Appraisal of geochemical composition and hydrodynamic sorting of the river suspended material: Application of time-integrated suspended sediment sampler in a medium-sized river (the Sava River catchment)

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ABSTRACT

The suspended particulate matter (SPM) carried by the rivers shows a wide range of particle size classes, mineralogical and chemical compositions and is mainly influenced by hydrodynamic sorting and provenance during the transport. Here, we have investigated the composition of the SPM in the Sava River and its tributaries (Ljubljanica, Savinja and Krapina) using a time-integrated suspended sediment sampler (TIMS). The representativeness of material collected by TIMS was evaluated comparing fine-grained sediments, single-point SPM and SPM collected using a shallow and deep-positioned sampler. The main results have revealed that the mineralogical and geochemical composition of the material is largely dependent on hydrological conditions. The differentiation of element composition is especially emphasized at low water stage when most of the SPM consists of slow-settling mineral phases (clay minerals and metal oxyhydroxides) which can be trapped in the sampler. During periods of high discharges, differentiation is less prominent, and homogenization of the SPM occurs, mainly as a part of bed load is also taken into suspension. These conditions have proven unfavorable for sampler efficiency, as at least part of the finest particles could not be retained. Additional issues that may occur during TIMS employment relate to biologically driven carbonate precipitation, which is triggered by changes in physico-chemical conditions at low water table in the summer period. Increased concentration of Ca, related to that process, influences the elemental composition of the SPM, which is particularly important when anthropogenic impact or sediment source is assessed. Hence, in order to interpret the geochemical and mineralogical data collected by TIMS, these factors should be taken into account. Our findings emphasize the need for detailed studies of chemical composition of the SPM (time-integrated) in medium-sized rivers and point out the significance of evaluating sampling representativeness during different hydrological conditions.

Keywords: Geochemical composition; Hydrodynamic sorting; Time-integrated sampler; the Sava River catchment

1. Introduction

The suspended particulate material (SPM) refers to particles that suspend in the water column with a lower size limit of 0.20 or 0.45 µm in median diameter (Viers et al. 2009). It consists of inorganic (quartz, feldspars, carbonates, clay minerals, metal oxyhydroxides, heavy minerals) and organic (microorganisms and detritus) particulate matter (Gregory, 2006; Garzanti et al., 2011) usually present in flocculated form (Droppo and Ongley, 1994). The SPM has a major role in transfer of elements from source to sink. According to Horowitz (1991) and Audry et al. (2004), more than 90% of the riverine flux of metals is associated with fine-grained sediment. So, when dealing with the trace elements input/transfer/transport along a river, the investigation should focus on the SPM. However, most of the SPM-bound element load is related to high flow events which are extremely irregular. Another difficulty is to collect a representative sample and sufficient amount of the SPM for analyzing different chemical and/or physical characteristics. In order to meet these requirements, Phillips et al. (2000) developed a time-integrated suspended sediment sampler (TIMS), mainly designed for streams and small lowland rivers (Schindler Wildhaber et al. 2012; Smith and Owens, 2014). Heretofore, TIMS was used in different studies (Russel et al., 2000; McDonald et al., 2010; Droppo et al., 2019) and proven effective in several environmental and controlled laboratory conditions (Martínez-Carreras et al., 2012; Marttila et al., 2013; Perks et al., 2014). The amount of material collected was found sufficient and the representativeness of TIMS was also proven satisfying. The main objections were the poor assessment of the SPM mass flux (Goharrokhi et al., 2019) and lack of knowledge of how it operates in larger river systems (Smith and Owens, 2014).

TIMS was also used in our previous research (Lučić et al., 2019) to investigate the Sava River SPM and associated anthropogenic impact. The TIMS was set at one location in the Sava River in Zagreb during different discharge periods. The results have shown increased concentrations of some ecotoxic elements (As, Bi, Cd, Cr, Ni, Pb, Sb, Zn). Some issues opened during that investigation: the input of the material from different sources during different discharge periods and high concentration of calcite in spring sampling period was observed. A possibility of *in situ* calcite precipitation instigated by algal bloom was hypothesized.

This investigation has been conducted in order to obtain more information on the hydrodynamic sorting and representativeness of the SPM (time-integrated) transported in a medium size river. The case study was the Sava River and main tributaries (Ljubljanica, Savinja and Krapina) between its source and the city of Zagreb, as an example of medium size river in the anthropogenically impacted environment. The aims of the study were:

1. to characterize the spatial and time variation of the geochemical composition of the SPM sampled by TIMS in different hydrological conditions,
2. to assess potential influence of hydrodynamic sorting on suspended material,
3. to determine possible differences between shallow and deeper suspended load using two TIMS samplers at one location.

2. Materials & methods

2.1. Study area

The Sava River is a major Danube tributary which flows through Slovenia and Croatia, alongside the northern border of Bosnia and Herzegovina, and finally through Serbia. The upper course of river is 232 km long with drainage basin covering 12680 km^2 of surface area (Table 1). Other detailed geographical characteristics of the Sava River can be found in our previous work (Lučić et al., 2019).

The Sava River has its origin as two branches, the Sava Dolinka and Sava Bohinjka rivers which flow mainly through carbonate terrain (limestone and dolostone) until their confluence at the city of Radovljica. From there, the river passes through previously deposited fluvio-glacial terraces which alternate with Paleozoic rocks consisting of shales, quartz sandstones and conglomerates. Besides Permo-Carbonian clastic sediments, the central part of the Sava section in Slovenia is composed of Triassic carbonates, together with Paleogene and Neogene clastic rocks in the area before the border with Croatia (Placer, 2008). In Croatia, the drainage area of the river comprises terraced Quaternary deposits consisting of sands, marls and clays (Šikić et al., 1979).

The Ljubljanica River flows through Ljubljana Moor, paleo-swamp filled with Quaternary alluvial sediments (pebble, sand and clay) covering Paleozoic basement and Mesozoic limestone and dolostone. Because of the considerable thickness of fluvio-glacial sediments, the Ljubljansko Barje is one of the most important aquifers in Slovenia (Cerar and Urbanc, 2013).

The Savinja River, the second longest Slovenian river originates in the Kamnik-Savinja Alps in Triassic carbonates and flows through Oligocene tuffs and andesites, while in the lower part drains the Triassic carbonates and Miocene sandstones. As a result of its runoff characteristics, its catchment area contributes up to 40 % of the lower Sava River (in Slovenia) discharge in high rainfall events (Kobold and Sušelj, 2005).

The Krapina River has its origin in the Paleogene and Neogene of the Panonnian Basin. On the left side of the flow, the Krapina River is filled by many streams that drain the Medvednica mountain, consisting of rocks of different ages (from Silurian to Quaternary age) (Galović and Peh, 2014).

2.2. Sampling and preparation of samples

The design and principles of TIMS are thoroughly described in the papers of Philips et al., (2000) and Russel and Walling (2000). It is a PVC cylinder of 100 cm in length and 10 cm diameter, closed on one side with a simple screw cap and at the other with the conus shaped screw cap. At the center of each cap there is a 4 mm opening to allow the passage of water. The sampler is positioned parallel to the flow of the river with the conus part pointing opposite to the flow direction. Within the main body of the sampler, the flow velocity is reduced by a factor > 600, which induces sedimentation of the suspended sediment.

The sampler is intended to collect river suspended sediment in a prolonged period. The resulting composite sample integrates natural variations in the geochemical properties of sediment transported during different runoff events. The sample mass collected by the sampler is sufficient to satisfy a wide range of laboratory analyses. Samplers used in this study were slightly modified - we used larger inlet and outlet (6 mm diameter), while tube diameter was 11 cm in width.

Sampling was conducted during a hydrological year with campaigns organized from October 2016 to July 2017 at different frequencies (Table 2); at least two sampling campaigns were performed at each site. The samplers were positioned at five locations (Fig. 1). At four of the chosen locations, TIMSs were fixed by steel uprights near the riverbed since river channels were too shallow for two samplers. At Zagreb location, TIMS was tied under the pontoon and sunk 30 cm below the water surface. During the spring and summer periods, an additional sampler was fixed closer to the river bottom. The intention was to collect and compare shallow and deeper suspended load at the same location.

Figure 1.

Besides suspended material collected by TIMS, in the period of time-integrated sampling at the Sava River, single-point samples of suspended material were also taken, as well as the bottom river sediments. The frequency of sampling is shown in Table 2.

The sediments were sieved through a 63 μm sieve, using ambient water, to separate coarse sand fraction and approximate the sediment sample to TIMS and single-point samples; the fraction <63 μm was kept for analyses. The samples were used wet for the particle size analysis; for all the other analyses the material was freeze-dried (FreeZone 2.5; Labconco) and ground to fine powder using a ball-mill (Pulverisette 7; Fritsch).

For the single-point SPM samples, river water was taken in plastic 6 dm^{-3} bottles. A portion (500 cm^3) of each sample was used “as is” for the particle size determination; the rest of the samples was subsequently filtered in laboratory (0.45 μm cellulose acetate, Sartorius). The material remaining on the filter was then dried at 60°C and kept for the element analysis.

Materials collected by TIMS were transferred into large glass beakers and left to settle; the supernatant was then carefully decanted and sedimented material kept for analyses. A portion of sedimented material (~2g) was used “as is” for the particle size determination and the rest of it was freeze-dried for other analyses.

2.3. Methods

Particle size distribution (PSD) was determined using a laser-based particle size analyzer (LS 13320; Beckman Coulter Inc.). The PSD was calculated using Mie theory of light scattering (optical parameters: refractive index = 1.53; absorption index = 0.1). PSD was determined for the samples in their native state as well as for the organic-free samples. To remove organic matter, samples were treated with 15% H_2O_2.

The mineral composition was identified by X-ray powder diffraction using a Philips X-Pert MPD diffractometer (40 kV, 40 mA, range scanned 4–63° 2θ). Bulk composition of 10 TIMS and 7 sediment samples was determined. For 6 chosen TIMS samples, the clay fraction (< 2 μm) was separated by centrifugation and analyzed on oriented slides after being air-dried, saturated by ethylene glycol, and heated for 1 h at 400° and 550°C. Proportions of minerals were evaluated semi-quantitatively using distinctive peak areas (Moore and Reynolds, 1997; Kahle et al., 2002), weighted by Schultz (1964) empirical factors, which represents rough estimate of mineral percentages.

Prior to geochemical analysis, sediment and TIMS samples were digested in the Microwave digestion system Multiwave 3000 (Anton Paar) by a two-step procedure:

1) 5 cm^3 HNO_3 (65%, pro analysi, Kemika) + 1 cm^3 HCl (37 %, VLSI Grade, Rotipuran) + 1 cm^3 HF (47-51%, supra pur, Fluka);

2) 6 cm^3 H_3BO_3 (≥99.5%, Sigma-Aldrich).

Due to small amount of sample, single-point SPM samples were dissolved by modified procedure:

1) 4 cm^3 HNO_3 + 1 cm^3 HCl + 0.2 cm^3 HF;

2) 1.25 cm^3 H_3BO_3.

Multi-elemental analysis of dissolved and particulate fraction was conducted using a High-Resolution Inductively Coupled Plasma Mass Spectrometer (HR ICPMS), Element 2 (Thermo Finnigan). Analytical quality control was provided by simultaneous analysis of blanks and certified reference material (Soil-NCS DC 77302) for which good recoveries (90-100 %) were obtained, depending on the element measured. Details of the method are provided in Fiket et al. (2017).

The hydrological data were provided by Meteorological and Hydrological Service of Croatia (DHMZ) and Slovenia (ARSO). Discharge measurements were performed by conventional current meter method. The SPM concentration was measured daily by filtration of surface water samples taken in the middle of the river course, 10 – 20 cm below the water level.

Statistical treatments were performed using a R package “robCompositions” while heat-maps were designed in package “gplots” in R platform (R Core Team, 2017).

3. Results and discussion

3.1. Hydrological and particle size characteristics

Five sampling campaigns conducted in Zagreb encompassed a wide spectrum of discharges and concentrations of suspended material (Fig. 2). Except for the calm summer period, all seasons were characterized by at least one increase in water discharge followed by corresponding variation of the SPM content. Ljubljanica and Savinja rivers have revealed similar trends of discharge fluctuations (Fig. A.1 and A.2). Somewhat different hydrological conditions were observed for the Krapina River in which high SPM concentration did not always follow the rise of the water level (Fig. A.3), mainly as a result of different sediment sources (Morehead et al., 2003).

Figure 2.

In the Sava River SPM, TIMS and sediment samples, predominant particle-size fraction was silt, regardless of the sampling period (Appendix B; Fig. 3). Sediments were dominated by finer particle size ranging from 11.1 to 34.7 µm, compared to single-point SPM (19.6 – 56.3 µm) and TIMS samples (40.6 – 56 µm). After organic matter removal, a notable increase in clay content and consequently lower mean grain size (Mz) was observed in all samples. These changes were more pronounced in TIMS samples than in sediments, which indicates that the flocculation process took place inside TIMS. Also, lower Mz in treated sediments compared to TIMS samples suggests that the part of the finest material carried in suspension could have passed through the sampler in case of a high flow rate. The flocculation of the SPM in the river channel could not have been be documented since the material retrieved from the single-point SPM sampling was not sufficient to apply H_2O_2 treatment. However, the differences in the PSD of 6 single-point SPM samples retrieved in Sava Zagreb, and comparable Mz results between single point SPM and TIMS, imply the presence of flocculation at least in some seasons.

Figure 3.

For the other rivers, the sediment particle size showed comparable variations (Appendix B), Mz of the Ljubljanica River ranging from 15.8 to 23.1 µm, similar to Savinja (15.4 – 23.2 µm) and Krapina rivers (15.1 – 18.4 µm). Regarding TIMS samples, the ones from the Krapina River had lower Mz (19.5 – 44.2 µm), compared to those from Savinja (24.7 – 71.6 µm) and Ljubljanica rivers (64.9 – 102.3 µm). In all H_2O_2-treated samples there was a decrease in Mz. The presence of coarser particles in TIMS of the Savinja River was a result of its stronger erosive power emphasized during the high-water level when the part of the bed load could also be taken into suspension (Singh, 2009). The abundance of sand-sized particles in all samples of the Ljubljanica River was largely the effect of erosion of soil aggregates along the watercourse (Woodward and Walling, 2007).

Grain-size data obtained for the shallow (TMZG4) and deep-positioned (TMBZG4) TIMS in Zagreb during the spring campaign differ in higher proportion of sand observed in deep-positioned sampler. In the summer sampling campaign deep-positioned TIMS (TMBZG5) contained higher share of clay fraction. However, when treated samples were compared, Mz in shallow positioned TIMSs decreased substantially while no such effect was observed for deep-positioned TIMSs. This could be related to the transport of aggregated soil particles in shallow relative to deeper load which contained more sand consisting of quartz, carbonates, tectosilicates and heavy minerals.

3.2. Mineralogical characteristics

The minerals present in all analyzed samples were quartz, calcite, dolomite, phyllosilicates and feldspars (Fig. 4). The most abundant minerals in sediment samples of the Sava River were quartz, calcite and dolomite. The dominance of each of them alternated, depending on the sampling period. In general, the highest amount of quartz was found in deeper positioned samplers and two shallow samplers from the late autumn and spring sampling campaigns. Regarding shallow positioned TIMS, higher quartz content probably resulted from stronger erosive power during high discharge. In such conditions, material is not sufficiently differentiated, mainly because of minimal chemical weathering and the dominance of physical erosion in the source area.

The origin of carbonates in the Sava River SPM and sediments is mostly detrital. Variation of dolomite content in TIMS samples can be related to both source supply and hydrodynamic sorting; higher density of dolomite affects its accumulation in finer sand and coarser silt classes (Garzanti et al., 2009; Garzanti and Ando, 2019). The origin of calcite could be double-natured. As assumed for the other minerals, in most of the sampling periods calcite was undoubtedly detrital in origin. Nevertheless, the high content of calcite found in sediment (55%) and shallow-positioned TIMS (69%) might be related to biologically mediated precipitation process (Olivier et al., 2011; Lučić et al., 2019) instigated in the summer period.

The higher content of phyllosilicates in TIMS compared to sediments was observed in periods of lower water discharges which suggests that phyllosilicates have preferential transport in surface load and have a good possibility to be retained in the sampler at slow flow rate. Their low content recorded in the SPM and sediment samples of the first and final sampling campaign was a consequence of dilution effect, mainly controlled by calcite and quartz abundance. Feldspar minerals did not show any variation visible from mineralogical analyses.

Clay mineral composition obtained for TIMS samples of the Sava River was characterized by prevalence of illite/mica minerals, followed by chlorite, smectite, kaolinite and vermiculite, present only in the summer sampling period (Table A.1). The comparison of clay minerals in shallow and deeper positioned TIMS, showed a higher amount of illite/mica and the absence of kaolinite in the latter, which implies that kaolinite does not prefer deeper transport (Gippel, 1995).

The slightly lower carbonate content was detected in all tributary samples, as the consequence of more siliciclastic lithologies (Fig. 4). All minerals showed opposite behavior relative to quartz. Additionally, TIMS samples had an increased quartz content compared to sediments. These results were corroborated with grain size analysis which reflected coarsening of the TIMS samples during high water stages.

Figure 4.

3.3. Geochemical composition of suspended material

The geochemical composition (50 elements) of the analyzed suspended sediments is given in the Appendix B. The comparison of TIMS samples showed a higher average Ca (107342 mg kg^{-1}) and Mg (22761 mg kg^{-1}) concentrations in the Sava River than in TIMSs positioned at other locations (Ca – 68310 mg kg^{-1} and Mg – 17716 mg kg^{-1}); the highest concentrations were observed during the summer sampling period, which corroborated mineralogical records. Magnesium concentrations proved to be sensitive to hydrodynamic sorting with the highest values in TIMSs during the greatest discharge in the Sava (26482 mg kg^{-1}) and Savinja (27506 mg kg^{-1}) rivers. Other major elements (Al, Fe, Ti, Na, K), being the part of aluminosilicates, showed the behavior opposite to Ca and Mg, with the highest concentrations in samples of the Krapina River. The rare earth elements (REE) and most of the trace elements displayed the highest concentrations in samples with more Al and Fe content.

3.4. Correlation analysis

Besides absolute element concentrations, geochemical data were also considered in terms of their composite nature (Reimann et al., 2012). This means that each variable is part of a whole and carry only relative information (Pawlowsky-Glahn et al., 2015). To follow this definition, before correlation analysis, we transformed geochemical data using special type of log-ratio transformation, called symmetric coordinates (balances), where elements are arranged according to a clustering procedure (Kynčlová et al., 2017; Reimann et al., 2017). The correlation analysis (Fig. 5) was conducted separately for all analyzed types of samples; A) TIMS, B) single-point SPM and C) fine-grained sediments. In these graphs, a similarity between TIMS and single-point SPM was observed. Fig. 5A (TIMS) is characterized by two large clusters. Starting from the upper-right corner, elements indicate their geogenic nature. Strong clustering is determined for Ga, Sc, V, Ni, Ge, Ti, Li, Al, Rb, K, LREE, Th, HREE, Nb, Y, and to a lesser extent for Tl, U, Cs and Mg, which are mostly detrital in origin. The second smaller subcluster consists of Fe, Na, and Cr, the presence of which is assumed in multiple mineral phases (phyllosilicates, feldspars and heavy minerals). Sr and Ca indicate their incorporation into the carbonate minerals, mostly calcite. The second large cluster of elements (Co, Ba, Pb, As, Mn, Bi, Be, Cd, Mo, Sn, Sb, Zn, Cu and W) probably emphasizes their anthropogenic nature and association with the finest particles (Chen et al., 2014).

In a single-point SPM (Fig. 5B) elements such as LREE, Th, Ga, Li, HREE, Al, V, Y, Nb, Ti, Sc, Cs, Tl, Ge, Rb, Co, Be, Ba, Na, W, Cr and Fe show moderate to strong mutual positive correlation, which suggests their association with clay minerals, oxyhydroxides and organic matter. Because most of the single-point samples were taken during low water level and strictly in a shallow part of the flow, this group represents geogenic element association dominating in a wash load where quartz, tectosilicates, heavy minerals and other fast-settling phases are sparse. The last cluster consists of two smaller ones. The first one is carbonate and feldspar related, and consists of U, Mg, Ca, Sr, K and Pb (Garçon et al., 2014); the second one is dominated by mainly anthropogenic group of elements which tend to concentrate in the finest part of shallow suspended load, such as Ni, Sn, Bi, Cd, Sb, As, Mn, Cu, Zn and Mo.

The fine-grained sediments (Fig. 5C) display somewhat different clustering and not so pronounced correlations. The upper-right corner suggests agglomeration of elements solely detrital in origin. Moreover, the strong positive correlations of Ti, W, Nb, Ge and Na probably suggest their presence in heavy minerals and tectosilicates which tend to concentrate in deeper suspended load (Garzanti et al., 2011). The second smaller subcluster consists of Ga, LREE, Li and Al mainly associated with clay minerals. An association of elements such as V, Fe, Cr, Sc, As, Pb, Co, Sb, Y and HREE may imply mafic component, especially within sediments of the Savinja and Krapina rivers (Salminen et al., 2005). The heat-map of fine-grained sediments does not reveal a prominent anthropogenic association of elements. Rather, they are positioned within the group of elements mostly related to phyllosilicates and feldspars (Rb, Be, Tl, Cu, Bi, Th, K, Ba, Zn, Mn and Cs). The second large cluster consists of two subclusters and point out carbonate components more dominant in the Sava River. Association of elements Cd-Sn is partly influenced by anthropogenic impact. Except for Sn, all grouped elements (Ni, Sr, U, Mg, Cd, Mo and Ca) have a similar ionic radius and can be incorporated into carbonates (Rambeau et al., 2010; Lerouge et al., 2017)

Figure 5.

3.5. Geochemical normalization

To assess the representativeness of time-integrated sampler for sampling in the Sava River and tributaries, we compared the geochemical composition of the material collected by shallow-positioned TIMS to other sampled material (fine-grained sediment (< 63 μm), deep-positioned TIMS and single-point SPM samples). In this way, important information about geochemical similarity/dissimilarity between material captured in TIMS and other materials present in a water column during different hydrological cycles could be attained. During low discharges, the most of fine-grained sediment is settled to the bottom, and clay/organic particles prevail in suspension. Somewhat different behavior can be observed during the turbulent water conditions when most of the fine-grained sediment, along with the part of fine sand, becomes the main component of the suspended load. Taking into account these components, we have covered all the material on the vertical profile and can reasonably conclude on the representativeness of the material collected by TIMS. The cross-section sampling was not performed; it is assumed that fine-grained material is rather homogeneously distributed across the horizontal profile (Walling et al., 2000; Perks et al., 2014). The geochemical normalization of materials was performed using enrichment factor (EF); all elements in a single-point SPM (average concentrations of all samples except during high water level) and fine-grained sediment were doubly-normalized to TIMS sample using a formula:

$$EF(E) = (E/Al)_{SPM/sediment} / (E/Al)_{TIMS} \quad [1]$$

where E is the element of interest normalized to insoluble element (Al) to minimize dilution caused by quartz, carbonates, or organic matter. Here, Al is chosen as the best reference non-mobile element, which is minimally affected by hydrodynamic sorting (Garzanti et al., 2013). EF > 1 indicates enrichment of element compared to TIMS, while EF < 1 indicates a depletion.

3.5.1. The Sava River

The chemical composition of suspended sediment usually changes throughout the hydrological cycles (Viers et al., 2008). The temporal variability of flow can cause sorting processes that are responsible for the geochemical differentiation of suspended material based on hydrodynamic properties. During the first autumn sampling campaign (Fig. 6A) the normalized elemental composition of sediment shows enrichment pattern for Co, Sn and Pb. Even though all analyzed materials are under the anthropogenic impact (Milačič et al., 2017), these anomalies suggest that the sediment is more influenced by anthropogenic contamination than the material collected by TIMS. In addition, slight enrichment of Cs, Be, LREE, Th, U, Mo, Fe, Ni, Cu, Zn, Ga and Tl in sediment compared to TIMS is related to elements mainly hosted in micas or associated with clay, Fe-Mn oxyhydroxides and organic matter, which indicates a minor loss of the suspended particles from the sampler. Contrary to sediment, an average of elements in all single-point SPM samples (average of 5 samples) shows lower concentrations of Na, Rb, Mg, Ca, Sr, Ba, Sc, Y, Eu, Lu, Ti, V, Nb, Cr, W, Co, Ni, Ge, Sn, and higher concentrations of K, Be, Th, Mn, Zn and Pb in relation to TIMS. The depletion of the first group of elements is caused by their tendency to accumulate in deep suspended load (Garzanti et al., 2011; Bouchez et al., 2011; Wu et al., 2013) and due to their hydrodynamic properties could be captured in the sampler at high water level when the part of bed load is also taken in suspension. It is assumed that Ca, Mg and Sr are mainly hosted in carbonates, Na, Sr and Eu in tectosilicates, while Lu, Ti, Nb, Cr, Ni, Ge and Sn can be hosted partly in ultradense minerals. Higher enrichment of Mn in single-point SPM is a result of its presence in clay minerals and oxyhydroxides, which dominate in a shallow suspended load and are likely to escape from sampler. Nevertheless, the normalized pattern of average SPM assumes reasonably good representativeness of material collected by TIMS.

Figure 6.

The second autumn sampling campaign (Fig. 6B) is characterized by more extreme hydrological conditions (Fig. 2). In that period, single-point SPM was sampled mostly at medium discharges. When compared to TIMS, sediment displays a similar pattern as observed in the previous period, i.e. minor enrichment of mostly geogenic (Na, Mg, REE and Th) and some of anthropogenic elements (Ni, Zn, Cd, Sn, Pb and As). With respect to most of the naturally-derived elements (from Li to Nb, W, Fe, Ga and Ge), average SPM values show good similarity to TIMS. Moreover, the SPM at high water level does not show significant enrichment which suggests that most of the material is captured inside the sampler. Depletions of Mg, Ca, Sr could be explained by more siliciclastic supply in conditions of high discharges, when the Sava River brings more material from the upper reaches. Opposite variations of Mo, Mn, Cu, Zn and Cd during high and low water levels are probably a consequence of their different source nature. During high discharges, the SPM is mainly detrital in origin and metal-poor (Ollivier et al., 2011). Contrary, low water conditions are characterized by metal-rich fraction which tends to adsorb onto clays, oxyhydroxides and organic matter (Horowitz and Elrick, 1987; Baran et al., 2019). Based on that, we can assume that TIMS sample represents averaged out SPM composition fairly well.

In the winter sampling period (Fig. 6C), single-point SPM samples were collected during low discharges (Fig. 2). In these conditions, for most of the period, the lowest SPM concentration was observed. Here geochemical differences between different water stages are more pronounced. High enrichment patterns for Mo, Mn, Ni, Cu, Zn, Cd, Sn, As, Sb and Bi at low water stage may emphasize prominent instant anthropogenic input and preferable adsorption onto clays/oxyhydroxides. During high discharges, siliciclastic and detrital influence is more visible from the depletion of Mg, Ca and Sr in comparison to the previous sampling period. Grain-size and mineralogical data suggest a good representativeness of material captured in the sampler. This is because both analyses showed a higher amount of clay fraction and phyllosilicates (Fig. 3 and 4) compared to sediment. Also, this is supported by no enrichment patterns in average SPM for most of the geogenic elements (Li. Na, K, Rb, Cs, Be, Ba, Sc, REE, Th, Ti, V, Nb, Fe, Ga and Ge). However, geochemical normalization of high water SPM and sediment samples showed slight enrichments of REE and Th in relation to TIMS. According to Garzanti et al., (2011) these elements can be enriched in both, shallow and deeper suspended load, mainly as a result of provenance effect, concentration in ultradense minerals, phyllosilicates and organic matter. Herein, we assumed that enrichment in SPM/sediment sample could reflect instant provenance signal and scavenging of Th and particularly MREE (Sm, Eu, Gd and Tb) onto Mn/Fe-oxyhydroxides and clays (Quinn et al., 2006).

The spring sampling campaign (Fig. 6D) is characterized by calm hydrological conditions, disturbed during the last three days of sampling (Fig. 2). In this period, the highest discharge and SPM concentration were observed. The results obtained for sample from deep-positioned TIMS corroborated previously stated inferences about hydraulic behavior of elements; enrichment/accumulation of Na, Mg, Ca, Sr, Ba, Ti, Nb, Cr, Ge and Sn in the bed load. Other enriched values of REE, V, Fe, Co, Ni and Cu suggest that these elements are not solely dominant in a shallow load, but also partly transported in a deeper load hosted in heavy minerals (Garzanti et al., 2011). Based on slight enrichment of mostly geogenic elements (K, Rb, REE, U) in sediment and SPM at high water stage, together with lower mean particle-size observed in sediment sample, a minor loss of finest particles from TIMS is presumed. Similarly to previous sampling period, consecutive enrichments of Mo, Mn, Ni, Cu, Zn, Cd, Sn and Pb are observed. This may suggest that comparing potentially anthropogenic elements in different materials should be taken with care since this group of elements represents fraction more sensitive to physico-chemical changes (pH, redox condition, temperature, electric conductivity, a form of elements, etc.) in water. Therefore, in evaluating time-integrated sampling in human-impacted rivers, focus should be put on naturally-derived elements that are more stable and associated with the residual fraction (Aguilar-Hinojosa et al., 2016; Baran et al., 2019).

As discussed earlier, the summer sampling period (Fig. 6E) was characterized by low discharges and unusually high concentration of Ca in shallow-positioned sampler. Considering that Ca tends to accumulate in coarser sediment fraction, that may imply the origin of Ca different than only detrital (Chen et al., 2014). An explanation could be intense biological production at low water stage during which the elements are accumulated by the long-chain organic acids (Rogerson et al., 2008). In addition, slow-moving water conditions in the sampler promoted biogenic calcite precipitation (Olivier et al., 2011), which resulted in unusually high concentration of calcium. These processes invoked the disturbance of the chemical composition of collected material which made the conclusion about sampler's representativeness more difficult to reach. This is most apparent in higher enrichment of all elements (except Ca and Mn) in the sediment compared to TIMS – that would imply the loss of fine material from the sampler which is in contradiction with the PSD results. Higher clay fraction content was determined in shallow TIMS after H_2O_2 treatment than in sediment, which suggests good effectiveness of TIMS in these low water conditions. However, high Ca content and the evidence of flocculation may mask the real characteristics of the collected material. Therefore, an estimation of the chemical composition in the summer sampling campaign should be interpreted with caution.

For the sampling location Radovljica (the Sava River headwaters), a smaller range of elements was analyzed (Fig. 7A). The results of single-point SPM have emphasized enriched patterns of mostly anthropogenic (Ni, Cu, Zn, Cd and Pb) and naturally derived (Rb, V and Mn) elements. As aforementioned, these disparities are related to organic- and metal-rich fraction abundant at low water levels. By observing grain-size distribution of the sediment samples, TIMS could be evaluated as quite effective. Higher Cr values may reflect anthropogenic impact (Milačić et al., 2017) or appearance of mafic minerals that concentrate at the riverbed (Hinterlechner-Ravnik and Pleničar, 1967; Garzanti et al., 2011).

Figure 7.

3.5.2. Tributaries

The results of normalized diagrams of the Ljubljanica, Savinja and Krapina rivers have shown somewhat different EFs compared to the Sava River (Fig. 7B, C and D). These tributaries have a dissimilar morphology and shallower channels, which promotes coarser particles to be collected by TIMS. This can also explain high quartz content determined in TIMS samples. Discrepancies found between single-point SPM and sediments reflect the influence of hydrodynamic sorting on geochemical and mineralogical composition. Because single-point SPM was collected only during low water stage, most of the particles that contain geogenic elements are likely to be captured by TIMS.

TIMSs positioned in the Ljubljanica and Savinja rivers (Fig. 7B and C) were characterized with higher concentration of Be and W, particularly in the summer period. The most probable explanation would be their interaction with organic matter (Tuna et al., 2012; Boschi and Willenbring, 2016) or the adsorption on the secondary Fe-Mn oxyhydroxides (Armiento et al., 2013; Bauer et al., 2017), rather than the selective entrainment of heavy minerals (Garzanti et al., 2010). As mentioned earlier, long-time sampling inside TIMS can probably cause a change of physico-chemical conditions at the sediment-water interface. The reductive dissolution of oxyhydroxide particles below this layer releases soluble Mn and induces its upward moving into the water column but subsequently trapping it back as Mn oxides when oxygenated water is encountered (Calvert and Pedersen, 1996; Tribovillard et al., 2006). Inside the TIMS, this precipitation resulted in strong binding of Be and W with Mn, and consequently their prominent depletions. This process could also be responsible for depletion patterns of Mn, Pb, Zn, As and Sb observed in sediment samples in comparison to TIMS of the Krapina River (Fig. 7D). As in the case of the Sava River, these variations can reflect their sensitivity to physico-chemical changes at the boundary between sediment and the overlying water (Baran et al., 2019). The higher EFs found in sediments for the most of detrital elements (Cs, Ba, Sc, REE, Th, U, Ga) indicate that their main carriers are not easiliy retained at high flow rate. This pertains particularly to the Savinja (Fig. 7C), as the hydrologically most demanding river, in which higher loss of particles is expected. Since Ljubljanica and Krapina are typical lowland rivers with lower discharge and lower enrichment patterns, more efficient retention of particles in TIMS is likely to occur.

4. Conclusions

In this study, we have combined hydrological observations, granulometric, mineralogical and geochemical data of the SPM in a medium-size river to characterize element behavior and representativeness of material collected by time-integrated mass-flux sampler (TIMS). To evaluate TIMS in real-environment conditions, we have compared different sampled materials (SPM collected by TIMS, single-point SPM samples and fine-grained sediment (< 63 µm)). The main findings are as follows:

1. The flocculation process in the river channel induces coarser particle size in the single-point SPM and the SPM collected by TIMS compared to fine-grained sediments (< 63µm), which otherwise represent their suitable representative. After organic matter removal, a notable increase in clay content and lower mean grain size were observed.
2. The mineral composition of all samples is dominated by quartz, carbonates, phyllosilicates and feldspars which are mainly detrital in origin. However, a high content of calcite in sediment (55%) and shallow TIMS (69%) determined in the summer period can be the result

of biologically instigated carbonate precipitation, supported by lower water table and almost stagnant water conditions.

3. The geochemistry of analyzed materials is mostly influenced by the hydrodynamic sorting and provenance; different compositions during different hydrological regimes are found. In calm hydrological conditions, surface load shows enrichment patterns of partly anthropogenic elements (Mo, Mn, Cu, Zn, Cd, As, Sb and Bi) adsorbed onto clay minerals, oxyhydroxides and organic matter. The differentiation of suspended material is not observed at high water stages when more detrital material is supplied, and part of a bed load is re-suspended.

4. During low and medium water table, samplers at the Sava River proved to be a reasonably good means of collecting representative time-integrated suspended material. However, different chemical composition of shallow and deep-positioned sampler, induced by hydrodynamic sorting, could be recognized. Somewhat problematic conditions can occur at high flow rate due to partial loss of the clay fraction and variation of elemental composition, particularly in human-impacted rivers. Therefore, using anthropogenic elements, mostly bound to that fraction, to compare materials sampled in different periods, requires additional caution. Moreover, changes in redox conditions and high biological activity in a summer period can invoke additional modifications of the chemical composition of the material and consequently distort the conclusion about the representativeness of the SPM. Hence, in order to interpret geochemical and mineralogical data (time-integrated) in sediment source modeling or assessing river sediment quality, these factors should be considered.

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Figure caption

Figure 1. Map of sampling sites (map sourced from https://maps-for-free.com/).

Figure 2. Water discharge and suspended particulate matter (SPM) concentrations at the Zagreb sampling site during five sampling campaigns (October and November 2016; February, April and July 2017). Data provided from Meteorological and Hydrological Service. Colored circles represent the frequency of collecting single-point SPM and sediment samples.

Figure 3. Particle size distribution curves of investigated samples from the Sava River, Zagreb; A) all samples and B) samples presented as average values.

Figure 4. Mineral composition of analyzed samples.

Figure 5. Heat-maps of correlation coefficients based on symmetric coordinates for different types of samples; A) TIMS, B) single-point SPM and C) fine-grained sediments. Samples from all locations are included.

Figure 6. Doubly-normalized chemical composition of fine-grained sediment and SPM from the Sava River, Zagreb. The elements are arranged following the periodic table groups.

Figure 7. Doubly-normalized chemical composition of fine-grained sediment and single-point SPM from the Sava River-Radovljica and tributaries. SPM average refers to at least four single-point SPM samples. The samples are normalized to TIMS. The elements are arranged following the periodic table groups.