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Abstract: Mineral composition and surface physicochemical properties, i.e., specific surface area (SSA), cation exchange capacity (CEC), and surface charge ( $\zeta$ -potential) of recent sediments and their submicron-sized mineral fractions from different sedimentological environments of the eastern Adriatic were investigated. The impact of organic matter on these properties was also examined. It was shown that illite and mixed-layered clay minerals (MLCM) were omnipresent and showed no size-related preferences while the occurrence of smectites, chlorites, and kaolinites varied. The content of smectites increased and of chlorites slightly decreased with particle size lowering. Sediments from the carbonate-rich environments did not contain smectites and chlorites and showed the highest content of kaolinite. For the first time, the poorly- and the well-crystallized kaolinite (Kl and KLD) were distinguished in the recent sediments of the Adriatic. While Kl prevailed in the submicron-sized fraction, KLD occurred only in micron-sized fractions. Authigenic submicron-sized aragonite was determined in a distinct environment of the semi-enclosed marine lake. The differences in mineral composition and particle size of sediments and their separated fractions were reflected in a wide range of the obtained SSA and CEC values. The highest values of SSA and CEC were determined in the submicron-sized fractions rich in phyllosilicates, 109 m<sup>2</sup>g<sup>-1</sup> and 87.4 cmol<sup>+</sup>kg<sup>-1</sup>, respectively. The submicron-sized fraction from aragonite-rich marine lake showed the lowest values of SSA (56.4 m<sup>2</sup>g<sup>-1</sup>) and CEC (38.8 cmol<sup>+</sup>kg<sup>-1</sup>), still unexpectedly high for carbonate-rich environments. The removal of organic matter resulted in a significant increase in SSA and CEC, up to 150% and 76%, respectively.

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To the Editorial Office:

Enclosed is the of the manuscript titled “**Size-related mineralogical and surface physicochemical properties of the mineral particles from the recent sediments of the eastern Adriatic Sea**” co-authored by Maja Ivanić, Goran Durn, Srečo D. Škapin, and Ivan Sondi, which we are submitting for the publication in the Chemosphere. Highlights and Graphical Abstract are included in the text of the manuscript.

***Type of the Manuscript:*** Original scientific paper.

**Statement:**

The above manuscript and its contents have not been published previously. It is neither under consideration for publication in any other journal.

We appreciate your consideration,

Prof. Ivan Sondi

## Highlights

- Micron and submicron-sized fractions of recent Adriatic sediments were investigated.
- Mineralogical and surface properties of mineral particles are size related.
- Phyllosilicate-rich submicron-sized sediment fraction showed highest SSA and CEC.
- The removal of organic matter resulted in a significant increase in SSA and CEC.
- Prevalence of submicron-sized authigenic aragonite induced low SSA and CEC.

# **Size-related mineralogical and surface physicochemical properties of the mineral particles from the recent sediments of the eastern Adriatic Sea**

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1     **Abstract**

2     Mineral composition and surface physicochemical properties, i.e., specific surface  
3     area (SSA), cation exchange capacity (CEC), and surface charge ( $\zeta$ -potential) of  
4     recent sediments and their submicron-sized mineral fractions from different  
5     sedimentological environments of the eastern Adriatic were investigated. The impact  
6     of organic matter on these properties was also examined. It was shown that illite and  
7     mixed-layered clay minerals (MLCM) were omnipresent and showed no size-related  
8     preferences while the occurrence of smectites, chlorites, and kaolinites varied. The  
9     content of smectites increased and of chlorites slightly decreased with particle size  
10    lowering. Sediments from the carbonate-rich environments did not contain smectites  
11    and chlorites and showed the highest content of kaolinite. For the first time, the  
12    poorly- and the well-crystallized kaolinite (KI and KI<sub>D</sub>) were distinguished in the recent  
13    sediments of the Adriatic. While KI prevailed in the submicron-sized fraction, KI<sub>D</sub>  
14    occurred only in micron-sized fractions. Authigenic submicron-sized aragonite was  
15    determined in a distinct environment of the semi-enclosed marine lake. The  
16    differences in mineral composition and particle size of sediments and their separated  
17    fractions were reflected in a wide range of the obtained SSA and CEC values. The  
18    highest values of SSA and CEC were determined in the submicron-sized fractions  
19    rich in phyllosilicates, 109 m<sup>2</sup>g<sup>-1</sup> and 87.4 cmol<sub>+</sub>kg<sup>-1</sup>, respectively. The submicron-  
20    sized fraction from aragonite-rich marine lake showed the lowest values of SSA (56.4  
21    m<sup>2</sup>g<sup>-1</sup>) and CEC (38.8 cmol<sub>+</sub>kg<sup>-1</sup>), still unexpectedly high for carbonate-rich  
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23    and CEC, up to 150% and 76%, respectively.

**Keywords:** surface properties, submicron-sized mineral particles, organic matter, marine sediments, eastern Adriatic Sea.

## 1. Introduction

Mineral particles, the main component of sediments, play a major role in biogeochemical processes in aquatic environment by controlling the fate and the behaviour of organic and inorganic compounds through complex physicochemical processes associated with their surfaces (Breiner et al., 2006; Hochella et al., 2008; Plathe et al., 2013). During the last decade, numerous studies have shown that the submicron-sized mineral particles, and particularly nanomineral solids, represent the most reactive mineral phases in the environment, comprising over 90% of potentially reactive surfaces (Breiner et al., 2006; Hochella et al., 2008; Plathe et al., 2013; Soni et al., 2017; Tang et al., 2009).

The micron- and the submicron-sized mineral fractions in sediments mostly consist of clay minerals, metal oxides, and oxyhydroxides and sulphides (Perret et al., 1994; Tang et al., 2009). It is generally accepted that carbonates occur as lithogenic and biogenic micron-sized constituents in recent sediments, and can rarely be found in the submicron-size fractions (Buffle et al., 1998; Perret et al., 1994), especially in the nanosized dimensions (Wilkinson and Reinhardt, 2005). However, investigations of carbonate minerals on the nanoscale are scarce and mostly focused on those of biogenic origin (Morse et al., 2007).

The surface reactivity of mineral particles, which results from their structural, chemical and surface properties, can be described by the specific surface area (SSA), the cation exchange capacity (CEC) and the surface charge ( $\zeta$ -potential). These properties are used to describe physicochemical reactions occurring at the

48 surfaces of mineral particles (Bišćan et al., 1991; Breiner et al., 2006; Zhuang and  
49 Yu, 2002) and are considered of great importance in different biogeochemical  
50 processes.

51 Mineral particles in sediments are associated with various inorganic and organic  
52 compounds that form micro- and macro-aggregates. It is assumed that more than  
53 90% of organic matter (OM) is associated with the surfaces of mineral particles  
54 (Hedges and Keil, 1995; Keil et al., 1994; Mayer, 1999). These organo-mineral  
55 aggregates alter the physicochemical properties of mineral surfaces and contribute to  
56 the preservation of OM (Kaiser and Guggenberger, 2003; Mikutta et al., 2005b;  
57 Ransom et al., 1998).

58 Investigation of the surface physicochemical properties of the micron- and  
59 submicron-sized mineral particles that are an integral part of the complex organo-  
60 mineral aggregates occurring in natural environments requires their separation from  
61 organic components (Citeau et al., 2006; Tang et al., 2009). The main endeavor  
62 during this process is minimizing the alterations of mineral surfaces caused by  
63 various physical and chemical treatments (Buffle and Leppard, 1995; Citeau et al.,  
64 2006).

65 Previous studies carried out in the Adriatic region have provided information on the  
66 primary sedimentological and mineralogical properties of recent sediments (Boldrin et  
67 al., 1992; Faganeli et al., 1994; Matijević et al., 2008; Pigorini, 1968; Pikelj et al.,  
68 2016; Ravaioli et al., 2003; Sondi and Juračić, 2010; Spagnoli et al., 2014; Tomadin,  
69 2000a), their surface physicochemical properties (Bišćan et al., 1991; Boldrin et al.,  
70 1992; Vdović et al., 1991) and their geochemical features (De Lazzari et al., 2004;  
71 Dolenec et al., 1998; Goudeau et al., 2013; Spagnoli et al., 2014).



Still, the impacts of different mineral phases, particle size, and OM on the surface physicochemical properties of recent sediments were not systematically investigated. For the first time, this study aims to investigate the size-related mineralogical and surface physicochemical properties of the mineral particles separated from recent sediments from different sedimentological environments of the eastern Adriatic (an estuary, a delta, deep-water open-sea areas, a marine lake, an indented marine bay). Particular attention was given to the investigation of the submicron-sized fraction. In addition, the impact of the OM on the surface physicochemical properties on these solids was examined.

## **2. Experimental**

### **2.1. Study area**

The sampling locations (S1-S8) were distributed along the eastern coast of the Adriatic Sea, as shown in Figure 1.

#### **Figure 1.**

The investigated sedimentological environments include coastal areas under a significant riverine influence (S1, S2, and S5), deep-water open-sea areas (S3, S4, and S8), a semi-enclosed karstic marine lake (S6) and an indented marine bay (S7). Sampling station S1 is in the northern Adriatic, in the outer region of the area receiving the Po River sediment load (Faganeli et al., 1994; Pigorini, 1968). Location S2 is in the karstic Krka River estuary, below the calc tufa barriers formed at the uppermost part of the estuary. The open-sea sampling stations S3 and S4 are

located at the central and the outer part of the Jabuka Pit depression, respectively. Location S5 is in the Neretva Channel, in front of the Neretva River mouth, where the river discharges its sediment load and forms a delta. The karstic marine lake (Malo Jezero) on the island of Mljet (S6) represents a unique sedimentological system due to the occurrence of intense short-term authigenic aragonite precipitation (Sondi and Juračić, 2010; Sondi et al., 2017). The indented Risan Bay (S7) is the innermost part of the Bay of Kotor, where hydrodynamic conditions allow deposition of fine-grained material (Bellafiore et al., 2011; Pikelj and Juračić, 2013). Location S8 is in the Albanian coastal area, under influence of the Drin River, the largest river on the eastern Adriatic coast.

## **2.2. Sampling and sample preparation**

Surface sediments (Fig. 1) were collected using a gravity corer (Uwitec, Austria). Immediately after sampling, sediments were frozen and stored at -20°C. Before the laboratory analyses, sediments were freeze-dried (FreeZone 2.5, Labconco, USA).

The sediment samples were treated as follows:

### **i. Native sediments**

Fractionation was performed on samples representing distinct environments of the northern (S1), central (S3) and southern (S6, S7) Adriatic. Sediments were rinsed in deionized water to remove salts and increase particle dispersion.

### **ii. NaOCl-treated sediments**

Fractionation was performed on all samples after OM was removed.

#### **2.2.1. The organic matter (OM) removal**

The OM was removed by the slightly modified treatment proposed by Kaiser and Guggenberger (2003). Sodium hypochlorite (NaOCl) was chosen due to its effective removal of the OM from carbonate-rich sediments at room temperature (Gaffey and Bronniman, 1993; Mikutta et al., 2005a). Samples were dispersed in deionized water and the pH of the dispersion was adjusted to 8.5 and constantly controlled during the treatment. After the NaOCl-treatment, sediments were sequentially rinsed with deionized water by centrifugation. After rinsing, samples were thoroughly stirred with deionized water in a beaker and left to settle in order to perform the particle size fractionation.

#### *2.2.2. Particle size fractionation*

Size fractions (<8  $\mu\text{m}$ , <4  $\mu\text{m}$ , <2  $\mu\text{m}$ , <1  $\mu\text{m}$  and <0.45  $\mu\text{m}$ ) were collected from the NaOCl-treated sediment samples and several native sediments (S1, S3, S6, and S7).

Different fractions were obtained from aqueous dispersions at 25°C by gravitational settling, a low-invasive fractionation technique that enabled separation of a sufficient amount of material. Fractionation was performed according to the periods presented in Table S1 (Supplementary). To determine if the particle falls into the desired size-range, the collected suspensions were analysed by dynamic light scattering (LS 13320 Beckman Coulter Inc., USA). Example of the particle size distribution (PSD) curves of the collected fractions is shown in Figure S1 (Supplementary). Only samples containing a minimum of 97 vol.% of particles of the required size were freeze-dried and used for further analysis.

It was demonstrated that the time required for the separation of mineral particles of the desired size significantly differed from the calculated values that are based on the Stokes' law (Table S1, Supplementary). Clifton et al. (1999) investigated the

efficiency of the size fractionation after Stokes' law and found that, even though the mean size (Mz) of particles was in the desired size-range, the number of misplaced particles ranged from 25-65%. The reasons for this discrepancy can be found in the Brownian motion of the submicron-sized particles and assumptions that all particles are spherical and of the same density, as Stokes' law anticipates. Obviously, this assumption cannot be applied to natural sediment samples.

## **2.3. Analytical methods**

### *2.3.1. Sediment characterization*

Particle-size distribution (PSD) measurements were performed by laser diffraction (LS 13320, Beckman Coulter Inc., USA). Prior to measurements, samples were dispersed in deionized water and treated with ultrasound for 3 minutes. The particle size was calculated with proprietary software using the Mie theory of light scattering (optical parameters: refractive index 1.53; absorption index 0.1). Sediments were classified according to Shepard's classification scheme (1954) and the modified Wentworth (1922) grade scale with the clay-silt boundary at 2  $\mu\text{m}$ .

### *2.3.2. Mineralogical analysis*

The total carbonate content was determined volumetrically with the Scheibler's apparatus (Allison and Moodie, 1965). Particle size and morphology were examined by the high-resolution scanning field-emission electron microscopy (HR-FE-SEM, Zeiss Supra 35 VP, Germany). The mineral composition of native sediments was determined by the X-ray powder diffraction (XRD) using a D4 Endeavor diffractometer (Bruker AXS, Germany). The mineral composition of fractions smaller than 2  $\mu\text{m}$ , 1  $\mu\text{m}$  and 0.45  $\mu\text{m}$  (where available) was determined using a Philips

164 diffractometer (graphite monochromator, Cu-K $\alpha$  radiation, proportional counter). The  
165 XRD patterns of random samples were obtained after air-drying. The XRD patterns of  
166 oriented samples were obtained after the following treatments: (a) K-saturation, (b) K-  
167 saturation and DMSO solvation, (c) K-saturation and ethylene glycol solvation, (d) K-  
168 saturation and heating for two hours at 350°C, (e) K-saturation and heating for two  
169 hours at 550°C, (f) Mg-saturation, (g) Mg-saturation and ethylene glycol solvation, (h)  
170 Mg-saturation and heating for two hours at 350°C and (i) Mg-saturation and heating  
171 for two hours at 550°C. The non-clay mineral phases were identified using the  
172 Powder Diffraction File (1996) data system and the Panalytical XPert HighScore (v.  
173 1.0d) program package. Identification of clay minerals was generally based on the  
174 methods outlined by Brindley and Brown (1980), and Moore and Reynolds (1989).  
175 The term “MLCM” was used for mixed-layer clay mineral(s), in which the type of  
176 interstratification and the constituting clay minerals were not recognized with  
177 certainty. The DMSO-treatment enabled the differentiation of the poorly-crystallized  
178 kaolinite that does not intercalate with DMSO (KI), from the well-crystallized kaolinite  
179 that forms intercalation compounds with DMSO (KI<sub>D</sub>) (Range et al., 1969). The  
180 semiquantitative estimates of clay minerals in the <2  $\mu$ m, <1  $\mu$ m and <0.45  $\mu$ m  
181 fractions were based on the relative intensities of the characteristic X-ray peaks.  
182 Estimated quantities of minerals were presented with Xs, but no quantitative value  
183 was assigned to each X.

### 184 *2.3.3. Determination of the total carbon, the total organic carbon (TOC) and the total* 185 *inorganic carbon (TIC) content*

186 The total carbon and the total organic carbon (TOC) were determined in a Leco IR–  
187 212 (USA) carbon analyser. The TOC, which is used as an indicator of the OM

content, was determined by combustion of acid insoluble matter, after treatment with hot 1:1 diluted 36.5% HCl. The content of TIC was calculated from the difference between the total carbon and TOC.

#### *2.3.4. The surface physicochemical characterization*

The specific surface area (SSA) measurements were performed by a single-point nitrogen adsorption using the BET method, on a FlowSorb II 2300 instrument (Micromeritics, USA). The cation exchange capacity (CEC) was determined using an ammonia selective electrode based on the method described by Busenberg and Clemency (1973). The electrophoretic mobility (EPM) was measured using a Zetasizer Nano ZS (Malvern, UK). For the measurements, 10 mg of sediment sample was dispersed in 50 ml of an inert electrolyte (1 mM NaCl) and left for a few hours to reach equilibrium. The electrophoretic mobility was measured at a constant temperature of 25°C. The software automatically calculated the  $\zeta$ -potential from the EPM using Henry's equation (Hunter, 1981). The instrument was calibrated prior to measurements with a polystyrene latex standard, supplied by the manufacturer. All the data processing was evaluated using Zetasizer software 6.20 (Malvern, UK).

### **3. Results and discussion**

#### **3.1. Granulometric characteristics of the investigated sediments**

The native sediments were classified as silty sand (S1), silt (S5-S8), and clayey silt (S2-S4) (Fig. S2a, Supplementary).

Coarser sediments were found in the northern Adriatic (S1), the Neretva Channel (S5), and the Albanian coastal area (S8). These environments coincide with areas

211 where rivers with a large discharge such as Po, Neretva, and Drin, deposit their load  
212 in marine coastal environments. The prevalence of silts was also characteristic for  
213 the carbonate-rich sediments at the Krka River estuary (S2) and Malo Jezero on the  
214 island of Mljet (S6), and for the Risan Bay (S7) where surface freshwater run-off  
215 significantly contributes to the size and the mineral composition of the sediment.  
216 Fine-grained sediments were found in the central Adriatic open-sea area (S3, S4),  
217 where due to specific hydrodynamic conditions of the Adriatic basin and the limited  
218 coastal influence, deposition of finer particulate material occurs. The obtained results  
219 are in agreement with the previous research that showed deposition of finer sediment  
220 in the central Adriatic area and coarser sediments in the northern part of the Adriatic  
221 and along its eastern coast (De Lazzari et al., 2004; Spagnoli et al., 2014; Tomadin,  
222 2000a; Vdović and Juračić, 1993).

223 Following the OM removal (Fig. S2b), all sediments were classified as clayey silts.  
224 This is the result of an increase in the share of clayey content and a decrease in  
225 particle size. Since most of the OM is found in organo-mineral aggregates (Arnarson  
226 and Keil, 2007), its removal caused their disintegration and the subsequent release  
227 of finer particles.

228 When comparing corresponding size fractions separated from the native and the  
229 NaOCl-treated sediment samples (Table S1, Supplementary), it was observed that  
230 the native sediment fractions  $<8\ \mu\text{m}$  and  $<4\ \mu\text{m}$  contained slightly coarser material  
231 and a correspondingly higher Mz. However, the Mz of fine fractions ( $<2\ \mu\text{m}$ ,  $<1\ \mu\text{m}$ ,  
232  $<0.45\ \mu\text{m}$ ) from both sets of samples was in the same size range. This implies that  
233 the removal of OM induced disintegration of macro-aggregates and had little effect on  
234 the OM bound to the clayey mineral particles.

Indeed, the results displayed in Figure 2a show an increase in the amount of TOC with decreasing particle size (sampling station S3). The strong affinity of the OM for finer particles was already established (Bišćan et al., 1991; Buffle and Leppard, 1995). This results in their strong association and greater resistance to chemical treatments (Kahle et al., 2003; Mikutta et al., 2005b).

Indeed, Keil et al. (1994) have shown that diverse classes of OM were associated with different types of mineral particles. Namely, coarser particles were enriched in carbon-rich OM while smaller, particularly clayey particles, contained nitrogen-rich OM. These diversities may lead to differences in the degradation rate of OM associated with the surfaces of mineral particles.

Finally, the persistence of clayey particles in the water column, together with their prolonged oxygen exposure time (Coppola et al., 2007), could lead to the removal of the more labile organic compounds, leaving the residual OM tightly bound to mineral surfaces and contributing to its resistance to the applied chemical treatment.

## **Figure 2.**

It is noteworthy that after the OM removal, similar PSD curves were obtained for the corresponding size-fractions in all investigated sediments (Fig. 3). A general lowering in modality, i.e. number of frequency peaks, with a decrease in the particle size occurred. Minor discrepancies were observed only for the carbonate-rich sediment from Malo Jezero (S6). In addition, the mineralogical analysis revealed presence of, in general, similar mineral phases in the corresponding size fractions of the



investigated sediments, as shown in section 3.2. A similar conclusion was reached by Keil et al. (1994) when exploring size fractions of sediments along the Washington margin (USA). Comparable granulometric characteristics of the corresponding size fractions could result from prevalence of similar mineral phases. The observed shift in the PSD curves of size fractions from the Malo Jezero (S6) sediment, characterized by slightly different mineral composition, supports this assumption. However, considering the strong affinity between OM and mineral surfaces, and its incomplete removal from the investigated samples (Table 1), it seems reasonable to presume that OM, through formation of aggregates, contributed to the observed similarity in PSD. Its influence was probably most exerted in fine fractions, due to its increased content in this size range (Fig. 2a).

A unimodal PSD curve with a small tail at 0.25  $\mu\text{m}$  and a Mz of 0.1  $\mu\text{m}$  was characteristic for all investigated fractions  $<0.45 \mu\text{m}$  (Fig. 3). Despite prolonged settling time, appreciable share of particles in smaller size range was not attainable. Plathe et al. (2013) suggested that in aquatic environments, nanoparticles in the size of 5-20 nm are mostly found in aggregates of  $\sim 100$  nm, and the efficiency of aggregate disintegration is limited. The obtained Mz of 0.1  $\mu\text{m}$ , observed in the finest fractions (Table S1, Supplementary), supports this assumption. According to Baalousha (2009), disintegration of micron-sized aggregates produces smaller aggregates that are 50 to 400 nm in size, which can be further disintegrated by a much slower process of surface erosion. Rapid aggregation of the nanosized particles and their limited disintegration could be a valid explanation for the observed difficulties in extracting them from the dispersion considering the settling time.

## **Figure 3.**

### **3.2. Mineralogical characteristics of the investigated sediments**

#### **3.2.1. Carbonate mineral phases**

The share of carbonates in native sediments varied from 14% to 69% (Table 1). Calcite, Mg-calcite, aragonite, and dolomite were determined as major or minor constituents (Table 1). According to their carbonate content, the investigated sediments can be divided into two groups. The first group, including sediments at sampling stations S1-S6, is characterised by a significant carbonate content (>27%), originating from weathering of the karstic rocks in the drainage area of the eastern Adriatic coast, the appearance of biomineral fragments, and the authigenic formation of carbonate minerals in the marine environment. Sediments at sampling stations S7 and S8, which contain significantly lower share of carbonates, ~15%, and calcite as the only carbonate mineral phase (Table 1), belong to the second group. Among the first group, sediments from the Krka River estuary (S2) and Malo Jezero (S6) contained the highest amounts of carbonates, 59% and 69%, respectively (Table 1). However, the origin and the mineral composition of carbonates in these two systems were different. In the Krka River sediment (S2) calcite was the only determined carbonate mineral phase (Table 1, Fig. 4f). Previous investigations of these sediments indicate its detrital origin with a small contribution of biogenic components (Juračić and Prohić, 1991). Contrarily, the XRD analysis of native sediment from Malo Jezero (S6) showed the presence of aragonite, Mg-calcite, and calcite (Table 1). Aragonite was the most abundant mineral phase. Sondi and Juračić (2010) have shown that biologically induced precipitation of aragonite, occurring during the short-

term whitening events, mainly contributed to the high share of carbonates, particularly aragonite in recent sediment of Malo Jezero (S6). The FE-SEM photomicrographs (Fig. 4d) revealed the prevalence of irregular needle-like mineral particles, typical for the occurrence of authigenic aragonite in the marine environment (Sondi and Juračić, 2010). In the fine fractions from these two sediments (Fig. 4 d,f), only occasional appearance of calcite grains was observed in sampling station S2, while irregular aragonite particles were abundant even in the submicrometer size-range (S6). The occurrence of aragonite and Mg-calcite in recent sediments of the Adriatic was mainly associated with biogenic production (Pikelj et al., 2016). Indeed, Mg-calcite was determined in the central Adriatic open-sea sediments (S3 and S4) (Table 1), where the abundance of skeletal detritus (Fig. 4e), indicates its biogenous origin. According to previous investigations, carbonates in the Adriatic sediments are found mainly in the coarse-grained fractions (Faganeli et al., 1994; Pikelj et al., 2016). A decrease in their share with decreasing particle size in majority of samples, and the absence of Mg-calcite in finer fractions from the open-sea sediment (S3) (Tables 1, 2), supports these assumptions.

#### **Figure 4.**

However, the XRD and FE-SEM investigation of different size fractions separated from the carbonate-rich sediment from Malo Jezero (S6) showed a considerable share of aragonite present in the submicron-sized fraction (Table 2, Fig. 4d). This finding is not in line with the general assumption that carbonate particles do not occur in the finest sediment fractions, especially in the nanosized dimensions (Buffle et al.,

1998; Wilkinson and Reinhardt, 2005). Their presence in sediment from Malo Jezero (S6) is a rare example of appearance of nanosized carbonates in recent sediments that highlights the important role of authigenic processes in their formation.

The lower share of calcite in sediments at sampling stations S7 and S8 (Table 1) is in agreement with the observation reported by Faganeli et al. (1994). These stations are located in the coastal areas of Montenegro and Albania where lithology of the hinterland mostly consists of flysch deposits, metamorphic, and igneous rocks (Dolenec et al., 1998; Pikelj and Juračić, 2013; Rivaro et al., 2004). The material formed by weathering of these terrains is transported by the Albanian rivers and is the main source of sediment deposited in the coastal area.

Dolomite was determined in sediments from the northern Adriatic (S1) and the Neretva Channel (S5). According to previous investigations, detrital dolomite in northern Adriatic originates from the drainage area of the eastern Alps (Faganeli et al., 1994; Pikelj et al., 2016; Ravaioli et al., 2003). Dolomite at sampling station S1 could also originate from the Late Glacial loess deposits. Namely, Durn et al. (2018a) found dolomite in the Late Glacial loess on the island of Susak (Northern Adriatic). The possible source of dolomite in the Neretva Channel (S5), where it was found even in the submicron-size fraction (Table 2), are flysch sediments. Particulate material entering the sedimentation system mostly originates from weathering of the Eocene flysch deposits in the upper drainage area (Jurina et al., 2015), in which dolomite is a common component in the Adriatic zone (Pikelj et al., 2016; Toševski et al., 2012).

### 3.2.2. Clay minerals

The XRD investigation of clay minerals in the investigated sediments showed presence of illite, smectite, chlorite, kaolinite, I/S MLCM and MLCM (Table 2). Although these results are generally in agreement with the earlier investigations (Ilijanić et al., 2014; Tomadin, 2000a), the new data were acquired based on the analysis of different micron- and submicron-sized sediment fractions of the Adriatic sediments, and provides a more detailed identification of clay minerals.

Illite was the most abundant and omnipresent clay mineral in the investigated sediments and equally present in all size fractions (Table 2). Mixed-layer clay minerals (MLCM and/or I/S MLCM) were also found in all investigated sediments and generally showed no size-related preferences (Table 2). Smectites were most abundant in sediments from the open-sea areas, and in general, their content increased with particle size lowering (Table 2). Chlorites occurred together with smectites, however their share mostly decreased in finer size fractions.

In the central Adriatic area, low hydrodynamic conditions allow deposition of very fine particulates (Spagnoli et al., 2014). The material deposited in this area consists of the clayey fraction delivered by currents flowing southward from the northern Adriatic, northwest from the southern Adriatic and the material of aeolian origin (Dolenec et al., 1998; Faganeli et al., 1994; Goudeau et al., 2013; Tomadin, 2000a). According to Tomadin (2000a), this area is supplied by the off-shore Padane flux, carrying fine-grained material rich in illite and chlorite which is delivered by the Po River, and with seasonal input of the coastal Apennine flux, transporting materials of Apennine source that are rich in smectites.

In the carbonate-rich sediments of the Krka River estuary (S2) and Malo Jezero (S6), smectites and chlorites were not determined (Table 2). These clay minerals mainly

377 originate from the flysch deposits located in the drainage area of the Adriatic.  
378 However, sampling stations S2 and S6 are surrounded by carbonates with no flysch  
379 terrains that could directly act as a source of smectites and chlorites. Due its distance  
380 from the coast, terrigenous supply in Malo Jezero (S6) is limited to soil erosion and  
381 aeolian deposition while its enclosure limits the water exchange, restricting potential  
382 input of material by currents. The small amount of the suspended load carried by the  
383 Krka River is retained by the calc tufa barriers located upstream from the sampling  
384 station S2. The main source of the flysch material deposited in the Krka River estuary  
385 is located downstream of the sampling station (Juračić and Prohić, 1991).

386 Kaolinites were found in sediments of the northern and the central Adriatic area (S1-  
387 S6), but they were not determined with certainty in sediments of the coastal areas of  
388 Montenegro and Albania (S7 and S8, respectively). Moreover, the results of this  
389 study for the first time allowed differentiation between the well-crystallised kaolinite  
390 ( $KI_D$ ) and the poorly-crystallised kaolinite (KI) in the investigated sediments. Results  
391 in Table 2 revealed that the  $KI_D$  was not present in the submicron-sized fractions,  
392 while the KI was equally abundant in the submicron and the clayey fractions.  
393 Rodriguez-Navarro et al. (2018) observed similar size-fractionation of kaolinite in the  
394 Saharan dust particles deposited in the Iberian Peninsula and ascribed it to different  
395 sources of dust. Coarser kaolinite particles of higher crystallinity were present in the  
396 silt fraction and the finer particles of poor crystallinity in the clay fraction. According to  
397 Tomadin (2000b), kaolinite in the Adriatic sediment is of both river-borne and aeolian  
398 origin. The wind-blown dust from different source areas in Africa has a significant  
399 effect on sediments in the Adriatic. However, since the contribution from the wind-  
400 blown transport in sediments is usually masked by the more significant river supply  
401 (Tomadin, 2000b), their presence can be revealed in sediments where the input of

402 terrigenous siliciclastic material is limited. Indeed, the two sediments from the  
403 carbonate-rich environments, Krka River estuary (S2) and Malo Jezero (S6), showed  
404 the highest content of the KI. It can therefore be argued, that the KI in the Adriatic  
405 sediments is of both river-born and aeolian origin, as Tomadin (2000b) postulated.  
406 However, kaolinite was determined in polygenetic soil, different palaeosols and loess  
407 sediments on the island of Susak (Durn et al., 2018a, b). Durn et al. (1999)  
408 postulated that kaolinite in the fine clay (KI) of the Istrian Terra Rossas is  
409 predominantly authigenic (pedogenic), while the  $KI_D$  is considered inherited from the  
410 parent materials. Durn et al. (2019) found that kaolinites (both KI and  $KI_D$ ) and illitic  
411 material are the dominant clay mineral phases in the analysed Terra Rossa and  
412 Calcocambisol from Istria.

413 It is important to note that the clay mineral assemblage at sampling station S1 (illite,  
414 chlorite, smectite, kaolinites and I/S MLCM) is identical to that found in the Late  
415 Glacial loess deposits on the island of Susak (Durn et al., 2018a). This points to the  
416 same provenance of the material from which the Late Glacial loess on the island of  
417 Susak and sediments at sampling station S1 were derived. Generally, clay minerals  
418 in the Adriatic sediments originate from the material delivered by the Po River and  
419 rivers draining the Apennines, from the Albanian rivers on the southeast part of the  
420 Adriatic and aeolian transport of Saharan dust (Tomadin, 2000a). However, during  
421 the Pleistocene, the North Adriatic was a closed basin and the sea level was up to  
422 100 m lower than today. Fluvial material was exposed to wind activity during the  
423 glacials and was subsequently deposited to form loess and aeolian sand. During the  
424 interglacials and interstadials, aeolian sedimentation was interrupted by the soil  
425 forming processes. Therefore, loess, aeolian sand, soils, and palaeosols have to be  
426 considered as a potential source of clay minerals in the recent Adriatic sediments

(e.g. Durn and Frechen, 2018c), in addition to flysch deposits, as documented by the clay mineral composition (e.g. smectite, chlorite, illite) of sediment in the Neretva Channel (S5).

### 3.2.3. Other mineral phases

Plagioclases were found in the recent sediment of the open-sea environment (S3), in sediments of the Neretva Channel (S5) and the Risan Bay (S7), while both plagioclases and K-feldspars were determined in sediments of the northern Adriatic (S1) and Malo Jezero (S6) (Table 1). The weathering of feldspars does not produce submicron-sized particles (Table 1).

Pyrite was found in sediments from the Krka River estuary (S2), Malo Jezero (S6), northern Adriatic (S1) and the Neretva Channel (S5) (Tables 1, 2). Formation of pyrite is associated with reductive conditions in sediments, induced by increased productivity and degradation of a large amount of OM of terrigenous origin in the investigated areas (Giani et al., 2012; Jurina et al., 2015). In reducing conditions and the presence of a sulfidic zone, pyrite can be formed during the post-depositional early-diagenetic processes. Indeed, the framboidal structure of pyrite of several microns in size, composed of uniform submicron-sized crystals (Fig. 4c) in sediment at sampling station S6 confirms its diagenetic origin (Wilkin et al., 1996).

**Table 1.**

**Table 2.**



### 3.3. Surface physicochemical properties of the investigated sediment samples

The SSA and CEC values of the investigated native sediments varied significantly according to the sampling sites and ranged from 11.3 to 27.8 m<sup>2</sup>g<sup>-1</sup>, and from 11.6 to 35.3 cmol<sub>c</sub>kg<sup>-1</sup>, respectively (Table S2). The highest values were obtained for sediments in the open-sea area (S3, S4), in the Albanian coastal area (S8), and the Risan Bay (S7). These sediments were fine-grained and mostly consisted of clay minerals (Table 2). The lowest values were determined in sediments under the dominant influence of rivers (S1 and S5). These sediments were coarser and consisted of sand and silt fractions (Fig. S2a). Similar values were also obtained for the silty carbonate-rich sediments at sampling stations S2 and S6. This is related to the significant occurrence of carbonate mineral phases, which exhibit low SSA and CEC values. The obtained results exemplify the predominant influence of particle size and mineral composition on the determined SSA and CEC values.

The ζ-potentials of native sediments, at pH of natural waters (7.4 – 9.5), were in a narrow range of values, from -30.7 mV to -26 mV (Table S2, Supplementary). It should be noted that the measurements were carried out on native samples dispersed in 1mM NaCl solutions and that the pH of dispersions were not adjusted to the same pH values. These results confirm previous findings on the crucial role of OM in the formation of the surface charge on mineral particles in natural environments (Breiner et al., 2006; Buffle et al., 1998; Plathe et al., 2013). Even a small amount of OM attached to the surfaces of mineral particles provides them with similar surface charges at pH values from 7 to 10 (Durn et al., 2019; Sondi et al., 1997). This is accomplished through complex processes of electrostatic attraction and ligand exchange between the hydroxyl groups on the mineral surfaces and carboxyl and

phenolic groups of the organic matter (Gu et al., 1994; Tombácz and Szekeres, 2004).

### **3.3.1. Influence of OM on the surface physicochemical properties of the investigated sediments**

The OM significantly affects physicochemical properties (SSA and CEC) of mineral surfaces (Bišćan et al., 1991; Boldrin et al., 1992; Kleber et al., 2004; Ransom et al., 1998; Zhuang and Yu, 2002). The extent of modification can be estimated through changes of these properties following the OM removal from mineral surfaces.

The applied NaOCl-treatment removed 53% to 82% of the OM from the investigated sediments (Table 1). After the OM removal, the SSA of sediments ranged from 25.1 to 52.4 m<sup>2</sup>g<sup>-1</sup>, and CEC from 18.5 to 39.1 cmol<sub>+</sub>kg<sup>-1</sup> (Table S2, Supplementary). The significant increase in SSA (47-150%) and CEC (5-76%) corresponds to the observed granulometric changes (Fig. S2, Supplementary), indicating disintegration of organo-mineral aggregates after the OM removal and exposure of new mineral surfaces. Numerous studies reported an increase of SSA after the OM removal (Boldrin et al., 1992; Durn et al., 2019; Kahle et al., 2003; Kaiser and Guggenberger, 2003; Kleber et al., 2004). However, contrary results were also reported (Bišćan et al., 1991; Jurina et al., 2015; Vdović and Juračić, 1993). The influence of OM on the surface physicochemical properties of mineral particles is complex and depends on the type of OM, marine vs. terrigenous (Bišćan et al., 1991), and the character of the underlying clay mineral surfaces (Zhuang and Yu, 2002). According to Bišćan et al. (1991), the impact of OM on the reactivity of mineral particles depends on the molecular weight and the porosity of the OM. The riverine type of OM, characterized by the degradable, hydrophilic organic compounds, and the more persistent

hydrophobic OM, which is characteristic for marine environments, exhibit complex and diverse influence on SSA and CEC of mineral surfaces (Bišćan et al., 1991). These interactions are additionally complicated by the observed size-dependent distribution of different organic compounds. According to Kiel et al. (1998), the share of amino acids increases in fine fractions, carbohydrates in silty fraction, while lignin phenols prevail in sandy fraction. Previous research showed that OM forms patches and occurs at specific localities on the surface of mineral particles (Mayer, 1999; Mikutta et al., 2005b; Ransom et al., 1997). If a significant part of the mineral surface remains exposed, it can be presumed that the role of the OM in lowering SSA and CEC of mineral particles is mostly in gluing grains into aggregates.

In addition, the results showed that the OM removal induced a more significant increase of SSA compared to CEC values (Table S2, Supplementary). If the binding of OM occurs on the more reactive sites on mineral surfaces, this indicates that the edge (amphoteric) surfaces of clay minerals would be mostly associated with OM (Kahle et al., 2003; Kaiser et al., 2002; Kaiser and Guggenberger, 2003; Mikutta et al., 2005b). This would leave the basal and the interlayer siloxane surfaces free to exchange cations with the surroundings. However, the role of OM cannot be neglected, and since its removal was incomplete (Table 1), the remaining OM could contribute to the determined CEC of the NaOCl-treated samples.

The incomplete removal of OM is also considered the main reason for the observed negligible effect of the NaOCl-treatment on the  $\zeta$ -potential values (Table S2, Supplementary). It was already established that the  $\zeta$ -potential of clay mineral surfaces was significantly influenced by a small amount of fulvic and polyacrylic acid

(Sondi et al., 1997). This supports the assumption that even small amounts of the OM govern the formation of surface charge of mineral particles.

### ***3.3.2. Size-related variations in the surface physicochemical properties of the investigated sediments***

A significant increase of SSA and CEC values occurred in finer size fractions in all investigated sediments (Fig. 5). The reason for this is the reduction in particle size and, more importantly, the presence of minerals with higher surface reactivity, e.g. clay minerals (illite, I/S MLCM, smectite, kaolinite, chlorite).

The significant impact of mineral composition on the increase of SSA and CEC values can be observed from the comparison of the two carbonate-rich sediments from the Krka River estuary (S2) and Malo Jezero (S6). While native sediments exhibited similar SSA and CEC values (Table S2, Supplementary), significant changes were observed with decreasing particle size (Fig. 5). In sediment at sampling station S2, a rise in SSA and CEC values was observed already in the fraction  $<8\ \mu\text{m}$ , while further reduction in grain size caused an additional increase of both parameters (Fig. 5). These results suggest that carbonate minerals, characterized by low surface reactivity, were predominantly found in coarser fractions, and efficiently removed by fractionation in the first step. The remaining clay minerals in finer fractions (illite, poorly-crystallised kaolinite and I/S MLCM), caused a more significant increase of SSA and CEC (Fig. 5). Contrarily, size fractions separated from sampling station S6 exhibited a minor increase with particle size lowering, and the lowest SSA and CEC values. The reason for this is the presence of carbonates (calcite, Mg-calcite and aragonite) in all size fractions (Table 2, Fig. 4d), a lower share of clay minerals (illite, kaolinite and MLCM) and the absence of I/S

MLCM (Table 2). This indicates a low surface reactivity of carbonates even when they are present in submicron-sized dimensions.

The increase of SSA and CEC in the finest fractions ( $<0.45\ \mu\text{m}$ ) was not observed as expected. The reason for this can be found in the increase of the TOC content (Fig. 2a), suggesting strong association of OM to mineral surfaces in the submicron-sized mineral phases (Kahle et al., 2003; Mikutta et al., 2005b). Mikutta et al. (2005b) showed that more SSA was occupied by the OM in the size fraction  $<0.2\ \mu\text{m}$  compared to coarser particles, e.g.  $0.2 - 2\ \mu\text{m}$ . In addition, it was shown that the interaction of clay minerals and the OM depends on the different types of OM and specific clay minerals (Ransom et al., 1998). In particular, Ransom et al. (1998) showed that the preservation of OM was higher in sediments rich in smectites, compared to chlorite-dominated sediments. Indeed, the results showed that samples with increased share of smectites in the finest fraction (Table 2) exhibited a decrease of SSA values. Complex interactions of specific clay minerals and OM could have, therefore, contributed to the observed changes in SSA and CEC of the finest fractions. A continuous size-dependent increase of both SSA and CEC determined in sediment from Malo Jezero (S6) supports these assumptions. Sediment from this location showed unique characteristics, with carbonates present in all size fractions and a minor share of the non-expandable clay minerals determined in the submicron-sized fraction (Table 2). The observed mineral composition could have contributed to a more straightforward relationship between the mineral surfaces and OM, mostly governed by weaker associations of carbonates and the OM. The presence of different types of OM, e.g. non-degradable terrigenous plant debris from the surrounding area (Lojen et al., 2010) and the plankton remains from intense primary

production during summer periods (Sondi and Juračić, 2010), could have induced the occurrence of particulate OM, not associated with mineral surfaces.

## **Figure 5.**

## **Conclusion**

For the first time, the mineral composition and the surface physicochemical properties of successive sediment size fractions from different sedimentological environments of the eastern Adriatic were investigated. Special attention was given to the submicron-sized sediment fractions and the influence of OM on the surface reactivity of mineral particles. It was shown that the mineral composition and the content of clay minerals were different in the studied environments and moderately varied among the separated micron/submicron-sized fractions. Illite and MLCM were omnipresent and showed no size-related preferences while the occurrence of smectites, chlorites, and kaolinites varied. The content of smectites increased in the submicron-size fraction, while the share of chlorite decreased with particle size lowering. Sediments from the carbonate-rich environments did not contain smectite and chlorite and showed the highest content of kaolinite. The poorly-crystallised kaolinite prevailed in the submicron-sized fraction and the well-crystallised kaolinite was limited to the micron fraction. Increase in the surface reactivity of mineral particles with the particle size lowering was related to smaller particle size and accumulation of minerals characterised by large SSA and CEC (e.g. clay minerals). Authigenic formation of the nanosized carbonate minerals resulted in their increased

presence even in the submicron-size fraction, resulting in lower SSA and CEC values. The OM removal induced disintegration of macroaggregates and exposure of mineral surfaces, reflected in an increase of SSA and CEC values.

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## **Supplementary information**

**Table S1.**

**Table S2.**

**Figure S1.**

**Figure S2.**

## **References**

Allison, L.E., Moodie, C.D., 1965. Carbonate. In: Black, C.A. (Ed.), *Methods of Soil Analysis, Part 2*, second ed., pp. 1379-1400 Agronomy Monography 9 ASA, CSSA and SSSA.

Arnarson, T.S., Keil, R.G., 2007. Changes in organic matter–mineral interactions for marine sediments with varying oxygen exposure times. *Geochim. Cosmochim. Ac.* 71, 3545-3556.

612 Baalousha, M., 2009. Aggregation and disaggregation of iron oxide nanoparticles:  
 613 Influence of particle concentration, pH and natural organic matter. *Sci. Total*  
 614 *Environ.* 407, 2093-2101.

615 Bellafiore, D., Guarnieri, A., Grilli, F., Penna, P., Bortoluzzi, B., Giglio, F., Pinardi,  
 616 N., 2011. Study of the hydrodynamical processes in the Boka Kotorska Bay with  
 617 a finite element model. *Dynam. Atmos. Oceans* 52, 298-321.

618 Bišćan, J., Rhebergen, I., Juračić, M., Martin, J.M., Mouchel, J.M., 1991. Surface  
 619 properties of suspended solids in stratified estuaries (Krka River estuary and  
 620 Rhône River delta). *Mar. Chem.* 32, 235-252.

621 Boldrin A., Juračić, M., Menegazzo Vitturi, L., Rabitti, S., Rampazzo, G., 1992.  
 622 Sedimentation of riverborne material in a shallow shelf sea: Adige River, Adriatic  
 623 Sea. *Mar. Geol.* 103, 473-485.

624 Breiner, J.M., Anderson, M.A., Tom, H.W.K., Graham, R.C., 2006. Properties of  
 625 surface – modified colloidal particles. *Clay Clay Miner.* 54, 12-24.

626 Brindley, G.W., Brown, G., 1980. Crystal Structures of Clay Minerals and Their X-  
 627 ray Identification. Mineralogical Society, London, pp. 495.

628 Buffle, J., Leppard, G.G., 1995. Characterization of aquatic colloids and  
 629 macromolecules. 1. Structure and behavior of colloidal material. *Envir. Sci. Tech.*  
 630 29, 2169-2175.

631 Buffle, J., Wilkinson, K.J., Stoll, S., Filella, M., Zhang, J., 1998. A generalized  
 632 description of aquatic colloidal interactions: the three-colloidal component  
 633 approach. *Envir. Sci. Tech.* 32, 2887-2899.



634 Busenberg, E., Clemency, C.V., 1973. Determination of the cation exchange  
 635 capacity of clays and soils using an ammonia electrode. *Clay Clay Miner.* 21, 213-  
 636 217.

637 Citeau, L., Gaboriaud, F., Elsass, F., Thomas, F., Lamy, I., 2006. Investigation of  
 638 physico-chemical features of soil colloidal suspensions. *Colloid Surface A* 287,  
 639 94-105.

640 Clifton, J., McDonald, P., Plater, A., Oldfield, F., 1999. Investigation into the  
 641 efficiency of particle size separation using Stokes' Law. *Earth Surf. Proc. Land.*  
 642 24, 725-730.

643 Coppola, L., Gustafsson, Ö., Andersson, P., Eglinton, T.I., Uchida, M., Dickens,  
 644 A.F., 2007. The importance of ultrafine particles as a control on the distribution of  
 645 organic carbon in Washington Margin and Cascadia Basin sediments. *Chem.*  
 646 *Geol.* 243, 142-156.

647 De Lazzari, A., Rampazzo, G., Pavoni, B., 2004. Geochemistry of sediments in  
 648 the Northern and Central Adriatic Sea. *Estuar. Coast. Shelf S.* 59, 429-440.

649 Dolenec, T., Faganeli, J., Pirc, S., 1998. Major, minor and trace elements in  
 650 surficial sediments from the open Adriatic Sea: a regional geochemical study.  
 651 *Geol. Croat.* 51, 59-73.

652 Durn, G., Ottner, F., Slovenec, D., 1999. Mineralogical and geochemical  
 653 indicators of the polygenetic nature of terra rossa in Istria, Croatia. *Geoderma* 91,  
 654 125-150.

655 Durn, G., Rubinić, V., Wacha, L., Patekar, M., Frechen, M., Tsukamoto, S., Tadej,  
 656 N., Husnjak, S., 2018a. Polygenetic soil formation on Late Glacial Loess on the

657 Susak Island reflects paleo-environmental changes in the Northern Adriatic area.  
 658 *Quatern. Int.* 494, 236-247.

659 Durn, G., Wacha, L., Bartolin, M., Rolf, C., Frechen, M., Tsukamoto, S., Tadej, N.,  
 660 Husnjak, S., Li, Y., Rubinić, V., 2018b. Provenance and formation of the red  
 661 palaeosol and lithified terra rossa-like infillings on the Island of Susak: A high-  
 662 resolution and chronological approach. *Quatern. Int.* 494, 105-29.

663 Durn, G., Frechen, M., 2018c. Quaternary of Croatia. *Quatern. Int.* 494, 1-4.

664 Durn, G., Škapin, S.D., Vdović, N., Rennert, T., Ottner, F., Ružičić, S., Cukrov, N.,  
 665 Sondi, I., 2019. Impact of iron oxides and soil organic matter on the surface  
 666 physicochemical properties and aggregation of Terra Rossa and Calcocambisol  
 667 subsoil horizons from Istria. *Catena* 183, 104184.

668 Faganeli, J., Pezdič, J., Ogorelec, B., Mišič, M., Najdek, M., 1994. The origin of  
 669 sedimentary organic matter in the Adriatic. *Cont. Shelf Res.* 14, 365-384.

670 Gaffey, S.J., Bronnimann, C.E., 1993. Effects of bleaching on organic and mineral  
 671 phases in biogenic carbonates. *J. Sediment. Petrol.* 63, 752-754.

672 Giani, M., Djakovac, T., Degobbis, D., Cozzi, S., Solidoro, C., Fonda Umani, S.,  
 673 2012. Recent changes in the marine ecosystems of the northern Adriatic Sea.  
 674 *Estuar., Coast. Shelf S.* 115, 1-13.

675 Goudeau, M.L.S., Grauel, A.L., Bernasconi, S.M., de Lange, G.J., 2013.  
 676 Provenance of surface sediments along the southeastern Adriatic coast off Italy:  
 677 An overview. *Estuar. Coast. Shelf S.* 134, 45-56.

678 Gu, B., Schmitt, J., Chen, Z., Liang, L., McCarthy, J.F., 1994. Adsorption and  
 679 desorption of natural organic matter in iron oxide: mechanisms and models. *Envir.*  
 680 *Sci. Tech.* 28, 38-46.

681 Hardy, R., Tucker M., 1998. X-ray powder diffraction of sediments. In: Tucker, M.  
 682 (Ed.), *Techniques in Sedimentology*, Blackwell Scientific Publications, pp. 191-  
 683 228.

684 Hedges, J.I., Keil, R.G., 1995. Sedimentary organic matter preservation: an  
 685 assessment and speculative synthesis. *Mar. Chem.* 49, 81-115.

686 Hochella, M.F. Jr., Lower, S.K., Maurice, P.A., Lee Penn, R., Sahai, N., Sparks,  
 687 D.L., Twining, B.S., 2008. Nanominerals, mineral nanoparticles and Earth  
 688 systems. *Science* 319, 1631-1635.

689 Hunter, R. J., 1981. *Zeta Potential in Colloid Science*. Academic Press,  
 690 London/New York, pp. 386.

691 Ilijanić, N., Miko, S., Petrinc, B., Franić, Z., 2014. Metal deposition in deep  
 692 sediments from the Central and South Adriatic Sea. *Geol. Croat.* 67, 185-205.

693 Juračić, M., Prohić, E., 1991. Mineralogy, sources of particles, and sedimentation  
 694 in the Krka River estuary (Croatia). *Geološki Vjesnik* 44, 195-200.

695 Jurina, I., Ivanić, M., Vdović, N., Troškot-Čorbić, T., Lojen, S., Mikac, N., Sondi, I.,  
 696 2015. Deposition of trace metals in sediments of the deltaic plain and adjacent  
 697 coastal area (the Neretva River, Adriatic Sea). *J. Geochem. Explor.* 157, 120-131.

698 Kahle, M., Kleber, M., Torn, M.S., Jahn, R., 2003. Carbon storage in coarse and  
 699 fine clay fractions of illitic soils. *Soil Sci. Soc. Am. J.* 67, 1732-1739.

- Kaiser, K., Eusterhues, K., Rumpel, C., Guggenberger, G., Kögel-Knabner, I., 2002. Stabilization of organic matter by soil minerals - investigations of density and particle-size fractions from two acid forest soils. *J. Plant Nutr. Soil Sc.* 165, 451-459.
- Kaiser, K., Guggenberger, G., 2003. Mineral surfaces and soil organic matter. *Eur. J. Soil Sci.* 54, 219-236.
- Keil, R.G., Tsamakis, E., Fuh, C.B., Giddings, J.C., Hedges, J.I., 1994. Mineralogical and textural controls on the organic composition of coastal marine sediments: Hydrodynamic separation using SPLITT-fractionation. *Geochim. Cosmochim. Ac.* 58, 879-893.
- Keil, R.G., Tsamakis, E., Giddings, J.C., Hedges, J.I., 1998. Biochemical distributions (amino acids, neutral sugars, and lignin phenols) among size-classes of modern marine sediments from the Washington coast. *Geochim. Cosmochim. Ac.* 62, 1347-1364.
- Kleber, M., Mertz, C., Zikeli, S., Knicker, H., Jahn, R., 2004. Changes in surface reactivity and organic matter composition of clay subfractions with duration of fertilizer deprivation. *Eur. J. Soil Sci.* 55, 381–391.
- Lojen, S., Sondi, I., Juračić, M., 2010. Geochemical conditions for the preservation of recent aragonite-rich sediments in Mediterranean karstic marine lakes (Mljet Island, Adriatic Sea, Croatia). *Mar. Freshwater Res.* 61, 119-128.
- Matijević, S., Bogner, D., Morović, M., Tičina, V., Grbec, B., 2008. Characteristics of the sediment along the eastern Adriatic coast (Croatia). *Fresen. Environ. Bull.* 17, 1763-1772.

723 Mayer, L.M., 1999. Extent of coverage of mineral surfaces by organic matter in  
724 marine sediments. *Geochim. Cosmochim. Ac.* 63, 207-215.

725 Mikutta, R., Kleber, M., Kaiser, K., Jahn, R., 2005a. Review: organic matter  
726 removal from soils using hydrogen peroxide, sodium hypochlorite, and disodium  
727 peroxodisulfate. *Soil Sci. Soc. Am. J.* 69, 120-135.

728 Mikutta, R., Kleber, M., Jahn, R., 2005b. Poorly crystalline minerals protect  
729 organic carbon in clay subfractions from acid subsoil horizons. *Geoderma* 128,  
730 106-115.

731 Moore, D.M., Reynolds, R.C., 1989. X-ray Diffraction and the Identification and  
732 Analysis of Clay Minerals. Oxford University Press, Oxford, pp. 378.

733 Morse, J.W., Arvidson, R.S, Lüttge, A., 2007. Calcium carbonate formation and  
734 dissolution. *Chem. Rev.* 107, 342-381.

735 Perret, D., Newman, M.E., Nègre, J.C., Chen, Y., Buffle, J., 1994. Submicron  
736 particles in the Rhine river - I. physico-chemical characterization. *Water Res.* 28,  
737 91-106.

738 Pigorini, B., 1968. Sources and dispersion of recent sediments of the Adriatic  
739 Sea. *Mar. Geol.* 6, 187-229.

740 Pikelj, K., Juračić, M., 2013. Eastern Adriatic Coast (EAC): geomorphology and  
741 coastal vulnerability of a karstic coast. *J. Coastal Res.* 29(4), 944-957.

742 Pikelj, K. Jakšić, L., Aščić, Š., Juračić, M., 2016. Characterization of the fine-  
743 grained fraction in the surface sediment of the eastern Adriatic channel areas.  
744 *Acta Adriat.* 57(2), 195-208.

- Plathe, K.L., von der Kammer, F., Hassellöv, M., Moore, J.N., Murayama, M., Hofmann, T., Hochella, M.F.Jr., 2013. The role of nanominerals and mineral nanoparticles in the transport of toxic trace metals: Field-flow fractionation and analytical TEM analyses after nanoparticle isolation and density separation. *Geochim. Cosmochim. Ac.* 102, 213-225.
- Range, K.J., Range, A., Weiss, A., 1969. Fire-clay type kaolinite or fire-clay mineral? Experimental classification of kaolinite–halloysite minerals. *Proceedings of the 3rd International Clay Conference*, Tokyo 1, 3-13.
- Ransom, B., Kim, D., Kastner, M., Wainwright, S., 1998. Organic matter preservation on continental slopes: importance of mineralogy and surface area. *Geochim. Cosmochim. Ac.* 62, 1329-1345.
- Ravaioli, M., Alvisi, F., Menegazzo Vitturi, L., 2003. Dolomite as a tracer for sediment transport and deposition on the northwestern Adriatic continental shelf (Adriatic Sea, Italy). *Cont. Shelf Res.* 23, 1359-1377.
- Rivaro, P., Ianni, C., Massolo, S., Ruggieri, N., Frache, R., 2004. Heavy metals in Albanian coastal sediments. *Toxicol. Environ. Chem.* 86, 85-97.
- Rodriguez-Navarro, C. Di Lorenzo, F., Elert, K., 2018. Mineralogy and physicochemical features of Saharan dust wet deposited in the Iberian Peninsula during an extreme red rain event. *Atmos. Chem. Phys.* 18, 10089-10122.
- Shepard, F.P., 1954. Nomenclature based on sand-silty-clay ratios. *J. Sediment Petrol.* 24, 151-154.
- Sondi, I., Milat, O., Pravdić, V., 1997. Electrokinetic potentials of clay surfaces modified by polymers. *J. Colloid Interf. Sci.* 189, 66-73.

768 Sonđi, I., Juraćić, M., 2010. Whiting events and the formation of aragonite in  
 769 Mediterranean karstic marine lakes: new evidence on its biologically induced  
 770 inorganic origin. *Sedimentology* 57, 85-95.

771 Sonđi, I., Mikac, N., Vdović, N., Ivanić, M., Furdek, M., Škapin, S., 2017.  
 772 Geochemistry of recent aragonite-rich sediments in Mediterranean karstic marine  
 773 lakes: Trace elements as pollution and palaeoredox proxies and indicators of  
 774 authigenic mineral formation. *Chemosphere* 168, 786-797.

775 Spagnoli, F., Dinelli, E., Giordano, P., Marcaccio, M., Zaffagnini, F., Frascari, F.,  
 776 2014. Sedimentological, biogeochemical and mineralogical facies of Northern and  
 777 Central Western Adriatic Sea. *J. Marine Syst.* 139, 183-203.

778 Tang, Z., Wu, L., Luo, Y., Christie, P., 2009. Size fractionation and  
 779 characterization of nanocolloidal particles in soils. *Environ. Geochem. Hlth.* 31, 1-  
 780 10.

781 Tomadin, L., 2000a. Sedimentary fluxes and different dispersion mechanisms of  
 782 the clay sediments in the Adriatic Basin. *Rend. Lincei-Sci Fis.* 9/11, 161-174.

783 Tomadin, L., 2000b. Riverborne and wind-blown kaolinite in the present clay  
 784 sediments of the Adriatic Sea. *Acta Universitatis Carolinae, Geologica* 44, 2-4,  
 785 157-161.

786 Tombacz, E., Szekeres, M., 2004. Colloidal behavior of aqueous montmorillonite  
 787 suspensions: the specific role of pH in the presence of indifferent electrolytes.  
 788 *Appl. Clay Sci.* 27, 75-94.

789 Toševski, A., Grgec, D., Padovan, B., 2012. Some characteristics of Eocene  
 790 flysch genesis, composition and weathering in Croatian coast belt. *The Mining-  
 791 Geology-Petroleum Engineering Bulletin* 25, 47-62 (in Croatian).

792 Vdović, N., Bišćan, J., Juračić, M., 1991. Relationship between specific surface  
 793 area and some chemical and physical properties of particulates: study in the  
 794 northern Adriatic. *Mar. Chem.* 36, 317-328.

795 Vdović, N., Juračić, M., 1993. Sedimentological and surface characteristics of the  
 796 northern and central Adriatic sediments. *Geol. Croat.* 46/1, 157-163.

797 Wentworth, C.K., 1922. A scale of grade and class terms for clastic sediments. *J.  
 798 Geol.* 30, 377-392.

799 Wilkin, R.T., Barnes, H.L., Brantley, S.L., 1996. The size distribution of framboidal  
 800 pyrite in modern sediments: an indicator of redox conditions. *Geochim.  
 801 Cosmochim. Ac.* 60, 3897-3912.

802 Wilkinson, K.J., Reinhardt, A., 2005. Contrasting roles of organic matter on  
 803 colloidal stabilization and flocculation in freshwaters. In: Droppo, I.G., Leppard,  
 804 G.G., Liss, S.N., Milligan, T.G. (Eds.), *Flocculation in Natural and Engineered  
 805 Environmental Systems*, CRC Press, pp. 147-170.

806 Zhuang, J., Yu, G.R., 2002. Effects of surface coatings on electrochemical  
 807 properties and contaminant sorption of clay minerals. *Chemosphere* 49, 619-628.



**Table 1.** Mineral composition of the investigated native sediments, the OM removal efficiency and the TOC content before (native) and after the NaOCl treatment (treated<sub>NaOCl</sub>).

Sample	TOC, mass. %	OM removal efficiency %	carbonates mass. %	Mineral composition of the native sediment samples	
	Native / treated <sub>NaOCl</sub>			major constituents	minor constituents
S1	0.47 / 0.17	64	27	Quartz, Phyllosilicates	Feldspars, Calcite, Dolomite, Pyrite
S2	0.92 / 0.16	82	59	Calcite, Quartz, Pyrite	Phyllosilicates
S3	0.51 / 0.09	82	28	Calcite, Phyllosilicates	Mg-Calcite, Quartz, Feldspars
S4	0.35 / 0.17	53	37	Calcite, Phyllosilicates	Mg-Calcite, Quartz, Feldspars,
S5	0.63 / 0.11	82	30	Calcite, Dolomite, Quartz, Phyllosilicates	Feldspars, Pyrite
S6	1.52 / 0.30	81	69	Aragonite, Mg-Calcite, Pyrite	Calcite, Quartz, Phyllosilicates, Feldspars
S7	0.88 / 0.18	80	15	Phyllosilicates, Quartz, Feldspars	Calcite
S8	0.43 / 0.20	54	14	Quartz, Phyllosilicates	Feldspars, Calcite

**Table 2.** Mineral composition of the separated size fractions of the investigated

Sample	Size fraction (µm)	Mean size (µm)	Calcite	Mg-calcite	Aragonite	Dolomite	Quartz	Plagioclase	K-feldspar	Pyrite	Illite	Chlorite	Smectite	KI <sub>D</sub>	KI	MLCM	I/S MLCM
S1	<2	0.4	+				+	+	+	+	XXX	X	X	X	X		XX
	<1	0.3	+				+			+	XX		X		X		XXX
S2	<2	0.4	+				+			+	XX			X	XX		XX
	<1	0.2	+				+			+	XX				XX		XX
S3	<2	0.4	+				+	+			XXX	XX	XX	X	X	X	
	<1	0.2	+				+				XXX	XX	XXX		X	X	
S5	<2	0.4	+			+	+	+		+	XXX	XX	X	X	X	X	X
	<1	0.2	+			+	+			+	XXX	X	XX	X	X	X	X
S6	<2	0.5	+	+	+		+	+	+	+	XX			X	XX	X	
	<1	0.2	+	+	+		+			+	XX				XX		
S7	<2	0.4	+				+	+			XXX	X	X		?	X	
	<1	0.2	+				+				XXX	X	X		?	X	
	<0.45	0.1	+				+				XXX	X	X		?	X	
S8	<1	0.2	+				+				XXX	X	XX		?	X	XX
	<0.45	0.1	+				+				XX	X	XXX		?	X	X

“+” non-clay mineral present in the sample

“X” relative abundance of clay minerals based on X-ray diffraction (no quantitative value is assigned to X)

“KI<sub>D</sub>” Kaolinite that forms intercalation compounds with DMSO

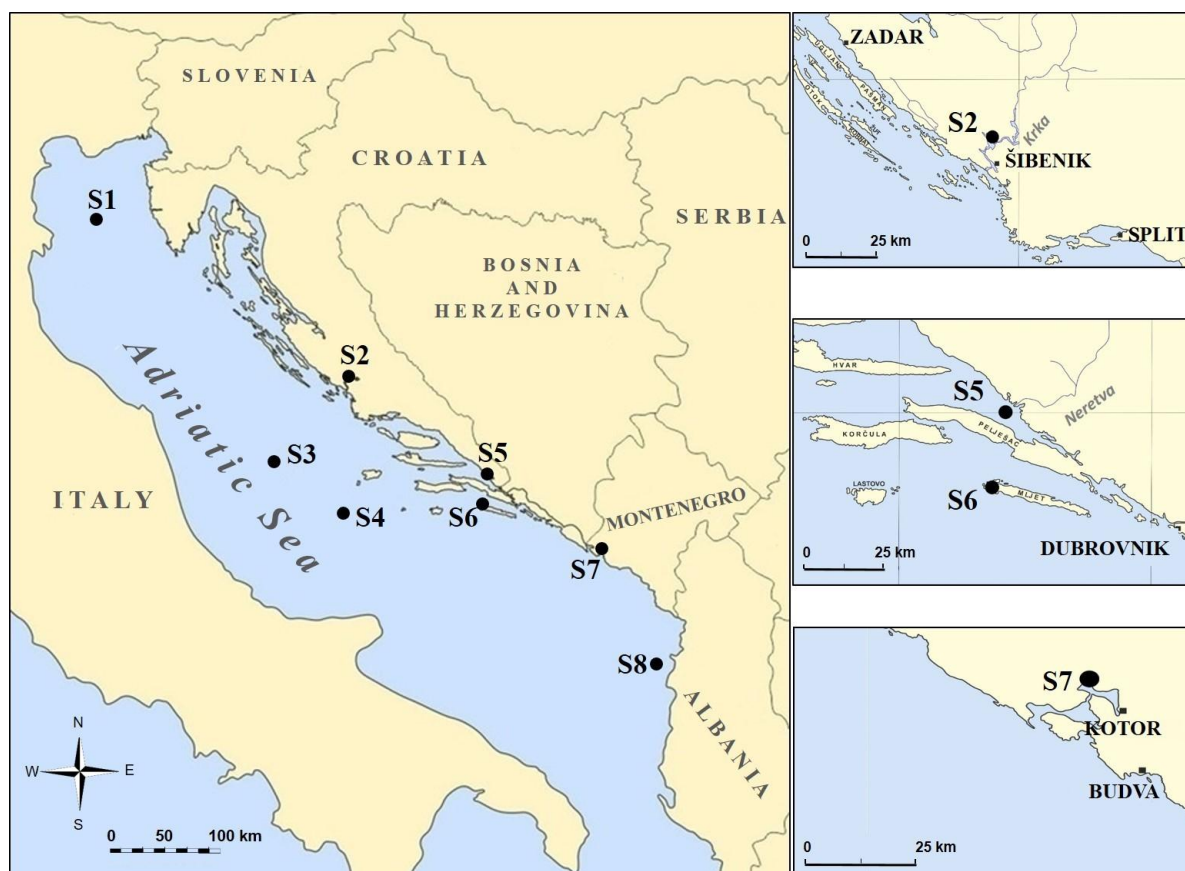
“KI” Kaolinite that does not intercalate with DMSO

“MLCM” mixed-layer clay minerals in which type of interstratification and constituting clay minerals were not recognized with certainty

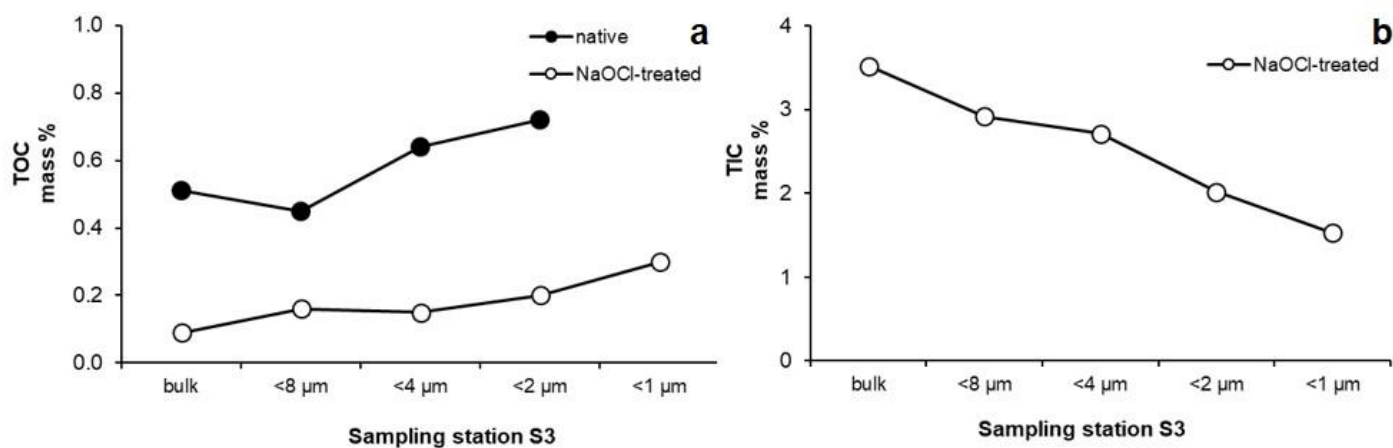
“I/S MLCM” Illite-smectite mixed-layer clay mineral

“?” mineral phase was not detected with certainty

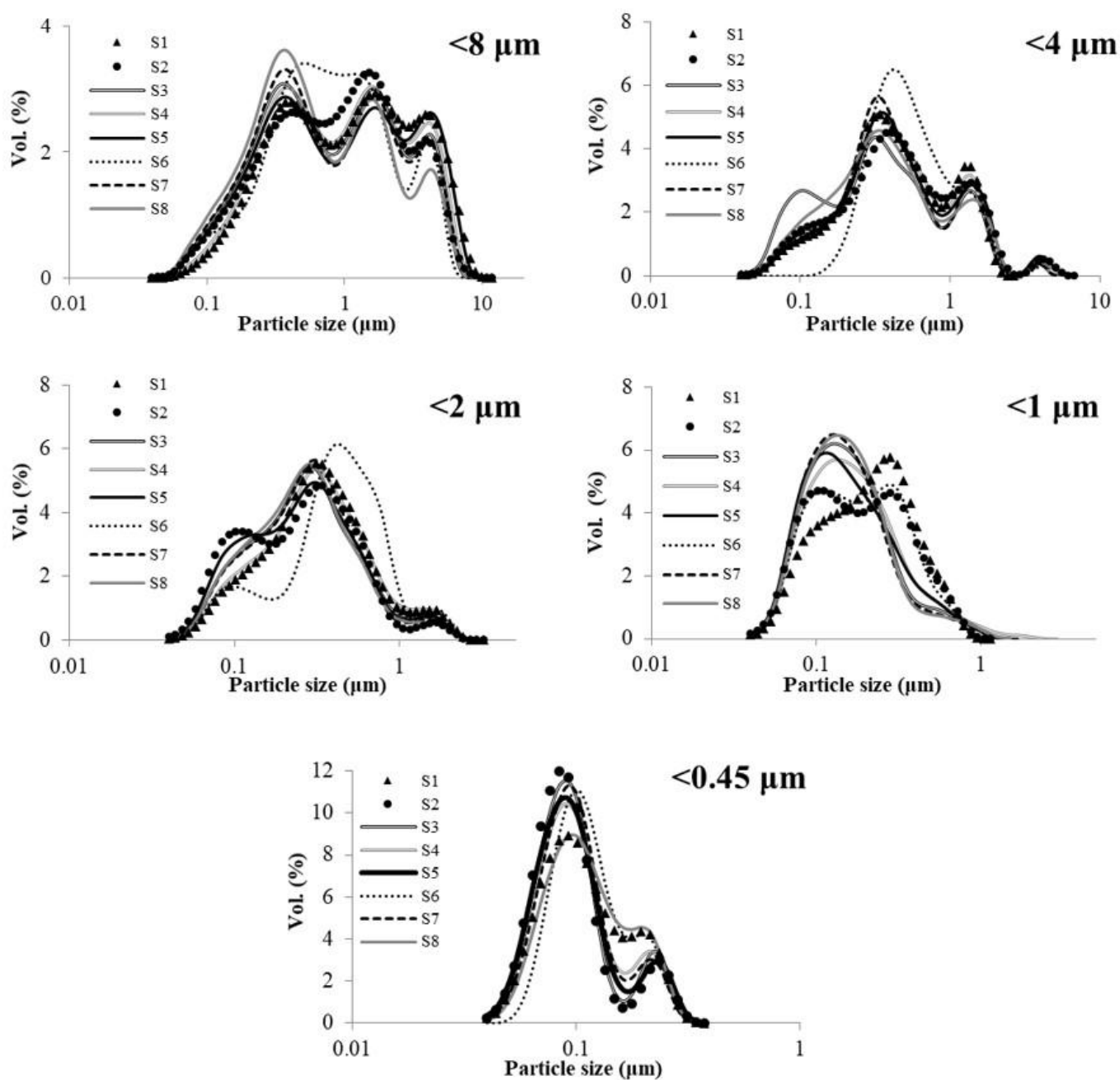
sediments.



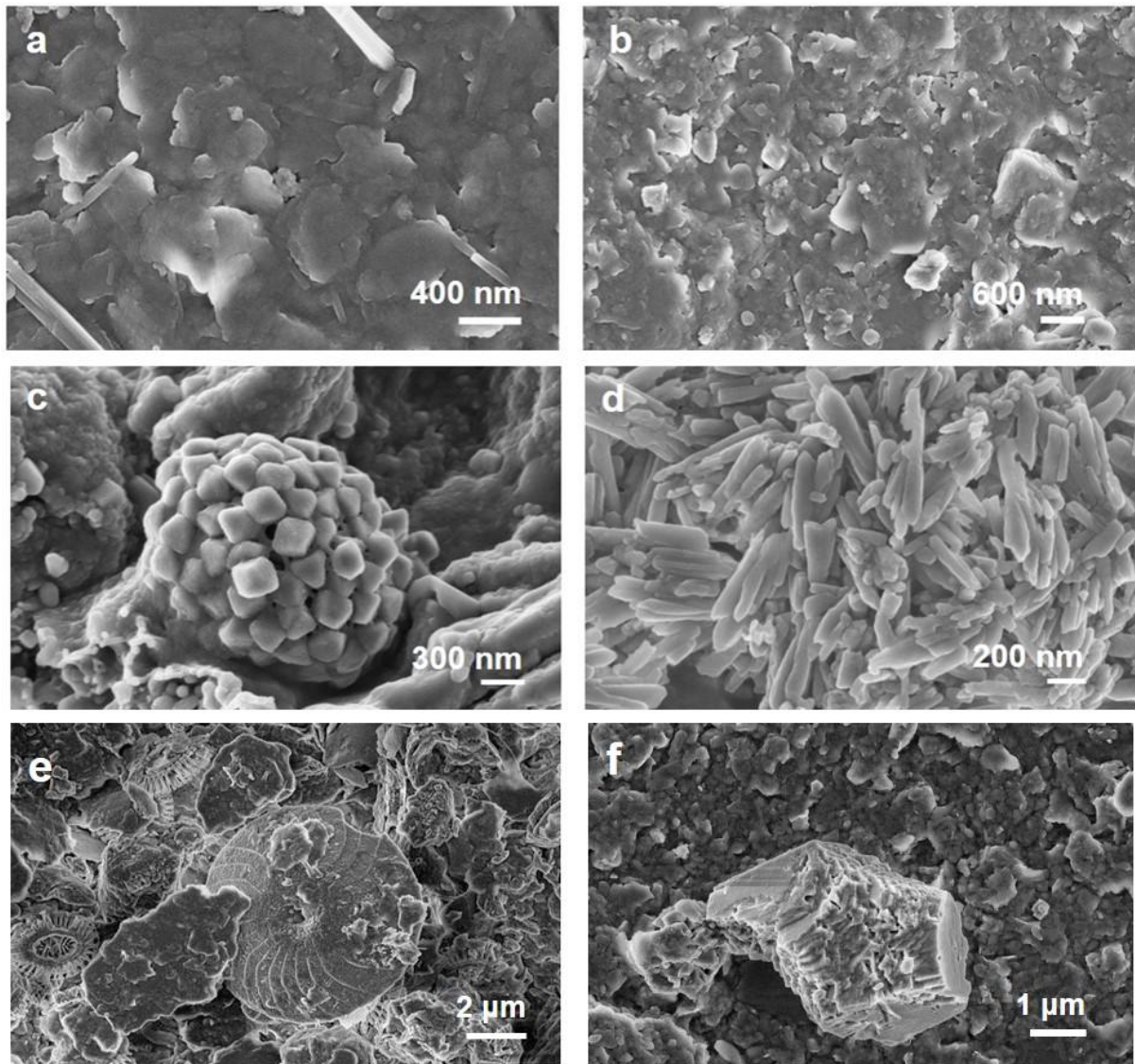
**Figure 1.** Map of the investigated area with sampling stations and their depth: S1 – northern Adriatic (36 m); S2 - Krka River estuary (6 m); S3 - central Adriatic open-sea (266 m); S4 - central Adriatic open-sea (166 m); S5 - Neretva Channel (30 m); S6 - Malo Jezero, island of Mljet (28 m); S7 - Risan Bay (33 m); S8 – open-sea in front of Albanian coast (100 m).



**Figure 2.** Size fractions separated from the sampling station S3 showing: (a) the TOC content in the native and the NaOCl-treated size fractions and (b) the TIC content in the NaOCl-treated size fractions.



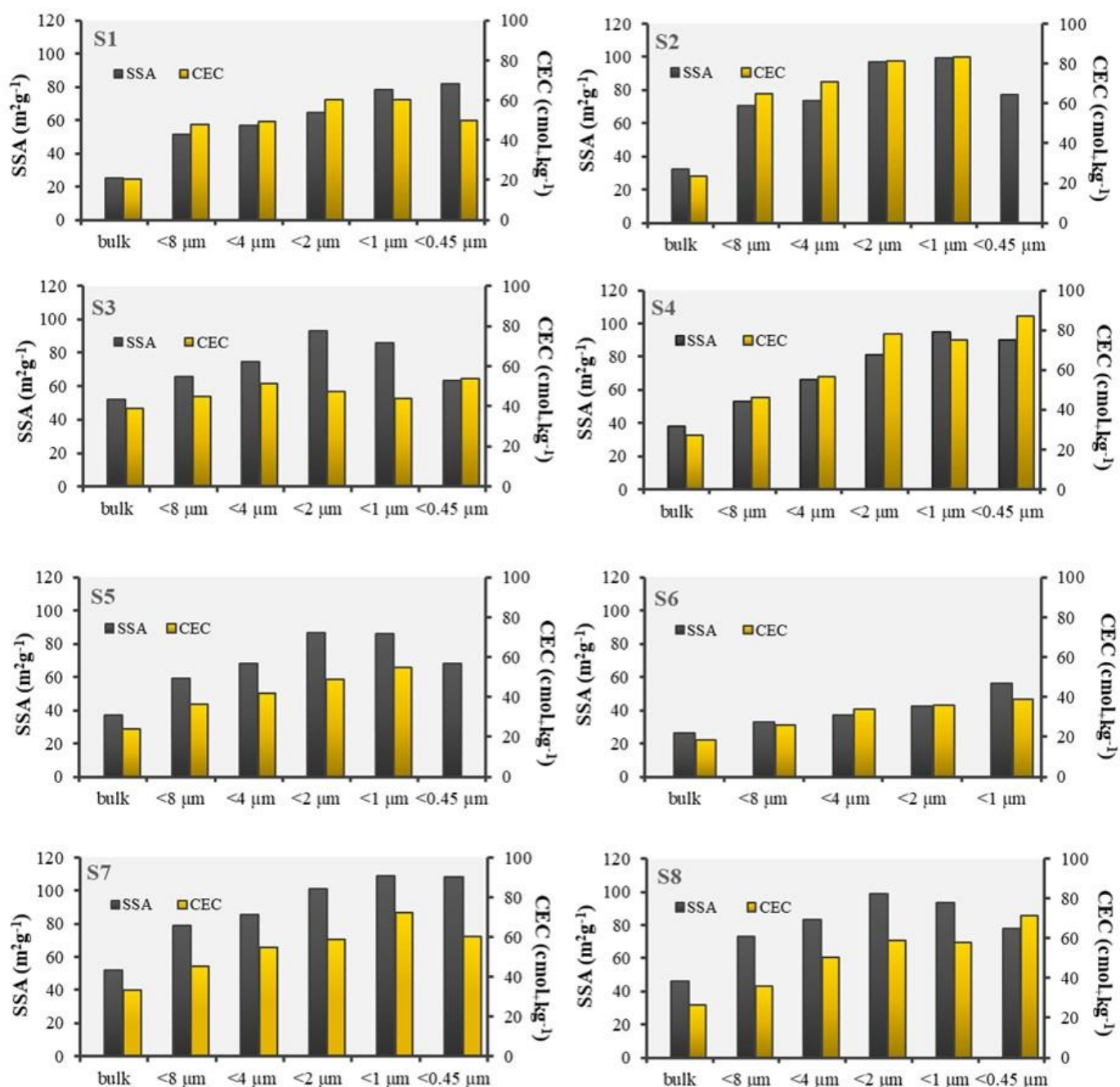
**Figure 3.** PSD curves of fractions ( $<8\ \mu\text{m}$ ,  $<4\ \mu\text{m}$ ,  $<2\ \mu\text{m}$ ,  $<1\ \mu\text{m}$ ,  $<0.45\ \mu\text{m}$ ) separated from the NaOCl-treated sediment samples.



**Figure 4.** FE-SEM photomicrographs showing: (a) phyllosilicates in sediment from the Albanian coastal area (S8) and (b) in sediment of the Risan Bay (S7); (c) diagenetic framboidal pyrite and (d) inorganically precipitated aragonite in sediment from Malo Jezero on the island of Mljet (S6); (e) prevalence of biogenic detritus in



sediment from the central Adriatic open-sea area (S3); (f) calcite in dominantly phyllosilicate submicrometer fraction from the Krka River estuary (S2).



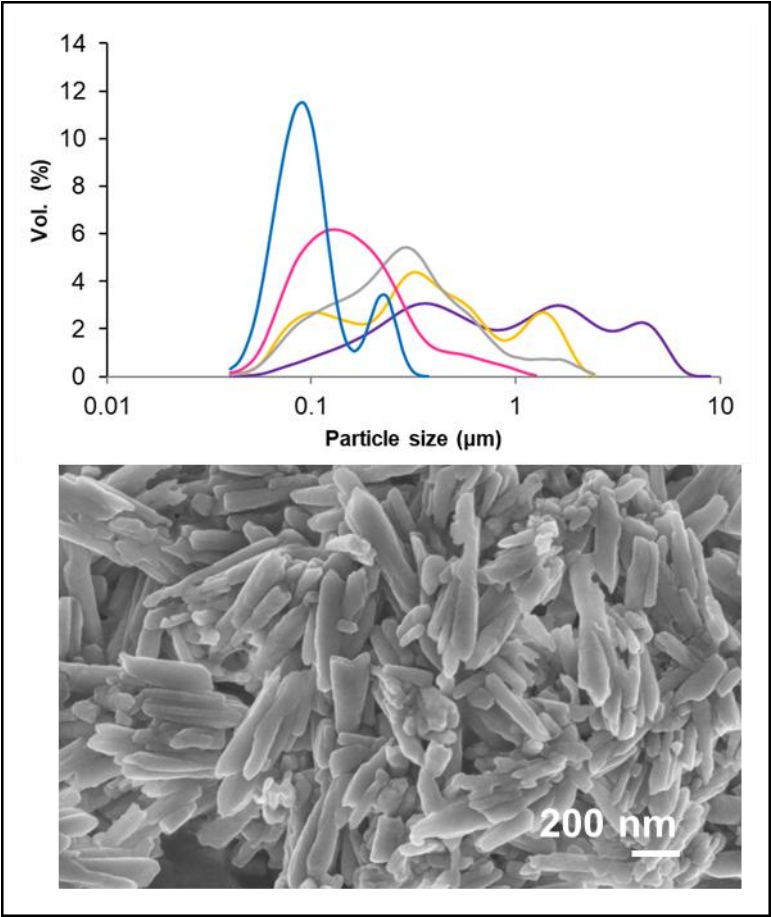
**Figure 5.** SSA and CEC of different size fractions of sediments after the OM removal.





## Supplementary Material

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**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: