weathering of clastic rocks composed of clay minerals as follows (1-5):

$$CaAl_2Si_2O_8 + 3H_2O + 2CO_2 \text{ (Anorthite)} \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^- \text{ (Kaolinite)} \quad (1)$$

In the case of weathering anorthite, only Ca^{2+} is present in carbonate reactions (precipitation of calcite).

$$NaAlSi_3O_8 + CO_2 + 11/2H_2O \text{ (Albite)} \rightarrow Na^+ + \tfrac{1}{2}\, Al_2Si_2O_5(OH)_4 + 2H_4SiO_4 + HCO_3^- \text{ (Kaolinite)} \quad (2)$$

In case of weathering of albite, Na^+ and HCO_3^- are in 1:1 stoichiometry ratio. The origin of K^+ can be mica shist.

Weathering of calcite and dolomite is presented below:

Calcite :

$$CaCO_3 + CO_{2(g)} + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^- \quad (3)$$

Dolomite :

$$Ca_{0:5}Mg_{0:5}(CO_3) + CO_2 + H_2O \Leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- \quad (4)$$

The carbon dioxide content of rain and soil water is particularly important in weathering processes (Gaillardet et al., 1999). The chemical composition of rainwater changes markedly after entering the soils (Gaillardet et al., 1999). The upper part of the soil is a zone of intense biochemical activity. One of the major biochemical processes of the bacteria is the oxidation of organic material, which leads to an increase of carbon dioxide in the soil gas (Gaillardet et al., 1999). Above the zone of water saturation, the soil gases may contain 10 to 40 times as much as carbon dioxide as the free atmosphere (reference value for partial pressure in atmosphere is 316 ppm (Clark & Fritz, 1997)). This CO_2 gives rise to a variety of weathering reactions, for example the congruent dissolution of calcite ($CaCO_3$) in limestone: $CaCO_3 + CO_2(g) + H_2O = Ca^{2+} + 2HCO_3^-$

and the incongruent reaction with K–spar:

$$(KAlSi_3O_8)\text{: } 2KAlSi_3O_8 + 2CO_2 + 11H_2O = Al_2Si_2O_5(OH)_4 + 2K^+ + 2HCO_3^- + 4H_4SiO_2 \quad (5)$$

The amount of CO_2 dissolved according to reaction (3) depends mainly on the temperature and its partial pressure. For example, for an atmospheric carbon dioxide pressure of 10^{-2} atmosphere and for a soil atmosphere of nearly pure carbon dioxide, the amount of calcium that can be dissolved (at 25 °C) until saturation is 65 and 300 ppm, respectively. The calcium and hydrogencarbonate ions released into soil water and groundwater eventually reach the river system. The water resulting from reaction (5) contains hydrogencarbonate, potassium, and dissolved silica in the ratios 1:1:2, and the new mineral, kaolinite, is the solid weathering product. The dissolved constituents of reactions (calcite) and (K-feldspar) eventually reach the river systems. The global silicate weathering fluxes and associated CO_2 consumption fluxes have been freshly estimated on the basis of data on the 60 largest rivers of the world (Gaillardet et al., 1999). Only active physical denudation of continental rocks was found to be able to maintain high chemical weathering rates and significant CO_2 consumption rates.

General geochemical characteristics of river water

Mean daily discharge data (Q), parameters measured in the field (T-temperature, D.O.-dissolved oxygen (mg/l)), geochemical and isotopic data of water (Pesnica catchment area) are presented in Table 1.

Most of the studied rivers in Slovenia (Kanduč et al., 2008) have a $Ca^{2+}+Mg^{2+}$: HCO_3^- ratio 2:1 indicating that geological composition (carbonates prevail) controls the composition of river waters. In Pesnica River catchment (studied locations Pesnica 1, Pesnica 2, Pesnica 3 and Pesnica 4) clastic rocks prevail (Fig. 1) meaning that most of the cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) are originated in clastic rocks (e.g. sandstones, claystones, marls) and also limestone, but to a minor extent.

Table 1. Field and laboratory measurement data (T, pH, conductivity, DO), discharge data (Q), major geochemistry data (Ca^{2+}, Mg^{2+}, Na^{+}, total alkalinity after Gran, SO_4^{2-}, NO_3^{-}), stable isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$), stable isotopic composition of particulate organic carbon ($\delta^{13}C_{POC}$).

No.	Location	Date	Q (m^3/s)	T (°C)	O_2 (mg/l)	pH	Cond (µS/cm)	Cl^- (mM)	NO_3^- (mM)	SO_4^{2-} (mM)	Na^+ (mM)	K^+ (mM)	Ca^{2+} (mM)	Mg^{2+} (mM)	TA (mM)	$\delta^{13}C_{DIC}$ (‰)	$\delta\ ^{13}C_{POC}$ (‰)	**SIcalc.**	**SIdol.**	**pCO_2 (bar)**	**pCO_2 (ppm)**	**Ca^{2+}+Mg^{2+} (mM)**
1	Pesnica 1	16.2.16	6.20	5.25	n.a.	7.21	n.a.	0.33	0.19	0.25	0.42	0.05	2.27	0.50	3.88	-13.7	n.a.	-0.2	0.5	-1.96	109648	2.77
2	Pesnica 2	16.2.16	6.20	5.25	n.a.	7.22	n.a.	0.42	0.14	0.25	0.44	0.06	2.33	0.50	3.79	-14.2	n.a.	-0.2	0.48	-1.98	104713	2.83
3	Pesnica 3	16.2.16	6.20	5.20	n.a.	7.14	n.a.	0.9	0.13	0.29	0.51	0.06	2.31	0.51	3.66	-13.7	n.a.	-0.29	-1.26	-1.91	123027	2.82
4	Pesnica 4 (Biš)	16.2.16	6.22	5.10	n.a.	7.01	n.a.	0.27	0.46	0.14	0.16	0.02	1.31	0.38	1.77	-13.5	n.a.	-0.94	0.3	-2.09	81283	1.69
1	Pesnica 1	18.3.16	0.91	4.35	n.a.	7.15	n.a.	0.35	0.05	0.34	0.54	0.05	3.28	0.79	4.85	-11.4	n.a.	-0.13	-1	-1.84	144544	4.07
2	Pesnica2	18.3.16	0.91	4.35	n.a.	7.20	n.a.	0.36	0.05	0.34	0.57	0.05	3.37	0.80	5.65	-14.8	n.a.	0.14	-1.77	-1.90	125893	4.17
3	Pesnica 3	18.3.16	0.91	4.35	n.a.	7.30	n.a.	0.35	0.05	0.33	0.53	0.05	3.15	0.77	5.20	-12.3	n.a.	-0.15	-2.06	-1.80	158489	3.91
4	Pesnica 4 (Biš)	18.3.16	2.99	6.00	n.a.	7.40	n.a.	0.28	0.06	0.13	0.20	0.01	1.86	0.65	1.49	-14.2	n.a.	-0.48	-0.74	-2.56	27542	2.50
1	Pesnica 1	14.4.16	0.25	13.60	n.a.	7.12	n.a.	0.46	0.04	0.33	0.86	0.06	3.04	0.83	5.10	-11.6	n.a	0.05	0.13	-1.72	190546	3.87
2	Pesnica 2	14.4.16	0.25	13.60	n.a.	7.11	n.a.	0.47	0.05	0.32	0.89	0.06	3.13	0.83	5.20	-11.4	n.a.	0.06	0.01	-1.70	199526	3.96
3	Pesnica 3	14.4.16	0.25	13.60	n.a.	7.13	n.a.	0.40	0.00	0.32	0.65	0.06	1.74	0.79	4.50	-7.3	n.a.	-0.2	-2.14	-1.77	169824	2.53
4	Pesnica 4 (Biš)	14.4.16	1.47	15.90	n.a.	7.15	n.a.	0.20	0.00	0.04	0.19	0.011	2.01	0.77	3.80	-13.1	n.a.	-0.18	-0.77	-1.83	147911	2.78
1	Pesnica 1	16.5.16	1.69	14.00	n.a.	7.23	n.a.	0.29	0.06	0.28	0.41	0.05	1.76	0.53	3.40	-13.7	n.a.	-0.2	-1.26	-1.99	102329	2.29
2	Pesnica 2	16.5.16	1.69	14.00	n.a.	7.29	n.a.	0.33	0.07	0.29	0.52	0.06	2.61	0.64	3.50	-13.4	n.a.	0.02	-1.26	-2.04	91201	3.25
3	Pesnica 3	16.5.16	1.69	14.00	n.a.	7.31	n.a.	0.19	0.03	0,16	0.25	0.03	1.29	0.31	3.20	-7.1	n.a.	0.0	-1.44	-2.10	79433	1.60
4	Pesnica 4 (Biš)	16.5.16	4.16	14.00	n.a.	7.35	n.a.	0.19	0.25	0.114	0.12	0.01	1.27	0.38	1.24	-13.9	n.a.	-0.66	-2.61	-2.81	15488	1.65
1	Pesnica 1	13.6.16	0.18	17.10	17,60	7.50	n.a.	0.47	0.07	0.27	0.93	0.10	3.02	0.73	5.05	-12.3	n.a.	0.47	-0.24	-2.08	83176	3.75
2	Pesnica 2	13.6.16	0.18	17.10	18,70	7.52	n.a.	0.48	0.07	0.27	0.99	0.09	2.90	0.70	5.09	-12.1	n.a.	0.54	-0.53	-2.16	69183	3.60
3	Pesnica 3	13.6.16	0.18	17.10	21,20	7.58	n.a.	0.29	0.00	0.21	0.46	0.08	1.38	0.06	2.81	-4.2	n.a.	0.04	-0.23	-2.40	39811	1.44
4	Pesnica 4 (Biš)	13.6.16	0.64	17.10	17,00	7.59	n.a.	0.12	0.00	0.03	0.17	0.01	2.01	0.78	4.34	-13.1	n.a.	0.35	-1.6	-2.23	58885	2.79
1	Pesnica 1	15.8.16	0.634	17.3	21,50	7.40	n.a.	0.47	0.07	0.27	0.48	0.06	1.54	0.35	4.80	-11.8	n.a.	-0.19	-0.5	-1.69	204174	1.89
2	Pesnica 2	15.8.16	0.634	17.5	23,30	7.30	n.a.	0.40	0.01	0.21	0.34	0.05	0.84	0.28	2.70	-7.2	n.a.	-0.66	-0.5	-1.93	117499	1.12
3	Pesnica 3	15.8.16	0.058	17.6	26,40	7.20	n.a.	0.32	0.00	0.17	0.27	0.07	0.50	0.38	4.40	-8.1	n.a.	-0.98	-0.79	-2.25	56234	0.88
4	Pesnica 4 (Biš)	15.8.16	n.a.	17.7	19,70	7.3	n.a.	0.10	0.00	0.02	0.08	0.00	1.01	0.41	1.60	-13.4	n.a.	-0.19	-0.78	-1.92	120226	1.42
1	Pesnica 1	2.09.16	1.086	18.80	47.20	7.41	500	0.4748	0.07	0.41	0.47	0.05	2.11	0.43	6.69	-13.0	-27.6	0.39	-0.95	-1.85	141254	2.54
2	Pesnica 2	2.09.16	1.086	19.60	47.00	7.45	512	0.4687	0.10	0.38	0.47	0.04	2.08	0.43	5.74	-12.8	-27.8	0.32	-0.6	-1.92	120226	2.52
3	Pesnica 3	2.09.16	0.179	22.40	60.20	7.22	314	0.3690	0.05	0.27	0.29	0.06	0.96	0.28	2.97	-9.8	-28.5	-0.85	-0.64	-1.50	316228	1.24
4	Pesnica 4 (Biš)	2.09.16	n.a.	17.30	15.50	7.25	398	0.1509	0.00	0.09	0.09	0.00	1.05	0.46	4.19	-13.4	-29.5	-0.22	-1.89	-1.92	120226	1.52

n.a.-not analyzed

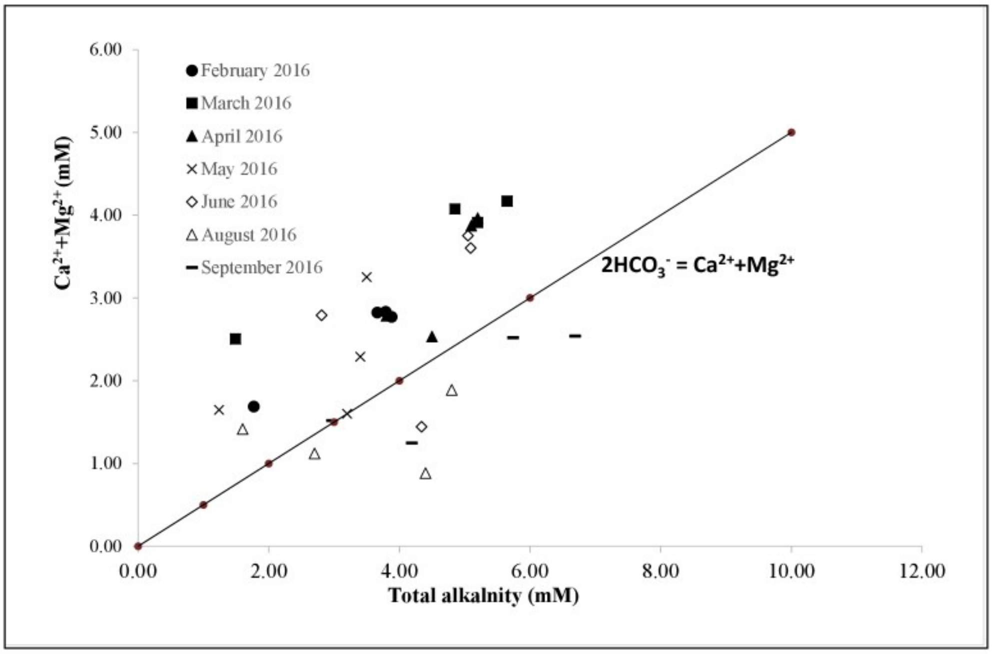

Fig. 2A. Ca^{2+}+Mg^{2+} ratio versus alkalinity with lines 1:2 indicating weathering of carbonates; deviation from the 1:2 line indicates weathering of clay minerals (albite, anortite) and mica schist (origin of K^+), which mostly contribute to alkalinity rather than to weathering of calcite/dolomite.

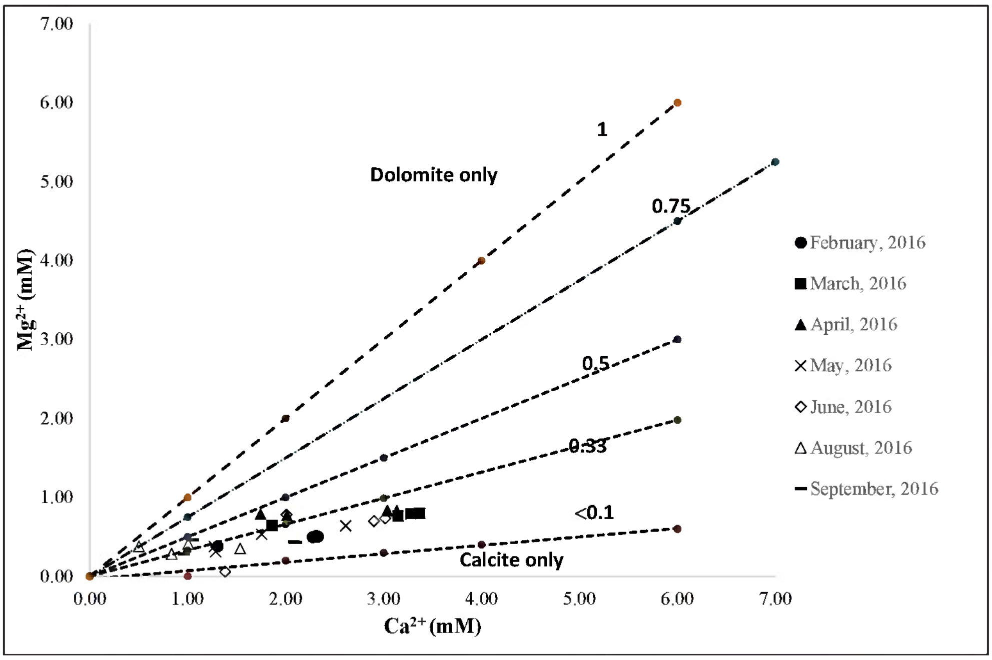

Fig. 2B. Mg^{2+} and Ca^{2+} concentrations indicating the dominance of dolomite or calcite in the Pesnica catchment

The relation of Mg^{2+} versus Ca^{2+} indicates the relative contributions of calcite and carbonate to weathering intensity in the Pesnica catchment. Most of the samples indicate that weathering of calcite is dominant over the entire Pesnica River catchment (Fig. 2B). A Mg^{2+}/Ca^{2+} ratio of around 0.33, typical for weathering of calcite with magnesium, is characteristic at all investigated locations in River Pesnica, only some samples having Mg^{2+}/Ca^{2+} of around 0.5. A Mg^{2+}/Ca^{2+} ratio of 0.33 is also characteristic of rivers comprising the Danube catchment, e.g., Sava River and its tributaries, Tisa River, Ilz River and Inn River (Kanduč et al. 2007; Szramek et al. 2007; Kanduč et al, 2013).

Thermodynamic modelling (pCO_2, $SI_{calcite}$, $SI_{dolmite}$)

From Fig. 3 it can be seen that the highest pCO_2 was observed in September 2016 with a value of 316227.8 ppm (-1.50 bar) at location Pesnica 3 and the lowest value of 15488.2 ppm (-2.81 bar) at location Pesnica 4 (Fig. 3 A, Table 1). pCO_2 concentrations in the river system depend mainly on conditions, such as temperature, pH and alkalinity. High concentrations of CO_2 can arise from higher groundwater discharge and/or respiration in streams because of the input of organic matter. All the samples were supersaturated with CO_2 with respect to the atmosphere ($10^{-3.5}$ bar = 316 ppmv) according to thermodynamic conditions in the investigated period in 2016 (Fig. 3A).

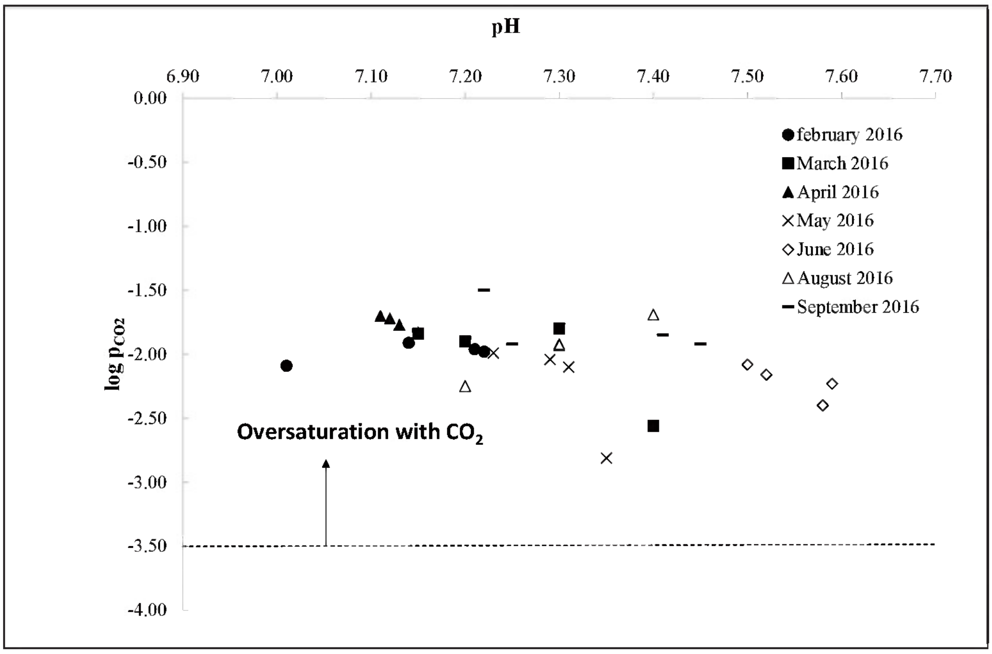

Fig. 3A. pCO$_2$ versus pH in river water system. All samples have pCO$_2$ values greater than atmospheric ($10^{-3.5}$ bar = 316 ppmv) causing increase in calcite saturation B. Saturation index of calcite (SI$_{calcite}$) versus dolomite (SI$_{dolomite}$) in river water system. Saturation for calcite/dolomite is defined as log IAP/K=0.

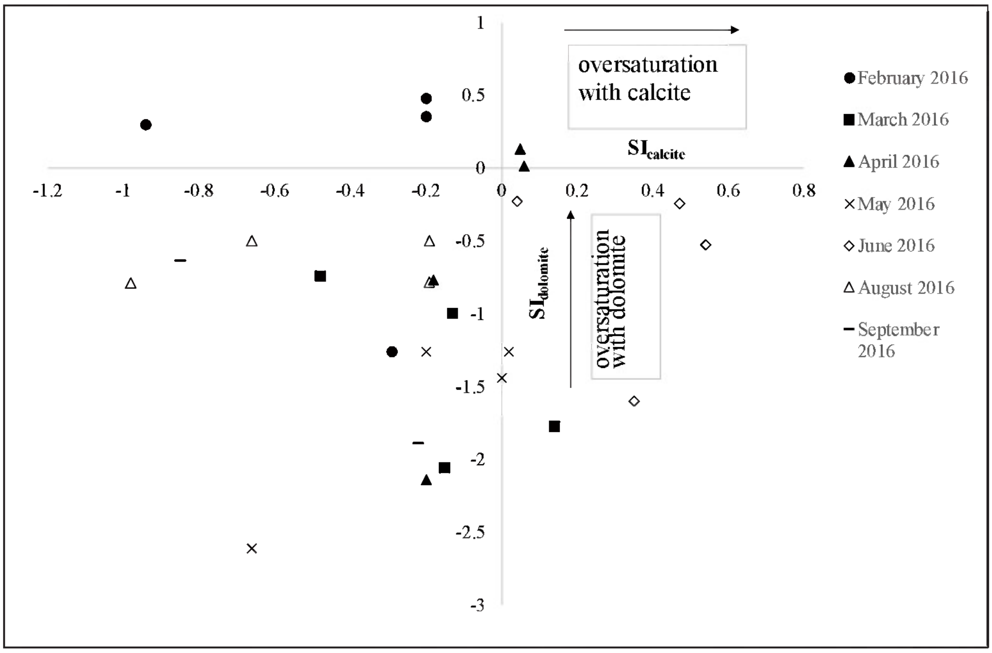

Fig. 3B. Saturation indices of calcite (SI$_{calcite}$) versus dolomite (SI$_{dolomite}$) in a river water system. Saturation for calcite/dolomite is defined as log IAP/K=0.

All samples in River Pesnica catchment were undersaturated with calcite and dolomite, only some samples in September 2016 season were oversaturated with calcite (Fig. 3B). SI$_{calcite}$ ranged from -0.98 to 0.54 and SI$_{dolomite}$ ranged from -2.61 to 0.48. It has been clearly shown that most of the investigated rivers in the world constitute sources of CO$_2$ to the atmosphere (Mayorga et al., 2005). Oversaturation with SI$_{calcite}$ is traced only in April at locations 1 and 2 before dam and oversaturation with dolomite only in June.

Isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) and particulate organic carbon ($\delta^{13}C_{POC}$)

Values of the isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) can help decipher the contributions of organic matter decomposition, carbonate mineral dissolution, equilibration with atmospheric CO$_2$ to DIC and in-stream biological processes (Kanduč et al., 2007). Figure 4 shows $\delta^{13}C_{DIC}$ versus alkalinity for Pesnica river water from February 2016. $\delta^{13}C_{DIC}$ in Pesnica catchment ranges from -14.8

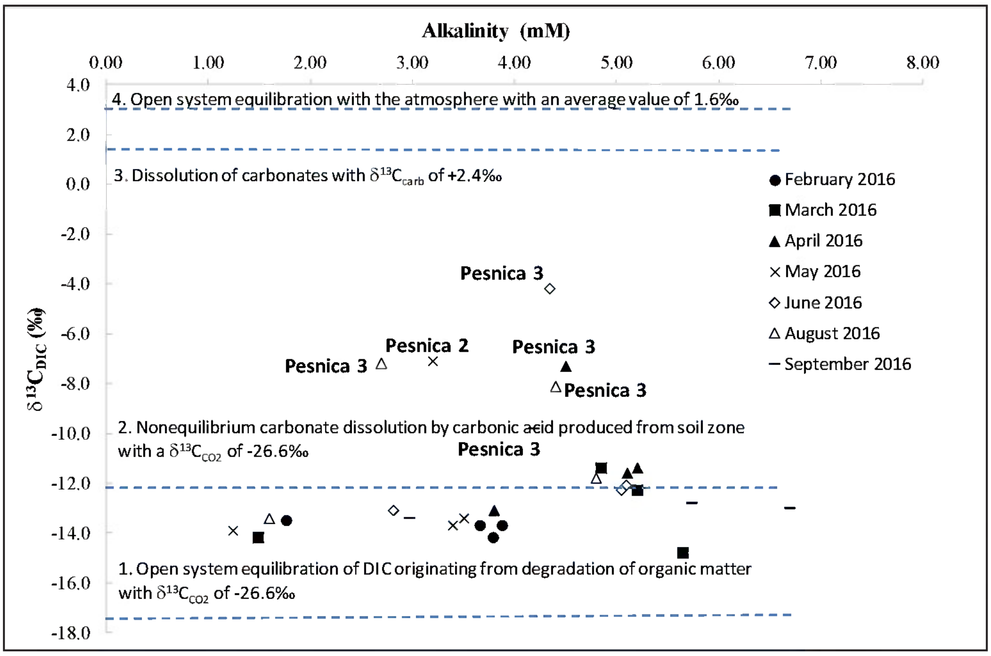

Fig. 4. Seasonal variation of $\delta^{13}C_{DIC}$ values versus alkalinity in Pesnica river water system, with lines indicating biogeochemical processes in river water. These include (see equilibration lines): 4. Open system equilibration with the atmosphere with an average valueof 1.6 ‰ 3. Dissolution of carbonates according to the average $\delta^{13}C_{CaCO3}$ (+2.4 ‰, Kanduč et al., 2013) of all measured samples composing the recharge area of river water, causing +1‰±0.2 ‰ enrichment in ^{12}C in DIC (Romanek et al., 1992), 2. Nonequilibrium carbonate dissolution by carbonic acid produced from soil zone CO_2, 1. Open-system equilibration of DIC with soil CO_2 originating from degradation of organic matter with $\delta^{13}C_{soil}$ = -26.6 ‰.

to -4.2 ‰ (Table 1). An average $\delta^{13}C_{POC}$ value of -26.6 ‰ (Kanduč et al., 2013) was assumed to represent the isotopic composition of DOC that was transferred to DIC (Dissolved Inorganic Carbon) by in-stream respiration. Open-system equilibration of DIC with CO_2 enriches DIC in ^{13}C by about 9 ‰ (Mook et al., 1974), which corresponds to the value of -17.6 ‰ shown in Figure 4. Non-equilibrium dissolution of carbonates, with one part of DIC originating from soil CO_2 (- 26.6 ‰), and the other from carbonates with an average $\delta^{13}C_{Ca}$ of +2.4 ‰, leads to an intermediate $\delta^{13}C_{DIC}$ value of -12.1 ‰ (Kanduč et al., 2012). Given the isotopic composition of atmospheric CO_2 (-7.8 ‰, Levin et al., 1987) and the equilibrium fractionation with $\delta^{13}C_{DIC}$ of +9 ‰, DIC in equilibrium with the atmosphere should have a $\delta^{13}C_{DIC}$ of about +1 ‰ (Fig. 4). Biogeochemical processes such as dissolution of carbonates and open-system equilibration with the atmosphere can be neglected in the Pesnica catchment since river water is composed mostly of clastic rocks (sandstones, marls, claystones).

Higher values of $\delta^{13}C_{DIC}$ are observed at Pesnica 3 location (March, 2016) and slightly more negative values $\delta^{13}C_{DIC}$ at Pesnica 2 (above the Pernica lake). From Figure 4 it can be seen that most of the samples from Pesnica River catchment fall around the line of nonequilibrium carbonate dissolution by carbonic acid produced from the soil zone with $\delta^{13}C_{CO2}$ of -26.6 ‰. Samples from Pesnica 3 (retention) have $\delta^{13}C_{DIC}$ values less negative up to -4.2 ‰ (June 2016) indicating that respiration can alter $\delta^{13}C_{DIC}$ to more positive $\delta^{13}C_{DIC}$ values in-stream, especially in summer months (Fig. 4). Controls of longitudinal variation in $\delta^{13}C_{DIC}$ in rivers have been studied by Roach et al., 2016. At location Pesnica 2 (before dam) and Pesnica 3 (after dam) $\delta^{13}C_{DIC}$ values are less negative indicating CO_2 reduction in river system and enrichment with ^{12}C isotope (Fig. 4).

According to the model of Devol & Hedges (2001), suspended matter (particulate in continuation) may be divided into three fraction (Kanduč, 2010 & references therein). Isotopic composition of carbon in particulate organic matter ($\delta^{13}C_{POC}$) was measured only in September and ranged from -29.5 to -27.6 ‰. At Biš location more negative $\delta^{13}C_{POC}$ (-29.5 ‰) was observed in comparison to characteristic degraded organic matter (-26.6 ‰). For comparison, the $\delta^{13}C$ value of particulate organic carbon ($\delta^{13}C_{POC}$) in the main channel of the Kamniška Bistrica River, a pre-alpine gravel-bed river with prevailing intensive agriculture in the catchment, varies from -28.6 to -25.4 ‰ and from -29.9 to -25.2 ‰ in the tributaries (Kanduč et al., 2013). Phytoplankton binds CO_2 from DIC in water leading to a ^{13}C fractionation of around -20 ‰, producing biomass with $\delta^{13}C_{POC}$ ranging from -32.0 to -45.0 ‰. At the River Pesnica catchment $\delta^{13}C_{POC}$ ranges from -27.6 to -29.5 ‰, meaning that photosynthetic activity was not so significant at our investigated locations.

Composition of suspended matter differentiates by SEM/EDXS

The composition of suspended matter differentiates from Pesnica catchment area at investigated locations: Pesnica 1, Pesnica 2 (above Pernica lake), Pesnica 3 (below the Pernica lake) and Pesnica 4- drainage channel Biš (Fig. 1). At Pesnica 1 and Pesnica 2 sampling sites (Figs. 5A, B) we can observe that aluminosilicates (K, Al, Si) prevail in suspended matter, while at sampling location Pesnica 3 we observe high biological activity (diatoms) (Fig. 5C-b) and at Pesnica 4 (drainage channel Biš) inorganic fibers prevail (Fig. 5D), which could be of anthropogenic origin. All SEM Figures have corresponding spectra, meaning that elements: Al, Si, O, K, Na, Mg prevail with traces of Ti and Fe representing detrital geological material composed of aluminosilicates (e.g. anorthite, albite, mica schist). From Fig. 5B with a corresponding spectrum, a pattern similar to that in Figure 5A is seen. Figure 5C-a with a corresponding graph shows that suspended matter is composed of diatoms; spherical structures are also observed. The spectrum shows that material is composed of Si, Al, O, Fe, K, Ca, Na, Mg (Fig. 5C-c). Diatoms are composed of Si-oxide, while spherical structures with corresponding spectrum have a microporous structure and are composed of Fe, Si, O, Ca. Fig. 5D with corresponding spectrum represents suspended matter composed of Si, O, Fe, Mg, Na, K, Ca with traces of Zn and Fe (Fig. 5D). Fibrous and microporous particles that were observed and analysed under higher magnification are composed of Al, Si, Fe and P, which could be attributed to anthropogenic input in the river system.

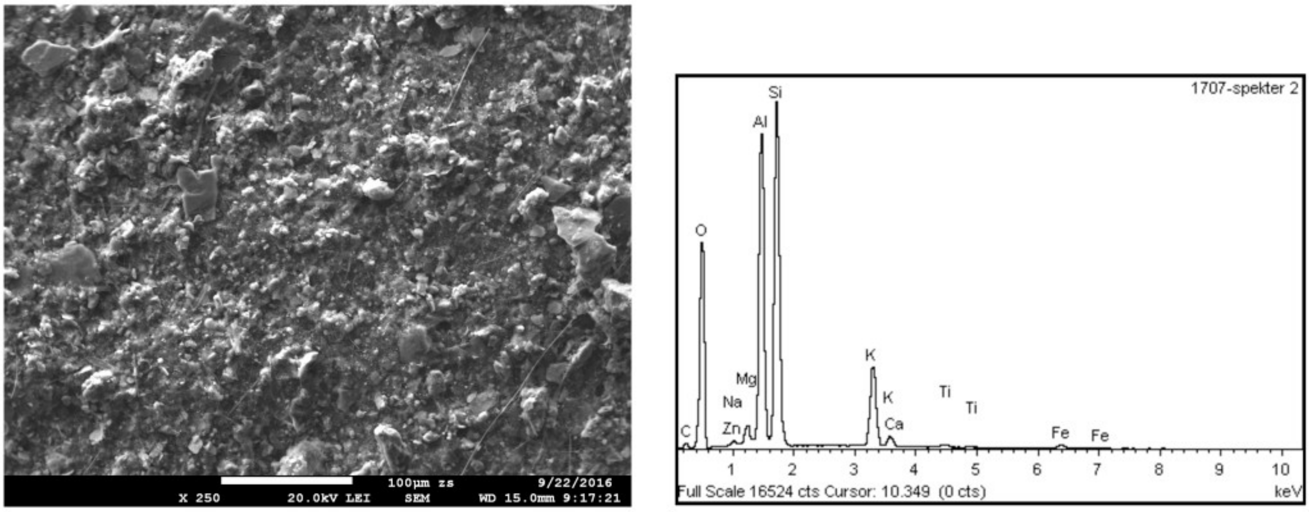

Fig. 5A. SEM micrograph and corresponding EDXS analysis/spectrum of samples of suspended matter at Pesnica 1.

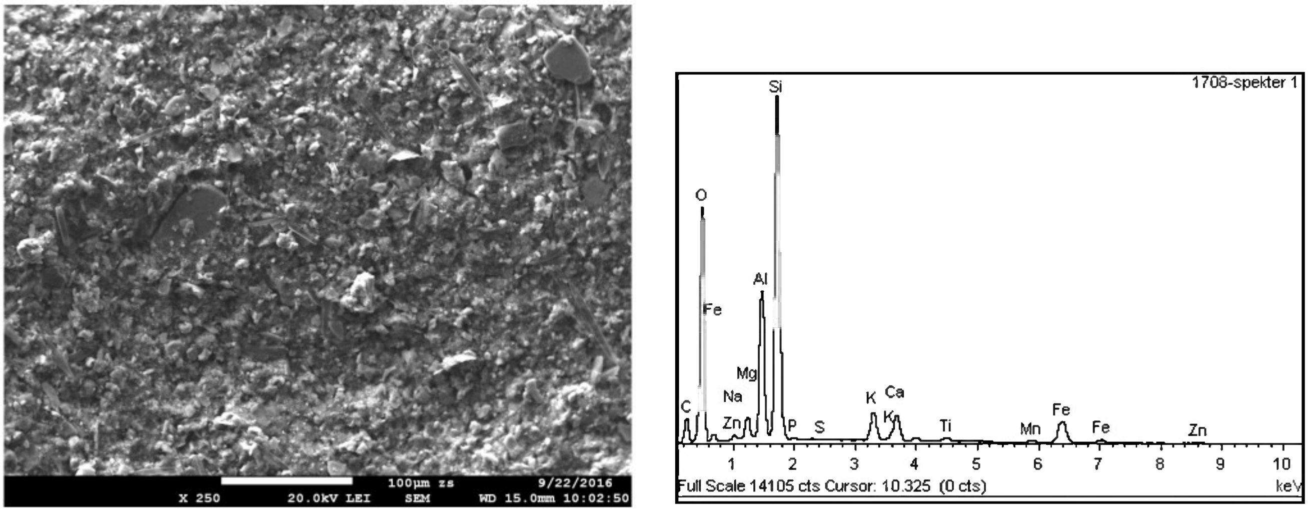

Fig. 5B. SEM micrograph and corresponding EDXS analysis/spectrum of samples of suspended matter at Pesnica 2 (above reservoir).

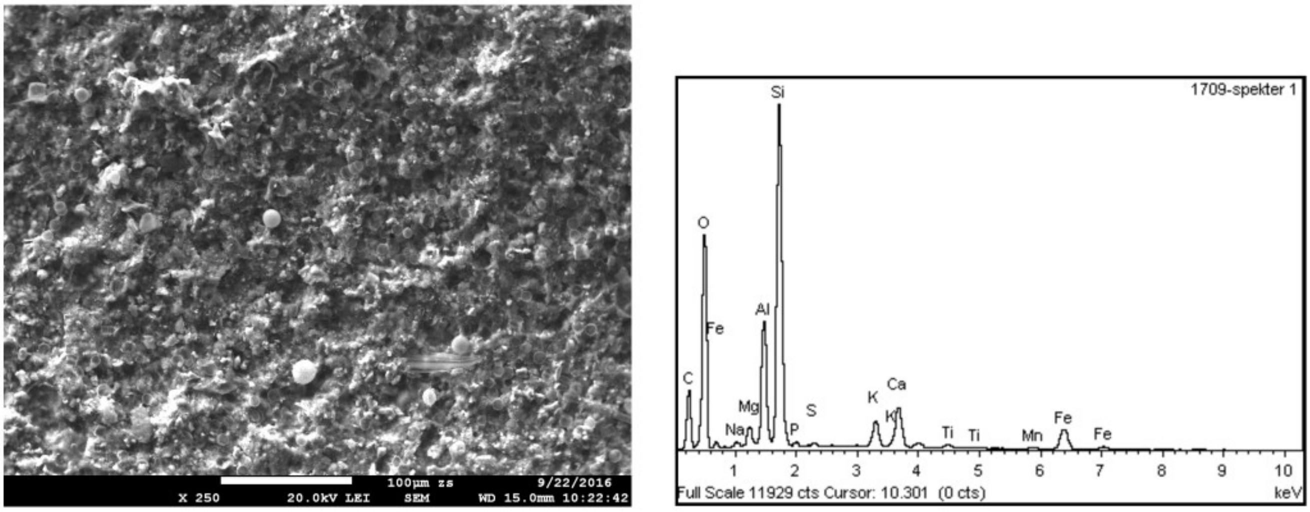

Fig. 5C-a. SEM micrograph and corresponding EDXS analysis/spectrum of samples of suspended matter at Pesnica catchment area from location Pesnica 3 (below the reservoir, retention).

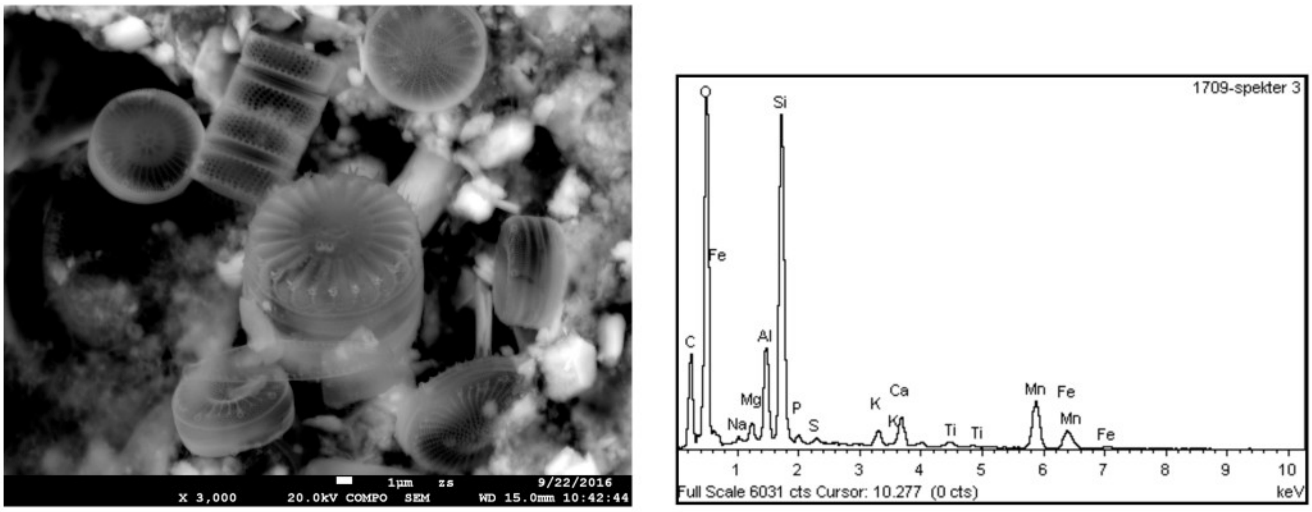

Fig. 5C-b. SEM micrograph and corresponding EDXS analysis/spectrum of samples of suspended matter at Pesnica catchment area from location Pesnica 3 (below the reservoir, retention).

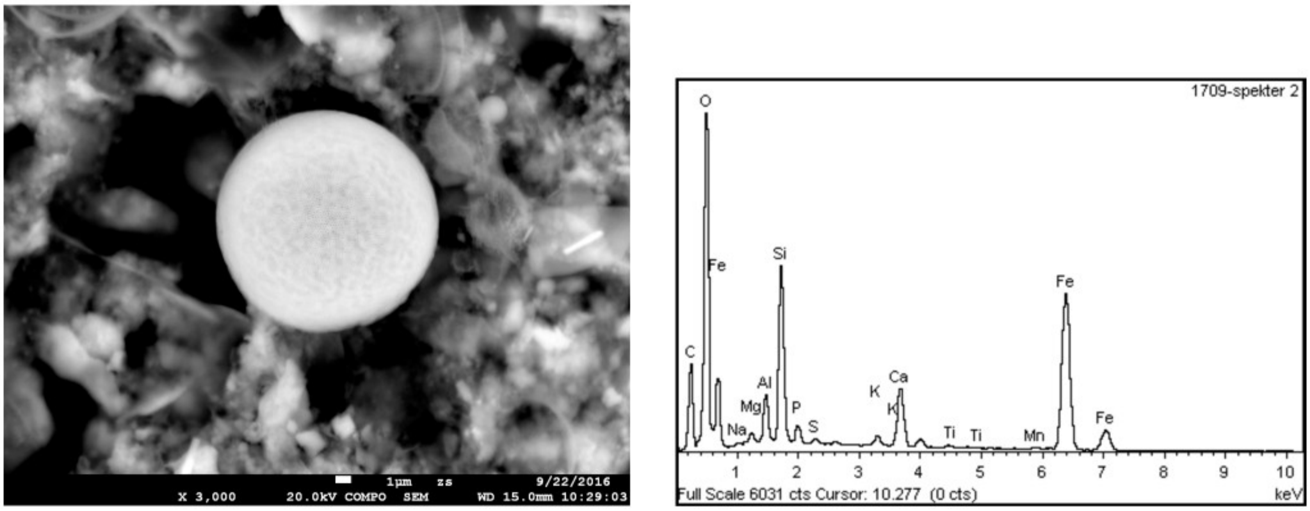

Fig. 5C-c. SEM micrograph and corresponding EDXS analysis/spectrum of samples of suspended matter at Pesnica catchment area from location Pesnica 3 (below the reservoir, retention).

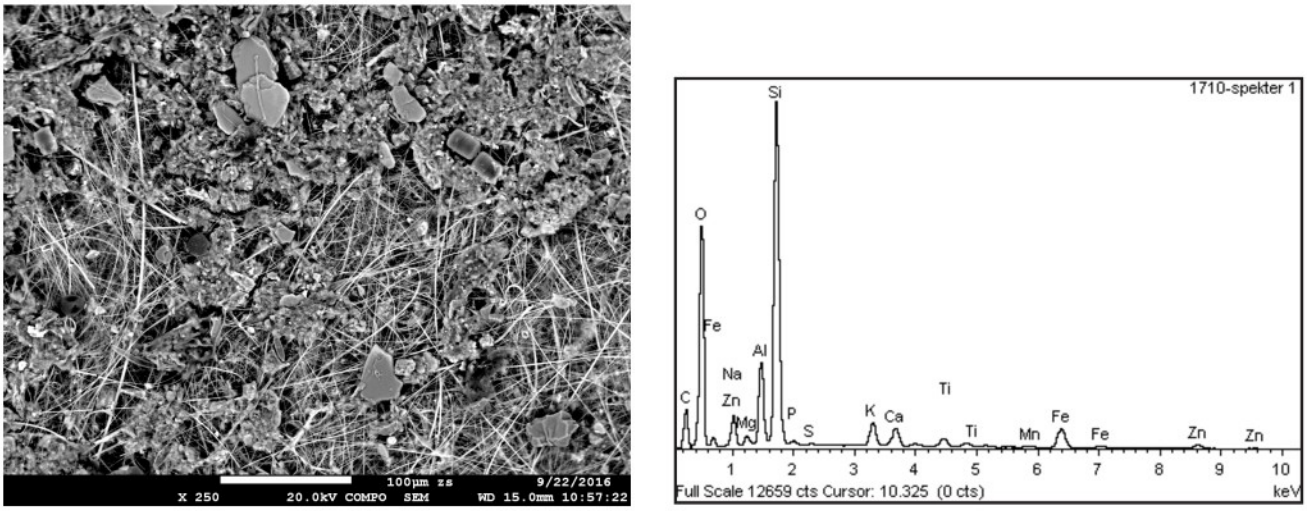

Fig. 5D. SEM micrograph and corresponding EDXS analysis/spectrum of samples of suspended matter at Pesnica catchment area from location Pesnica 4 (drainage channel Biš).

Conclusion

Pesnica River water solute chemistry is dominated by HCO_3^-, Ca^{2+} and Mg^{2+}. Seasonal (spring, summer and autumn) concentrations of total alkalinity ranged from 1.24 to 6.69 mM. From a geochemical point of view, we found out that dissolution of clastic material influences the geochemical composition of river water. Most locations of surface water were near equilibrium with respect to calcite ($SI_{calcite}$ from -0.98 to 0.54) and dolomite ($SI_{dolomite}$ from -2.61 to 0.48) in all sampling seasons or, otherwise, generally undersaturated. According to the calculated pCO_2 values, surface water is a source of CO_2 to the atmosphere. pCO_2 in Pesnica catchment ranged from 15488 to 316228 ppm. Alkalinity and isotopic composition of $\delta^{13}C_{DIC}$ values were used to trace carbon cycling in surface waters. Seasonal $\delta^{13}C_{DIC}$ values (from February 2016 to September 2016) ranged from -14.8 to -4.2 ‰ indicating different biogeochemical processes in Pesnica River catchment. $\delta^{13}C_{DIC}$ values around and below -12 ‰ indicate that the most important process in Pesnica River catchment in our study is degradation of organic matter. At a location below the reservoir Pernica lake (Pesnica 3 location), higher $\delta^{13}C_{DIC}$ values have been observed since April 2016. The highest value of $\delta^{13}C_{DIC}$ of -4.2 ‰ was observed in June 2016. This was due to the presence of large amounts of algae from phytoplankton and phytobenthos in reservoir upstream of the sampling location, as confirmed using SEM microscopy. $\delta^{13}C_{POC}$ ranged from -29.5 to -27.6 ‰ and indicated different degree of suspended material at investigated locations.

Microscopic SEM/EDXS analyses revealed that at Pesnica 1 and 2 detrital clastic material prevails in the samples, while at location Pesnica 3 phytoplantonic and/or phytobenthic algae prevail, presumably originating from Pernica Lake, while at location near drainage channel Biš, particles originating from wetland plants are observed in addition to degraded organic material.

These first results on suspended matter in the River Pesnica catchment provide first data, that will help in evaluation of anthropogenic impacts, especially in relation to future impacts and for long term planning for sustainable management (e.g. regulation of river channel, deforestation and agriculture activity). The application of stable isotopes in river management studies is useful tracer for determining the origin of dissolved solutes and evaluation of biogeochemical processes, and has been widely used in other catchments in Slovenia (e.g. Sava River, Kamniška Bistrica River, Krka River, Idrijca River).

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