



Terrestrial nanoparticle contaminants and geospatial optics using the Sentinel-3B OLCI satellite in the Tinto River estuary region of the Iberian Peninsula

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ABSTRACT

The Tinto River is known globally for having a reddish color due to the high concentration of dissolved metals in its waters. The general objective of this study is to analyze the dispersion of nanoparticles (NPs) and ultra-fine particles in terrestrial and geospatial suspended sediments (SSs) using Sentinel-3B OLCI (Ocean Land Color Instrument) satellite images; by examining water turbidity levels (TSM_{NN}), suspended pollution potential (ADG₄₄₃_{NN}) and presence of chlorophyll-a (CHL_{NN}). The images were collected in the estuary of the Tinto River, in the city of Nerva, Spanish province of Huelva, between 2019 and 2021. The following hazardous elements were identified in nanoparticles and ultra-fine particles by FE-SEM/EDS: As, Cd, Ni, V, Se, Mo, Pb, Sb and Sn. Sentinel-3B OLCI satellite images detected a 2019 TSM_{NN} of 23.47 g⁻³, and a 2021 reading of 16.38 g⁻³.

1. Introduction

The study of aquatic quality in marine estuaries with a high load of toxic elements is of fundamental importance in order to understand the different dynamics related to the potential for contamination of water and sediments, capable of causing environmental risks and having possible influence on human health (Neckel et al., 2021; Wang et al., 2022). Also, the transport of contamination to oceanic regions compromises biodiversity along with the livelihood of human economic activity, such as fishing (Orte et al., 2018; Ronchi et al., 2019; Geng et al., 2022; Wang et al., 2022). Almeida et al. (2020) and Neckel et al. (2021) highlight that metals consist of elements with electropositive bonds, some of which are red, yellow or silver in color. In the marine environment metals can contain dangerous elements capable of causing excessive harm to human health in addition to that of marine species.

According to Orte et al. (2018), Mo et al. (2022) and Najafi et al. (2022), the consequences of the contamination of water bodies and

sediments generate high environmental risks for entire continental regions. As contaminants spread, most exert an influence on the pH of marine areas, especially estuary regions. The buildup of hazardous elements in estuarine ecosystems is due to the release of industrial effluents directly into rivers without treatment of any kind (Najafi et al., 2022). Furthermore, mining, livestock and agricultural irrigation return flows carrying chemical pesticides also lead to the accumulation of dangerous elements in estuaries and river beds (Singh et al., 2020; Kuprijanov et al., 2021; Neckel et al., 2021). Dangerous elements of metallic origin present a high potential for ecological risk. Sun et al. (2018), Singh et al. (2020) and Fang and Wang (2022) define dangerous metallic elements as the following: manganese (Mn), copper (Cu), lead (Pb), zinc (Zn), iron (Fe), nickel (Ni), cadmium (Cd), chromium (Cr), cobalt (Co) and arsenic (As). It is possible for high concentrations of these dangerous elements to be present in the soil naturally in regions of soil with abundant minerals. Soil runoff from such regions contributes to different optical tones in the coloration of local water resources (Neckel

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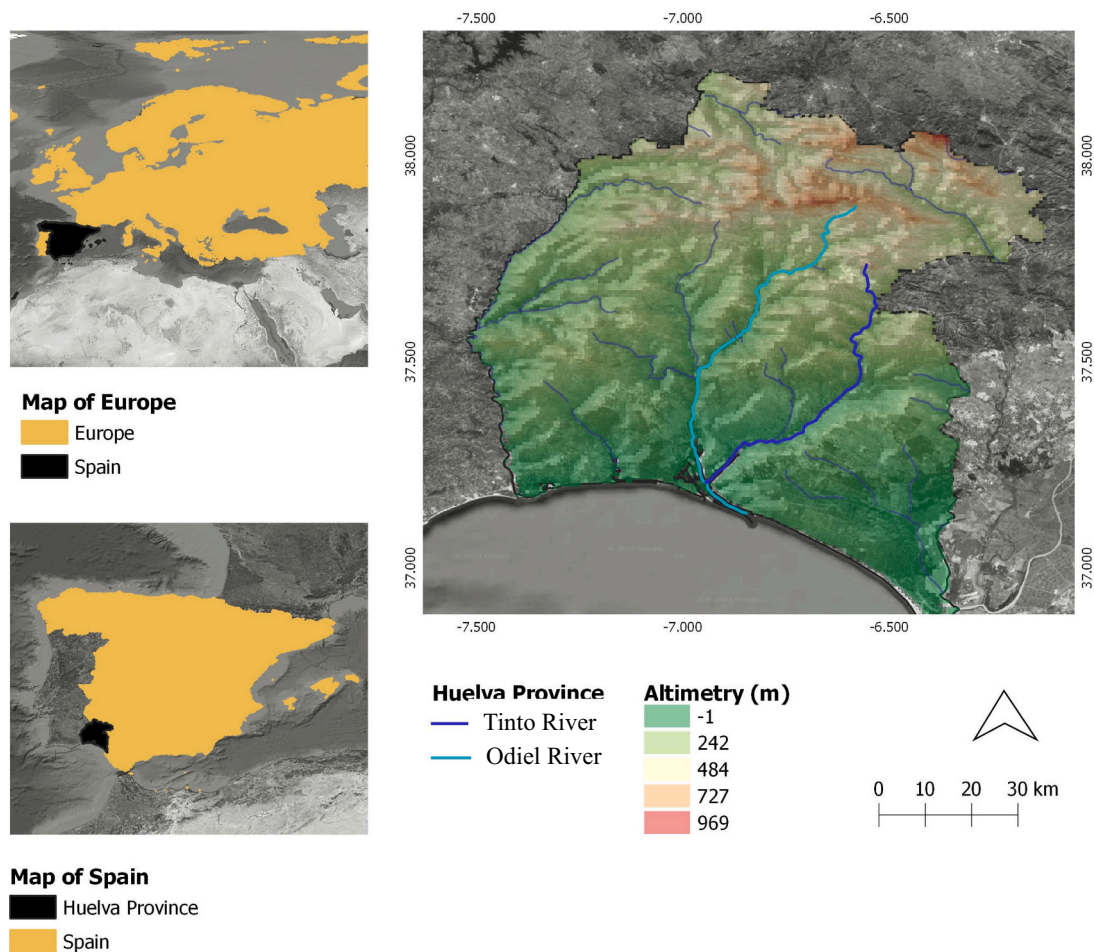


Fig. 1. Location of the Tinto River estuary, located in the city of Nerva, Spanish province of Huelva.

et al., 2021; Zhuang et al., 2021; Derakhshan-Babaei et al., 2022; Li et al., 2022).

Optically visible gradations of water color are visible to the naked eye in addition to satellites overhead. This difference in color is most often due to the presence of metallic elements in aqueous solution that vary according to pH variation (Ordóñez et al., 2022; Riminucci et al., 2022).

The object of this research, the Tinto River, is located in the Spanish province of Huelva on the Iberian Peninsula. This river got its name due to the reddish color of its waters, which may contain elements that are dangerous to human health, the environment and marine fauna and flora (Ferris et al., 2004; Fernández-Remolar et al., 2005; Aguilera et al., 2007; Gammons et al., 2008; Trigueros et al., 2012; López-Arce et al., 2019).

Numerous pyrite mining activities take place within the Tinto River estuary region, located in southwest Spain, giving rise to high concentrations of Al, Fe, Mg, S and Si in the river's waters (Ferris et al., 2004). The Tinto River was studied by the National Aeronautics and Space Administration (NASA) in January 2004 because its reddish color is similar to Planet Mars. NASA tested equipment on and analyzed levels of metal in the sediments of the Tinto River bed (Fernández-Remolar et al., 2005). The results of this testing showed that the Tinto River gets its reddish color from an intense process of geochemical weathering. Water reacts with the local bedrock of basaltic composition, forming and accumulating nanoparticles in sediments. These nanoparticles cause a high concentration of sulfate to be accumulated in sedimentary basins. Local springs have high proportions of iron and sulfuric acid. These springs run into the Tinto River, and through aqueous homogenization

lead to the reddish color of the river (Fernández-Remolar et al., 2005).

Aguilera et al. (2007) demonstrated the presence of high concentrations of Zn, Cu and Ni in animal and aquatic plant samples collected from the Tinto River. The study also showed that the pH of Tinto River water displayed average variations from 0.9 to 2.5 in different seasons. Studies by Gammons et al. (2008) demonstrated that the waters of the Tinto River concentrate high chemical acidity potentials (pH 2.3 to 3.1) with a high predominance of Fe. Trigueros et al. (2012) and López-Arce et al. (2019) also found the presence of high Pb contamination of plants and leaves collected on the banks of the Tinto River. This finding has a high potential for environmental degradation capable of negatively compromising marine fauna and flora.

This study is therefore justified due to the importance of continuing studies in the estuary region of the Tinto River based on past studies carried out by Ferris et al. (2004), Fernández-Remolar et al. (2005), Aguilera et al. (2007), Gammons et al. (2008), Trigueros et al. (2012) and López-Arce et al. (2019). These studies identified high levels of contamination harmful both to human health and the quality of marine ecosystems, thus enabling subsidies for future environmental recovery projects.

In the case of the Tinto River, field collection of riverine sediments allows for the identification of the predominance of chemical substances and hazardous elements (HEs) present in NPs, often suspended and transported with SSs, as emphasized by studies carried out by Silva et al. (2021), Zhao et al. (2021) and Hojjati-Najafabadi et al. (2022). Another analytical factor to be considered for analysis of the Tinto River is geospatial analysis by the Sentinel-3B OLCI satellite, which is characterized as one of the most advanced methods in the world to evaluate

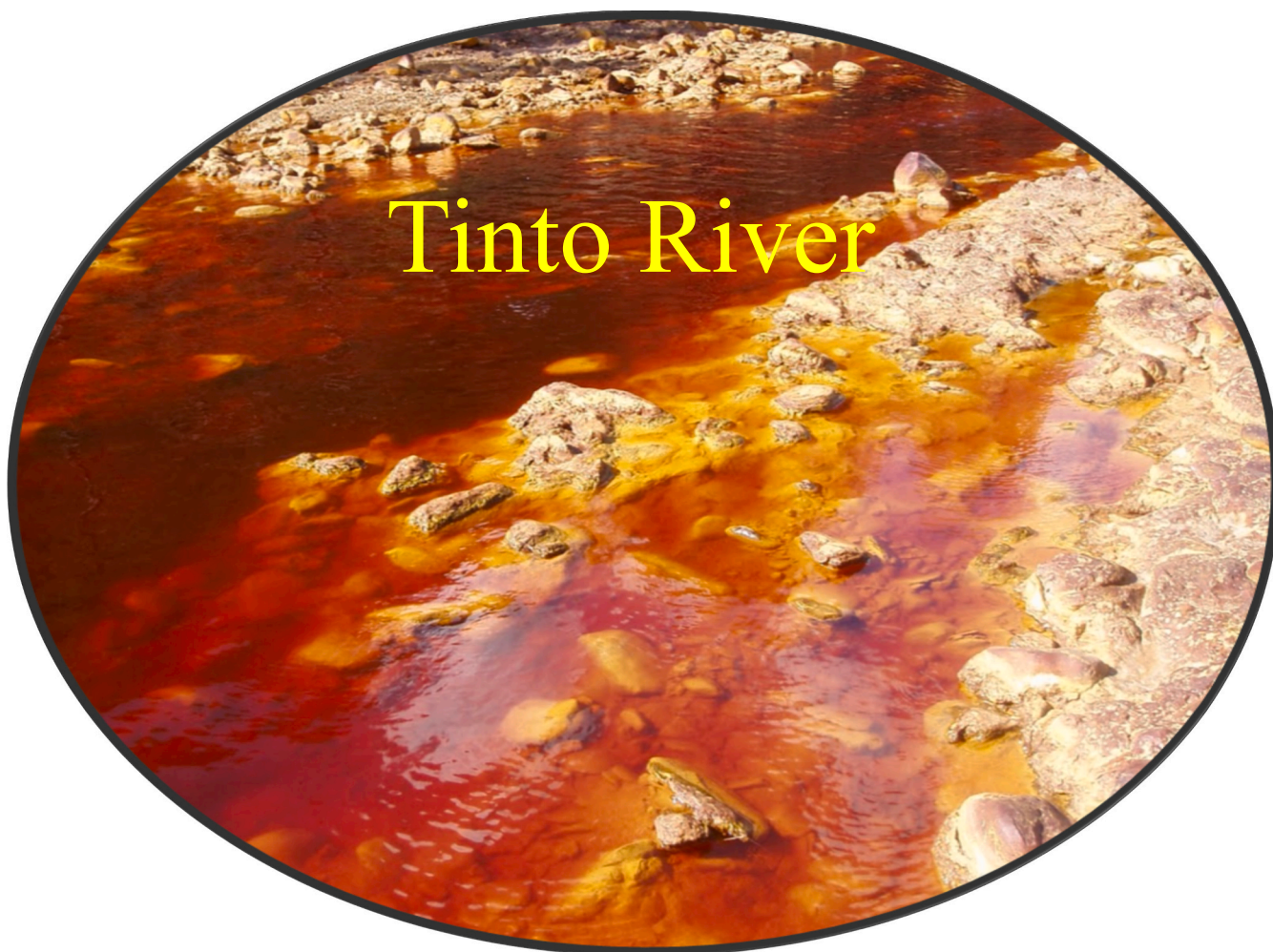


Fig. 2. Representation of the Tinto River, with its reddish color.

ADG_443_NN, TSM_NN and CHL_NN in marine estuaries (Xi et al., 2020; Neckel et al., 2021).

The general objective of this study is to analyze the dispersion of NPs and ultra-fine particles in terrestrial and geospatial SSs through Sentinel-3B OLCI satellite images collected in the estuary of the Tinto River, in the city of Nerva, Spanish province of Huelva, between 2019 and 2021. The satellite images are examined for levels of TSM_NN, ADG_443_NN and CHL_NN. This study is of fundamental importance for the creation of public policies capable of consolidating future environmental recovery projects in the estuary region of the Tinto River. In addition to using collected NPs in the field on SSs, geospatial collections were used with unpublished images from the Sentinel-3B OLCI satellite, further enhancing the relevance of this study to the international scientific community.

2. Materials and methods

2.1. Study area

The Tinto River estuary region covers an area of 739 km², forming part of the Gulf of Cádiz (Fig. 1), a part of the Atlantic Ocean, located adjacent to the Iberian Peninsula, south of Portugal and southwest of Spain, in the Spanish province of Huelva (Fernández-Remolar et al., 2005). What makes the Tinto River unique is its acid sulfide drainage (Trigueros et al., 2012; López-Arce et al., 2019). The absence of regional bedrock capable of neutralizing acids, together with the intense mining of iron, has caused unusually extreme conditions of acidity (low pH) and

toxic concentrations of metals and metalloids; from the headwaters, where the concentration of mining activities begins, to the mouth of the Tinto River (Ferris et al., 2004; Fernández-Remolar et al., 2005; Aguilera et al., 2007; Gammons et al., 2008; Trigueros et al., 2012; López-Arce et al., 2019). Generally, fish, amphibians, insects and plants do not live in the waters of the Tinto River due to their acidity (Nolen et al., 2022).

However, the Tinto River (Fig. 2) is not totally lifeless, as there are abundant extremophile organisms (microorganisms and certain species of algae) that inhabit it, as they have the ability to adapt to these particular conditions that would kill most other organisms (Olías and Nieto, 2015). This arouses great scientific interest due to the existence of a wide variety of eukaryotic organisms which resemble the conditions found on Planet Mars (Olías and Nieto, 2015).

With a total length of approximately 100 km, the Tinto River meets the Odiell River before flowing into the Gulf of Cádiz in the Atlantic Ocean. 519,229 inhabitants live in close proximity to the river as it flows through the Spanish province of Huelva (Aemet, 2022) (Fig. 1). The regional climate is characterized as Mediterranean, with long, hot, dry summers and mild winters. The average annual temperature is 23.9 °C, and average annual precipitation is 525 mm, divided as follows: winter, 220 mm; spring, 115 mm; summer, 15 mm and autumn, 173 mm (Aemet, 2022).

Another factor that stands out on the banks of the Tinto River is mining activities, with the extraction of iron oxide being the most predominant according to the Ministry of Ecological Transition and the Demographic Challenge of Spain. A total of 116,000 tons of iron oxide was extracted along the river's banks in 2018, with an additional



Fig. 3. Visual detail of the sediments dredged by the port of the city of Nerva.

147,000 tons extracted in 2019. The year 2020 saw extraction fall to only 77,000 tons due to the interruption of services caused by the COVID-19 pandemic (Metdc, 2022).

The Tinto River also receives industrial waste and contaminants as it flows through the urban area of Nerva. The river deposits a high amount of sediment in the port area, where the sediments for analysis in this study were collected (Fig. 3). When diluted Tinto River waters first enter the Atlantic Ocean, the precipitation of dissolved metals occurs. This is due to the fact that the Tinto River waters are exceptionally acidic, whereas the oceanic waters are of relatively neutral pH (Fernández Caliani et al., 1997). In this area of the estuary, the ocean and the estuary

move and deposit large amounts of quartz and clays (Harmesa et al., 2022). Industrial mining on or near the banks of the river in the post-Roman era has created a very serious problem of contamination by metals in the Tinto River. The river also contends with discharges from oil refineries, paper mills, fertilizer producing industries and others that, combined, significantly degrade the water quality of the Tinto River.

2.2. Sample collection, laboratory analysis of SSs and geospatial application with satellite images

The data collection and analytical procedures of this study were divided into two methodological steps. The first was sample collection and laboratory analysis of the levels of NPs present in the collected SSs. The second comprised geospatial collections using Sentinel-3B OLCI satellite images at the same 40 sites from which samples were taken. Neckel et al. (2021) emphasizes that carrying out studies involving sediment analysis, integrated with satellite studies, is one of the most complete forms of investigation of contaminants on a global level. In this case, through field studies, the verification of the types of hazardous elements present in the identified sediments can be confirmed through geospatial analysis. Using the Sentinel-3B OLCI images, the quantity of solid particles of sediment present in the water during a certain period of study is able to be ascertained (Neckel et al., 2022).

The SS collections carried out in the field at 40 points along the Tinto River were spaced between 300 and 800 m downstream from each upstream collection point, as laid out by studies conducted by Neckel et al. (2021) and Tarrés et al. (2022). A total of 40 SS samples were collected during both the summer (August 5, 2019 and August 15, 2021) and winter (March 10, 2019 and March 16, 2021). After collection, the SS samples were stored in a sterilized glass container, transported in a sealed polystyrene box and submitted to the Environmental Chemistry Laboratory of the Universidad de La Costa, Colombia. A combined total of 160 samples were collected in 2019 and 2021. For better accuracy and reliability of this study, these samples were tripled in the laboratory,

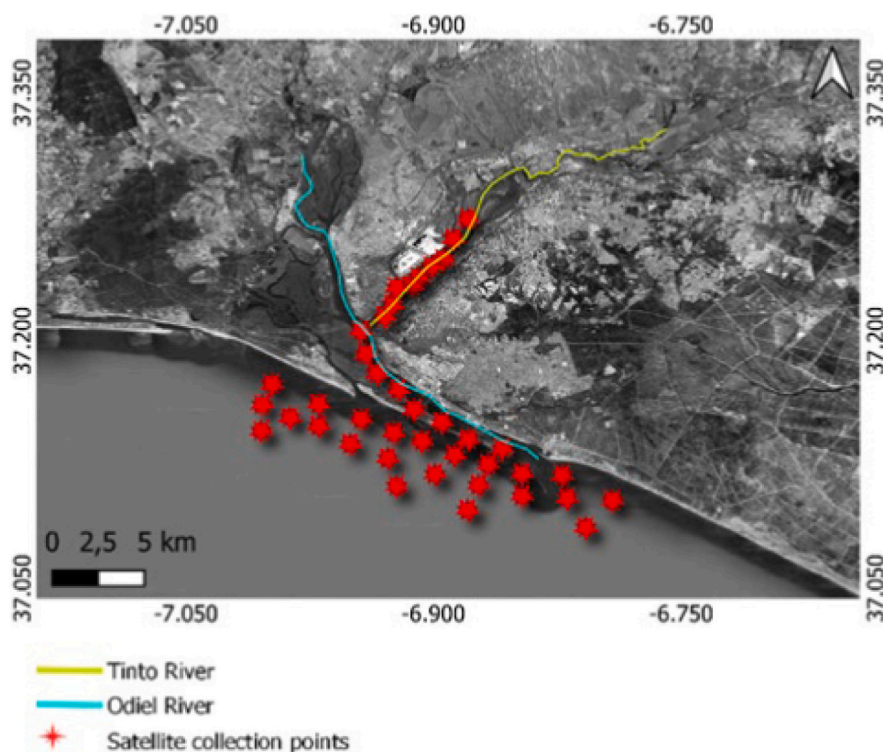


Fig. 4. Location of SS sample collection points and points collected by Sentinel-3B OLCI satellite images in the Tinto River estuary region in the city of Nerva.

now comprising 480 specimens for analysis. Samples were processed by X-ray Diffraction (XRD) analysis according to Alderton (2021) and Fahoul et al. (2022), which allows for the possibility of identifying mineralogical phases present in the structures of the SSs collected in the Tinto River estuary (Fig. 4). Subsequently, the sampled SSs were analyzed via powder diffractometer (PANalytical Xpert-PRO), enabling an understanding of the wave conduction of the metallic elements present in the SSs, thus allowing for chemical identification (Mejdi et al., 2020) and a greater reliability attributed to the results of this study. Integrating use of FIB-SEM (Focused Ion Beam Scanning Electron Microscopy) allowed for two electron beams to consider focused ions capable of revealing coincidences between the sampled sediment material (Silva et al., 2020; Rausch et al., 2022). This was followed by the use of HR-TEM (high-resolution transmission electron microscopy) (Dietrich et al., 2022; Zhang et al., 2022), which enabled the identification of HES present in the NP structures of the SSs analyzed from the 40 points sampled in the Tinto River estuary.

The second analytical procedure performed in this study consisted of the use of images from the Sentinel-3B OLCI satellite, based on Neural Network (NN) algorithms, to evaluate the levels of TSM_{NN}, ADG₄₄₃ NN and CHL_{NN} in the same identical 40 locations from which SS samples were collected (Fig. 4). The Sentinel-3B OLCI was selected for use in this study due to the fact that it presents satellite images spanning 2019 and 2021, with cloud-free images in image resolutions calibrated by the European Space Agency (ESA) with an average normalization of 0.83 µg/mg, totaling a maximum error of 6.62 %. The calibration (0.83 µg/mg) of the images used was performed by the ESA, enhancing the reliability of this study by reducing the error. Calibration involves geometric correction through modeling activities of these satellite images in relation to the coordinate system (Tang et al., 2021; Neckel et al., 2022). The ESA performs this error correction so that the resulting images not only present an excellent spatial, spectral and temporal resolution, but are viewed with greater reliability (Tang et al., 2021; Xu and Liu, 2021; Neckel et al., 2022; Shin et al., 2022).

Images of the 40 sample points were collected directly from the Sentinel-3B OLCI image library using Geographic Information System (GIS) software SNAP (Sentinel Application Platform) version 8.0.4. Images with 300 m resolution, dated: April 27, 2019 and April 13, 2021 for the spring season; August 28, 2019 and August 22, 2021 for the summer season; October 25, 2019 and November 2, 2021 for the autumn season; and March 22, 2019 and January 8, 2021 for the winter season were utilized for this study. Spreadsheets were generated using statistical data to be modeled in JASP software version 0.14.1.0. According to Wang et al. (2019) and Tarpanelli et al. (2020) the Ocean and Land Color Instrument (OLCI) sensor aboard Sentinel-3B provides a satisfactory technical approach to mapping land surface water bodies using 300 m of spatial resolution. By utilizing a spatial resolution of 300 m, it is possible to carry out studies involving long-term water quality with high frequency (Wang et al., 2019; Tarpanelli et al., 2020). The images used for this study were unpublished and unavailable to the public at the time this research was conducted. Permission for their use was obtained through the European Space Agency (ESA), in partnership with the National Aeronautics and Space Administration (NASA), by accessing the researchers' login.

The process of collecting and analyzing physical SS samples allowed us to understand the presence of HES in the NPs of the SSs analyzed. Combined with the images of the Sentinel-3B OLCI satellite, it was then possible to combine the confirmation of the presence of these dangerous and harmful chemical elements in the marine environment to potential human health concerns in the Tinto River estuary region. This reinforces the importance of using this analytical methodology as laid out by Kravitz et al. (2020), Mikelsons and Wang (2021), Neckel et al. (2021) and Vanhellemont and Ruddick (2021). These studies point out the need to carry out field studies, compared with geospatial satellite results, for a better understanding of hydrological conditions in micro and macro regions of the world.

Table 1

Hazardous elements, amorphous phases and minerals detected.

	Abundance	Hazardous elements
Amorphous phases	X	Li, Mg, Sr, Ba, Sc, Ti, V, Cr, Mn, Co, Ni, Zn, As, Se, Y, Zr, Nb, Mo, Ag, Sn, Sb, Ge, W, Hg, Pb
Silicates		
Albite	x	Ti, Cr
Chlorite	x	Ti, Cr, Pb
Diopside	x	N.D.
Illite	X	Ti, V, Cr, Mn
Kaolinite	X	N.D.
Muscovite	X	Cr, Cd
Olivine	x	N.D.
Quartz	X	N.D.
Sulphides		
Arsenopyrite	x	As, Se, Hg, Pb
Chalcopyrite	x	As, Cu
Galena	x	Pb, Cu
Marcasite	x	As, Se, Cd, Sb,
Pyrite	x	Zn, As, Se, Mo, Cd, Hg, Pb, As, Pb
Pyrrhotite	x	As, Mo
Sphalerite	x	Zn, Mo
Carbonates		
Aragonite	x	N.D.
Ankerite	x	N.D.
Calcite	x	N.D.
Dolomite	x	N.D.
Siderite	x	Cr, Mn, Co, Ni
Phosphate		
Monazite	x	F, Ce, La, Th, Nd, Sm
Sulfates		
Alunogen	x	As, Cr
Anglesite	x	Pb
Anhydrite	X	N.D.
Argentojarosite	x	As, Se, Pb
Barite	x	Ba, Sc, Cr, Zn
Bassanite	x	N.D.
Beaverite	x	As, Cu, Pb,
Beaverite	x	Cu
Copiapite	x	Sr, Ti, V, Cr, Mn, Co, Ni, Zn, As, Se, Mo, Ag, Sn, Sb, Hg, Pb
Coquimbite	x	Mg, Sr, Sc, Ti, V, Cr, Mn, Co, Ni, Zn, As, Se, Y, Ag, Sn, Sb, W, Hg, Pb
Epsomite	x	N.D.
Ferrohexahydrate	X	N.D.
Gypsum	X	N.D.
Hexahydrate	x	N.D.
Jarosite	X	V, Cr, Co, Ni, Zn, As, Se, Zr, Nb, Mo, Ag, Sn, Sb, W, Hg, Pb
Melanterite	X	Al, Mg, Mn
Natrojarosite	x	As, Se, Mo, Ag, Sn, Sb, Hg, Pb
Pickeringite	x	N.D.
Plumbojarosite	x	As, Se, Pb
Schwertmannite	X	Mg, Ti, V, Cr, Co, Ni, Zn, As, Se, Zr, Nb, Mo, Ag, Sn, Sb, W, Hg, Pb
Symplectite	x	As, Mo
Rozenite	X	As, Al, Mg
Oxides and hydroxides		
Ti-dioxides (anatase and rutile)	x	Ti, Cr, As
Hematite	X	Sr, Sc, Ti, V, Cr, Mn, Co, Ni, Zn, As, Se, Sb, W, Hg, Pb
Goethite	X	Li, Mg, Sr, Ba, Sc, Ti, V, Cr, Mn, Co, Ni, Zn, As, Se, Y, Zr, Nb, Mo, Ag, Sn, Sb, W, Hg, Pb
Gibbsite	X	Cr, Mn, Co, Ni, Zn, As, Se, Pb
Scorodite	x	As, Se

X = main components (detected by both XRD and electron microscopes) and x = trace components (detected only by microscopy).

The results collected from the Sentinel-3B OLCI satellite images were submitted using spreadsheets for JASP software version 0.14.1.0. for performing K-means cluster analysis. Maroni et al. (2021) laid out a process for obtaining data vectors, represented by clusters, based on centroids. Consequently, the application of the results by variation of

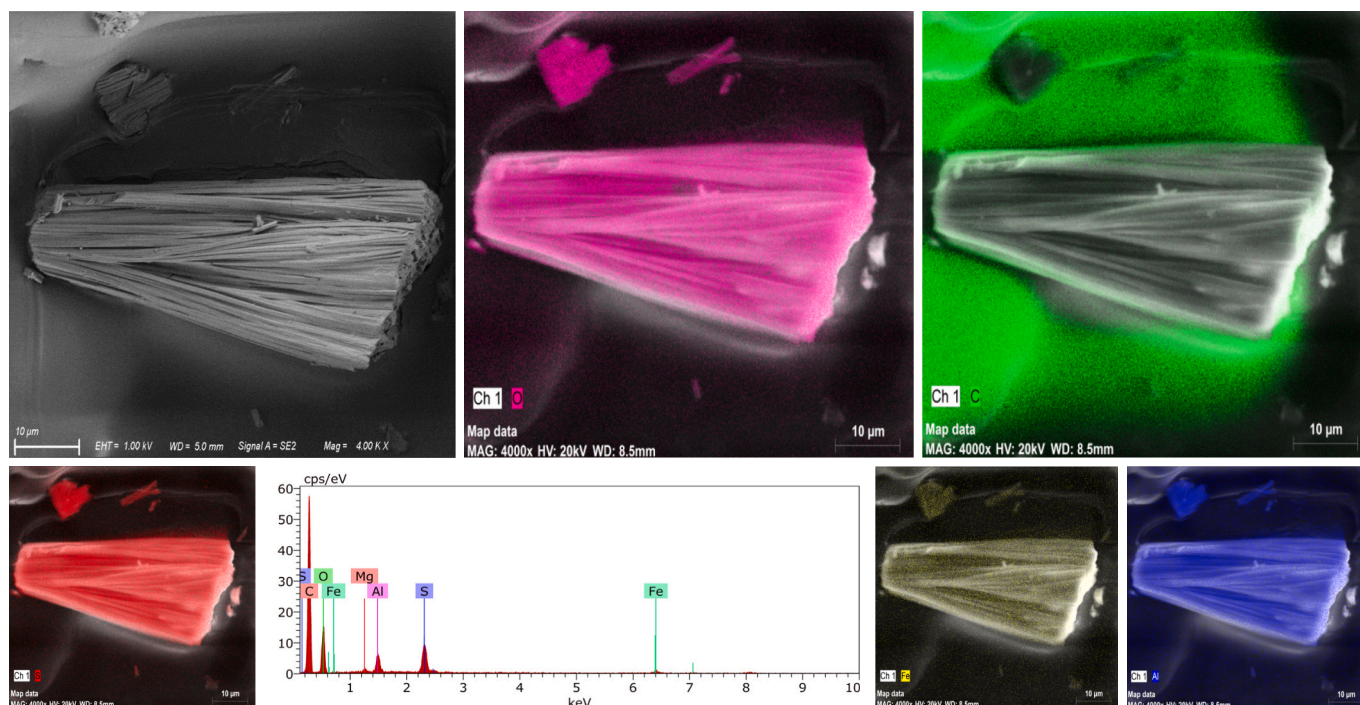


Fig. 5. Presence of melanterite and rozenite identified in the sampled SSs.

clusters was based on the position of the centroids, being recalculated and updated as the average center of the resulting clusters. Algorithmic applicability of the data space partition of the sum of squares of errors (SSE) was located in the internal area of the cluster, assigned to the closest centroid, according to the mean identified in the Silhouette index (Maroni et al., 2021; Abdalameer et al., 2022). Naghizadeh and Metaxas (2020) and Maroni et al. (2021) emphasize that the Silhouette index consists of the average cluster, considering the properties of each categorized cluster with values greater than 1 and high reliability between the clustering results. The lower limit, less than -1 indicates an incorrect coherence correlation applied to the results. For Dal Moro et al. (2021), the application of clusters allows for a better graphic and representative understanding to the reader in relation to the results obtained in research, thus reinforcing the need for this particular application of clusters in this study.

3. Results and discussion

3.1. Sampling carried out in the field

The results of the field sampling of SSs collected from 40 points in the estuary region of the Tinto River are shown in Table 1. They reveal that most of the analyzed sediments are composed mainly of quartz, clays, acid sulfates and iron and aluminum hydroxides. Table 1 also helps to ratify that both sulfates, oxides and hydroxides contain high loads of toxic elements in their structures. After all, they are adsorbents of such water contaminants (Ahmed et al., 2021; Sonal and Mishra, 2021; Varsha et al., 2022; Sonal and Mishra, 2021; Varsha et al., 2022). In this case, identified in the SSs collected in the Tinto River estuary. Consequently, one of the main mineralogical groups detected were Fe and Al sulfates. According to Neckel et al. (2021) and Mosa et al. (2022), excess Fe and Al in water can generate harm to marine fauna and flora, in addition to increasing the risks of human contamination.

Furthermore, the Tinto River drains its waters, together with its sediments, into the Gulf of Cádiz, a fishing region where local residents and large fishing companies make up the local, fishing based economy. It is likely that those eating the fish caught in this area experience a greater

intake of Fe and Al upon digestion of the fish (Shaibur and Das, 2022). Fe and Al consumed in excess, become elements hazardous to human health, present carcinogenic risks, and threaten human health when accumulated in the human body in high concentrations (Ahmed et al., 2019; Rashid et al., 2022). Kenkhuis et al. (2022) highlight that Fe in the human body can be absorbed differently between individuals, which compromises the establishment of tolerated levels of exposure. Excess consumption of Fe has been linked to increased rates of Alzheimer's disease in the population, thus stimulating neurodegenerative disorders.

This study points out that both melanterite and rozenite were the few crystals detected without amorphous material in their structures (Fig. 5). This does not mean that they cannot also occur with amorphous compounds (Neckel et al., 2021; Silva et al., 2021), being easily detected by FE-SEM/EDS. When evaluating the carbon mapping, it can be confirmed that not even organic agglomerates are associated with the formation of melanterite and rozenite. Sometimes there was interaction between organic matter and such minerals in the samples. A similar phenomenon occurred in a study by Xiao et al. (2022), demonstrating a high capacity of cumulative connection between organic matter and minerals.

Table 2 proves the complex chemical composition of the elements most frequently detected by EDS coupled with both HR-TEM. The abundant presence of C, S, and O was detected in almost all 2523 particles studied, as well as the elements Zn, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cr and Ti. The presence of S is mainly due to the presence of sulfates and sulphides present in the analyzed samples, while the presence of Si, Al, Na, Mg, Fe, Ca, Zn, P is due especially to the silicates, carbonates, and phosphates shown in Table 1. It is worth mentioning the high amount of hazardous elements such as, Pb, Cd, among others is also present in both Tables 1 and 2.

Regarding the identification of sulfates and amorphous phases of the 2523 particles detected by FIB-SEM, only 538 were composed only of mineralogical phases, and of these only 83 contained only one mineral (the others were all composed of mixtures of several minerals). The remaining 1985 particles presented as agglomerated particles that contained several phases, and only 492 did not contain amorphous phases. The other 1493 contained organic and inorganic amorphous

Table 2

Minerals detected from the suspended sediments in the Tinto River estuary region identified in the 40 sampled points.

Minerals detected in the SSS	Abundance
Fullerenes (C ₆₀ , C ₇₀ , C ₈₀)	▼
Amorphous organic nanophases	▲
Silicates	
Quartz, SiO ₂	▲
Chlorite, Na _{0.5} Al ₆ (Si,Al) ₈ O ₂₀ (OH) ₁₀ .H ₂ O	▲
Clinoptilolite, (NaK) ₆ (SiAl) ₃₆ O ₇₂ ·20H ₂ O	▼
Illite, K _{1.5} Al ₄ (Si _{6.5} Al _{1.5})O ₂₀ (OH) ₄	▼
Kaolinite, Al ₂ Si ₂ O ₅ (OH) ₄	▲
Melilite, CaAl ₁₂ MgSi ₃ O ₁₄	▼
Microcline, KAlSi ₃ O ₈	▼
Montmorillonite, (Na,Ca)(Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ ·n(H ₂ O)	▼
Mullite, Al ₆ Si ₂ O ₁₃	▼
Muscovite, KAl ₂ (AlSi ₃)O ₁₀ (OH) ₂	▲
Talc, Mg ₃ Si ₄ O ₁₄ (OH) ₂	▲
Zircon, ZrSiO ₄	▼
Sulphides	
Arsenopyrite	▼
Bismuthinite, Bi ₂ S ₃	▼
Cattierite, CoS ₂	▼
Chalcopyrite, CuFeS ₂	▼
Cinnabar, HgS	▼
Galena, PbS	▼
Marcasite, FeS ₂	▼
Molybdenite, MoS ₂	▼
Millerite, NiS	▼
Pyrite, FeS ₂	▲
Pyrrhotite Fe _(1-x) S	▼
Sphalerite, ZnS	▼
Carbonates	
Aragonite, CaCO ₃	▼
Ankerite, (Fe,Ca,Mg)CO ₃	▲
Calcite, CaCO ₃	▲
Dolomite, CaMg(CO ₃) ₂	▼
Oligonite, Fe(Mn, Zn)(CO ₃)	▼
Siderite, FeCO ₃	▲
Phosphates	
Brushite, CaPO ₃ (OH)·2H ₂ O	▼
Monazite, (Ce, La, Th, Nd, Y)PO ₄	▲
Xenotime, (Y,Er)PO ₄	▲
Sulfates	
Ammoniojarosite, [(NH ₄)Fe ₃ (SO ₄) ₂ (OH) ₆]	▲
Anhydrite, CaSO ₄	▲
Alunogen, Al ₂ (SO ₄) ₃ ·17H ₂ O	▼
Alunite, (K,Na)Al ₃ (SO ₄) ₂ (OH) ₆	▼
Aluminite, Al ₂ SO ₄ (OH) ₄ ·7H ₂ O	▼
Barite, BaSO ₄	▼
Bassanite, CaSO ₄ ·1/2H ₂ O	▼
Bloedite, Na ₂ Mg(SO ₄) ₂ ·4H ₂ O	▼
Butlerite, Fe(OH)SO ₄ ·2H ₂ O	▼
Calcantite, CuSO ₄ ·5H ₂ O	▼
Copiapite, MgFe ₄ (SO ₄) ₆ (OH) ₂ ·18H ₂ O	▲
Coquimbite, Fe ₂ (SO ₄) ₃ ·9H ₂ O	▲
Epsomite, MgSO ₄ ·7H ₂ O	▲
Ferrohexahydrite, FeSO ₄ ·6H ₂ O	▲
Halotrichite, FeAl ₂ (SO ₄) ₄ ·22H ₂ O	▲
Hexahydrite, MgSO ₄ ·6H ₂ O	▲
Glauberite, Na ₂ Ca(SO ₄) ₂	▼
Gypsum, Ca[SO ₄]·2H ₂ O	▲
Jarosite, KFe ₃ ³⁺ (SO ₄) ₂ (OH) ₆	▲
Melanterite, FeSO ₄ ·7H ₂ O	▲
Natrojarosite, NaFe ₃ (SO ₄) ₂ (OH) ₆	▼
Pickeringite, MgAl ₂ (SO ₄) ₄ ·22H ₂ O	▲
Rozenite, FeSO ₄ ·4H ₂ O	▲
Schwertmannite, Fe ₁₆ ³⁺ O ₁₆ (OH) ₁₂ (SO ₄) ₂	▲
Sideronatrite, Na ₂ Fe[SO ₄](OH)·3H ₂ O	▼
Szomolnokite, FeSO ₄ ·H ₂ O	▲
Thenardite, Na ₂ SO ₄	▲
Tschermigite, NH ₄ Al(SO ₄) ₂ ·12H ₂ O	▼
Oxides and hydroxides	
Anatase, TiO ₂	▼
Ilmenite, FeTiO ₃	▲
Brucite, Mg(OH) ₂	▼
Brookite, TiO ₂	▼

Table 2 (continued)

Minerals detected in the SSS	Abundance
Chromite, (Fe,Mg)Cr ₂ O ₄	▼
Hematite, Fe ₂ O ₃	▲
Goethite, Fe(OH) ₃	▲
Gibbsite, Al(OH) ₃	▲
Maghemite, Fe ₂ O ₃	▲
Magnesianferrite, MgFe ₂ O ₄	▼
Magnetite, Fe ₃ O ₄	▲
Rutile, TiO ₂	▲
Amorphous inorganic phases	▲

X = XRD; M = Mössbauer spectroscopy; S = SEM; T = TEM; OP = optical microscopy; R = Raman; IR = Infra-red spectrometry; LC = liquid chromatography, coupled to a high-resolution mass spectrometer (HRMS) using atmospheric pressure photoionisation (APPI);▲ = abundant; ▼ = minor portion.

phases agglomerated with minerals or contained only amorphous material. Such agglomerations of mineralogical phases with amorphous phases were better studied thanks to analysis by FIB-SEM/EDS. After all, with such a technique it was possible to cut the particles and study their inner layers, in addition to preparing the nanometric particles to be better studied by HR-TEM.

The formation of agglomerates containing Al and Fe sulfate minerals containing amorphous phases is of paramount importance as they contain rare elements such as Ge (see EDS data and Ge mapping) (Fig. 6). This provides evidence that the combination of amorphous compounds and minerals (especially Fe and Al) can yield a good adsorption of contaminants. Recalling that the sediments obtained in the center of the river contained jarosite (Fig. 7), while the samples of sediments collected on the banks of the Tinto River contained jarosite pseudomorph. The formation of the pseudomorph is mainly due to rapid oxidation to arsenopyrite and/or pyrite. According to Qiu et al. (2017) and Wen et al. (2022), this is due to the presence of low humidity. Furthermore, such a pseudomorph formation of jarosite was only possible thanks to the use of FIB, as without cutting the amorphous clusters so that their interiors could be studied, it would not have been possible to detect such a formation of jarosite, not even its interactions with toxic elements, such as demonstrated by mapping the identified hazardous elements.

When evaluating the mapping of the elements, it can be observed that the jarosite crystals are responsible for adsorbing toxic elements such as arsenic, since on the sides of the jarosite crystals only amorphous phases of Si and Al were detected without containing toxic elements (Fig. 8). Such geological formation is probably due to the attack of sulfuric acid on clays that generate the amorphous compounds around the jarosites (Battler et al., 2013; Benavente et al., 2020). Here again, the importance of analyzing sediment samples by FIB-SEM/EDS is demonstrated (Silva et al., 2020; Neckel et al., 2021). On the contrary, in this study it would not be possible to understand the real behavior and geochemical mobility of potentially toxic elements to the environment and human health.

The high Eh (oxidative potential) and the low pH value of 2.2 at the sample collection points, demonstrating a high acidity, can be compared to the study by Aguilera et al. (2007) who found that the Tinto River displayed averages of variation from 0.9 to 2.5 in different seasons. The C detected was considered to be due to the chemical composition of the TEM-grid. Therefore, the most abundant elements in the 2583 particles smaller than 100 nm were O, S, Si, Al, Mg, K, N, Na, Fe, Ca, Zn, Cl, Ti, Mn and multiple hazardous elements such as, Cd, Ni, V, Se, Mo, Pb, Sb and Sn among others. Although of the 2821 particles larger than 50 nm detected by FE-SEM/EDS, only 712 contained hazardous elements. It cannot be ruled out, however, that their interiors contained such elements (Fig. 9). Therefore, FIB-SEM/EDS was crucial to cut more than 1200 particles so that they could be better analyzed by HR-TEM (Silva et al., 2020; Neckel et al., 2021), confirming, in this study, the efficiency in the detection of dangerous elements.

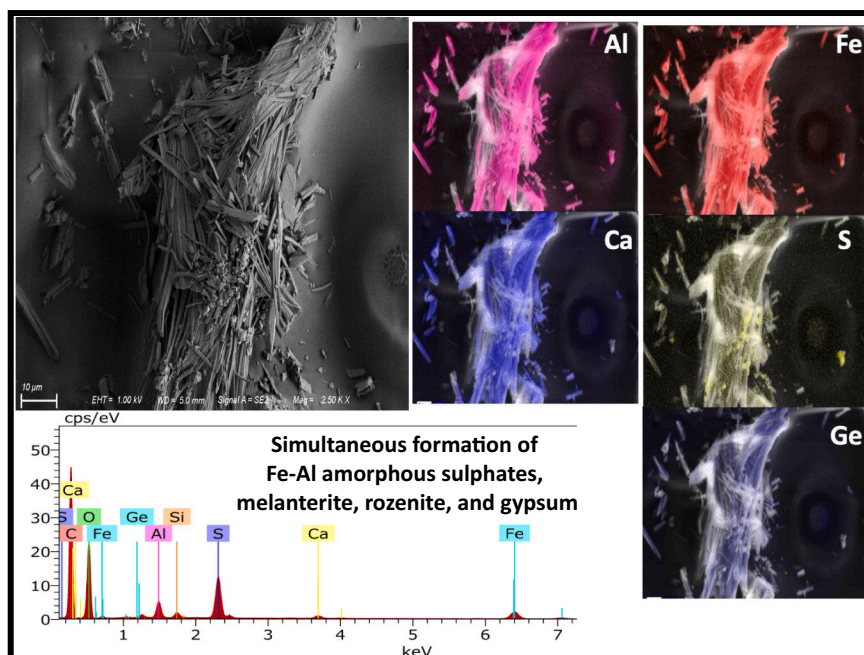


Fig. 6. Agglomerates containing Al and Fe sulfate minerals containing amorphous phases, melanterite, rozenite and gypsum.

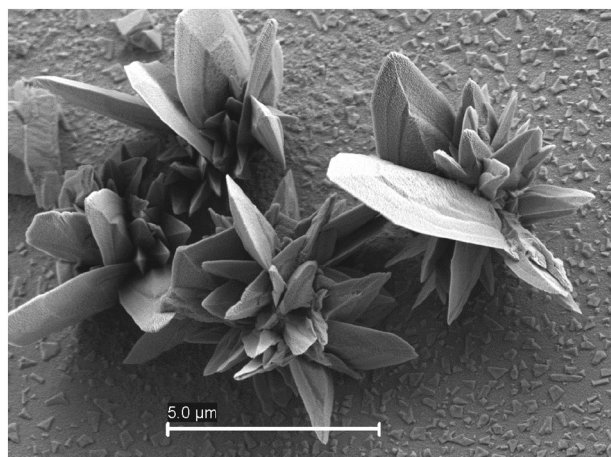


Fig. 7. Sediments obtained from the Tinto River, with the formation of jarosite.

3.2. Geospatial analysis using Sentinel-3B OLCI satellite imagery

The spring period where the average rainfall was 115 mm, Fig. 10 (A and B), presents the composites of the Sentinel-3B OLCI images for the suspended material, ADG_NN. It is observed that the maximum value in 2019 was 1.35 m^{-1} , and in 2021, the maximum value was 17.14 m^{-1} ; indicating that the concentration of suspended material increased 12.6 times. In the CHL_NN levels (Fig. 10 C and D), it is observed that the maximum value in 2019 was 9.15 mg/m^3 (chl a), and in 2021, the maximum value was 4.29 mg/m^3 (chl a). These values indicate that there was a decrease in organic matter and phytoplankton in the study area. As for TSM_NN (Fig. 10 E and F) it is observed that the maximum value in 2019 was 20.34 g^{-3} , and in 2021, the maximum value was 36.35 g^{-3} . Thus, an increase of 1,78 times can be observed, representing a greater impact on the Tinto River estuary. In 2020 there was a decrease in the emission of particles, due to the beginning of the restrictive measures adopted in the COVID-19 pandemic, as a consequence of the reduction of industrial production and the release of chemical elements

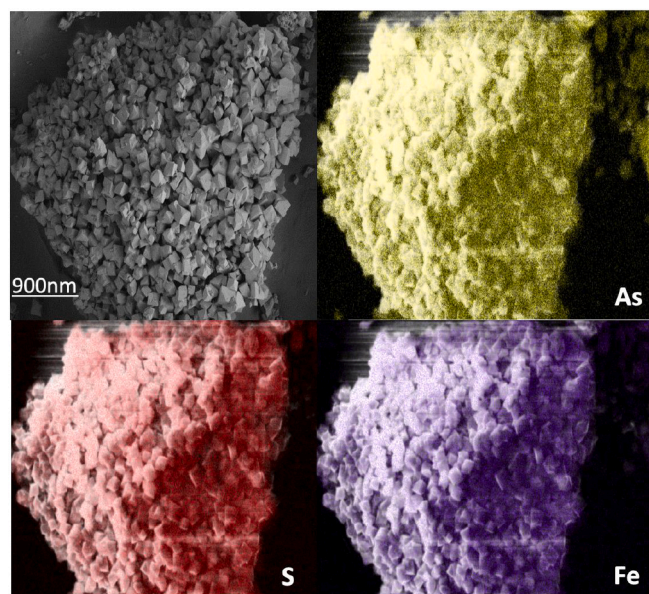


Fig. 8. Mapping the elements of jarosite crystals containing the following toxic elements: As, S and Fe Si.

harmful to human health in rivers on a global scale (Bodah et al., 2022; Buzzi et al., 2022; Jia et al., 2022). However, the data show that the water quality worsened within the analyzed period.

Fig. 11 presents the analyzed variables in the summer months. Through Fig. 11 (A and B) the difference regarding ADG_NN can be noted. For the year 2019 the maximum value was 2.43 m^{-1} , and for the year 2021 this level increased to 9.55 m^{-1} . This was an increase of 3.9 times greater than the previous period. As for the concentrations of chlorophyll-a observed in Fig. 11 (C and D), for the year 2019 it was 11.38 mg/m^3 (chl a), while in 2021 the maximum value was 5.12 mg/m^3 (chl a), this decrease in concentration is noted in all analyzed points. In turn, the TSM_NN (Fig. 11 E and F), in 2019 was 23.47 g^{-3} , and for 2021 it was 16.38 g^{-3} . According to Fonseca et al. (2016) and Neckel

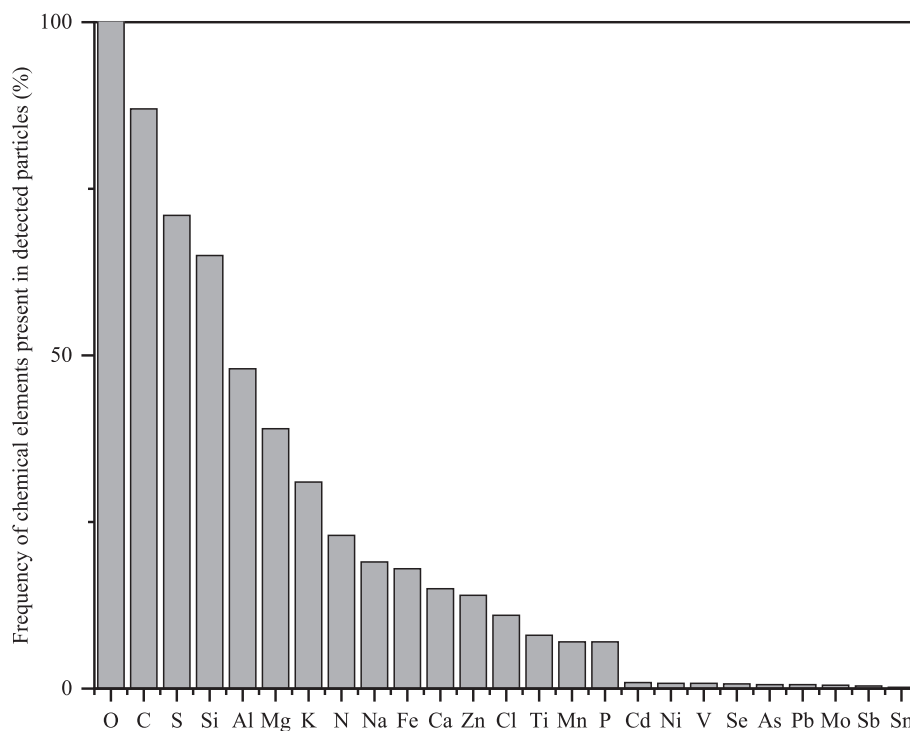


Fig. 9. The most abundant elements of the 2583 particles smaller than 100 nm analyzed from the SS samples of the Tinto River estuary region.

et al. (2021), this increase in water turbidity is due to the high presence of suspended solids (e.g.: clay, silt, colloids and silica), inorganic and organic material, in addition to the presence of algae and organisms of microscopic origin.

In the autumn period, it was observed (Fig. 12 A and B) that the ADG_NN for the year 2019 totaled 1.35 m^{-1} , and in 2021 an amount of 18.77 m^{-1} was identified. In the year 2021 compared to the year 2019, it was found that in the oceanic region the levels of dissolved materials have decreased, but in the waters of the Tinto River estuary there is a considerable increase in dissolved materials. In relation to chlorophyll-a concentrations for the year 2019 it was 9.15 mg/m^3 (chl a), for the year 2021 it was 4.78 mg/m^3 (chl a). When compared to the levels shown by the color scale line, observed- chlorophyll levels decreased from 2019 to 2021 (Fig. 12C and D). As for TSM_NN (Fig. 12 E and F), respectively, there was a very large difference in water quality, since in 2019 the maximum value identified was 20.34 g^{-3} , and in 2021 the identified value increased to 48.29 g^{-3} . Thus, it can be noted that the resulting turbidity is loaded with nanoparticles and ultra-fine particles that accumulate, forming sediments along the river through the decanting process (Neckel et al., 2021). Field study of these nanoparticles and ultra-fine particles detected by FE-SEM/EDS show that the elements are dangerous to human health and to the quality of the marine environment, elements such as: As, Cd, Ni, V, Se, Mo, Pb, Sb and Sn.

Fig. 13(A and B) presents the reality of the variables in the winter period. The ADG_NN, during the year 2019 presented levels of 1.14 m^{-1} , in 2021 a value of 11.93 m^{-1} was observed. Thus, there is an increase of 1,04 % in relation to the analyzed period. Smith et al. (2021) emphasize that dissolved material is exclusively related to effluent discharge into rivers, which can accumulate contaminants capable of negatively impacting human health and threatening the survival of local ecosystems. It is noteworthy then, that in the winter of 2021 as compared to 2019, it was found that in the Ocean region the levels of dissolved materials decreased, because the ocean has a greater capacity to disperse pollutants (Neckel et al., 2021).

The concentration of chlorophyll-a (Fig. 13 C and D) for the year 2019 was 10.20 mg/m^3 (chl a), and was 4.61 mg/m^3 (chl a) for the year 2021. The TSM_NN (Fig. 13 E and F) in 2019 was identified as 27.22 g^{-3} ,

and in 2021 it showed a reduction of 20.88 g^{-3} . This can be explained by the decrease in iron oxide mining activities on the banks of the Tinto River, according to data made available by the Ministry for Ecological Transition and the Demographic Challenge of Spain (Metdc, 2022).

Table 3 presents a statistical description of the data collected from the compositions of the Sentinel-3B OLCI images. The average value for all four seasons of 2019 for the variable TSM_NN was 22.70 g^{-3} , whereas 2021's average annual value was 24.47 g^{-3} . The standard deviation variability was lower in 2019, with a value of 29.48 compared to 2021, with a value of 40.89. The average value for all four seasons of 2019 for the variable CHL_NN was 5.46 mg/m^3 , with 2021's average annual value of 4.07 mg/m^3 . The variability (standard deviation) is lower for the year 2021, with a deviation of 3.92. In 2019 the deviation was 5.21. This demonstrates the variability in chlorophyll-a concentrations. Regarding the maximums, the year 2021 had a higher concentration of chlorophyll, with a value of 20.02. In the year 2019, when there were still no results from the pandemic, it had a total of 15.79 m^{-3} . According to Kim et al. (2022), the high environmental conditions of pollution provide a higher concentration of chlorophyll-a, where the river has the ability to decompose organic matter. Regarding this, the dissolved material at 443 nm (ADG_443_NN) readings displayed average 2021 values of 6.95 m^{-1} , and 2019 values of 1.53 m^{-1} . Regarding the maximum, it is observed that the year 2021 presented a higher concentration of dissolved material (50.20 m^{-1}), than 2019 (4.28 m^{-1}).

Through K-means analysis (Table 4) we considered the adjustment scores for the statistical model, where $K = 3$ clusters for a dataset of the 40 collection points. According to Dal Moro et al. (2021) the R^2 is the ratio between the sums of squares and the total sums of squares. The closer the value is to 1, the better the perceived fit of the model. In this study, the observed value of R^2 was 0.62, demonstrating that the model presents a good answer to the question of this research, thus demonstrating greater reliability. As for the Akaike Information Criterion (AIC) and the Bayesian Information Criterion (BIC), they were used to measure the goodness of fit of a model (Dal Moro et al., 2021), with satisfactory results in this sample. Thus, the silhouette index ranged from zero (0) to one (1), for $k = 3$ clusters, corresponding to 0.49, potentiating a regular trend of clustering, demonstrating that there was variability between the

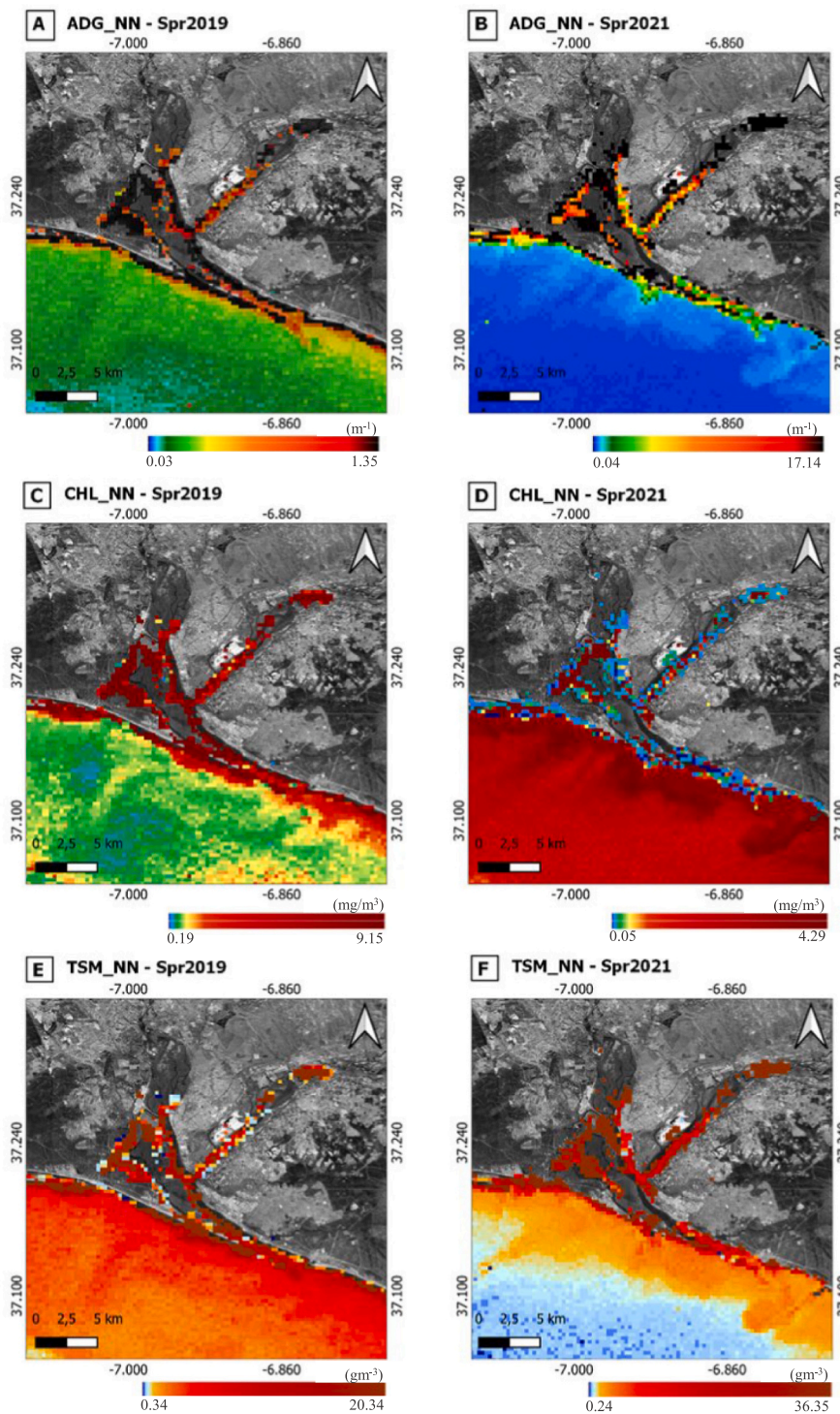


Fig. 10. Compositions of Sentinel-3B OLCI satellite imagery for the spring season analysis period: (A) 2019 surface dissolved material (ADG443_NN); (B) surface dissolved material (ADG443_NN) from 2021; (C) 2019 chlorophyll-a (CHL_NN) concentrations; (D) 2021 chlorophyll-a (CHL_NN) concentrations; (E) 2019 Water Turbidity (TMS_NN); (F) Water Turbidity (TMS_NN) of 2021.

period studied in the 40 points of the geospatial satellite image analyses of the Tinto River.

The number of points in each cluster showed variability in relation to the sum of squares, proportion of heterogeneity and silhouette index (Table 5). As for heterogeneity, the total value of 1 was proportionally divided. Thus, it is observed that Cluster 1 has an index of 0.64, being more heterogeneous. Clusters 2, 3 and 4 are homogeneous, with lower values. Another parameter capable of evaluating a cluster is the sum of

squares, the smaller the sum, the lower the variability (Dal Moro et al., 2021). Cluster 4 has the lowest sum of squares with 8796, so it can be considered the most homogeneous, with the variables: suspended material, chlorophyll-a and turbidity with similar values in relation to the other clusters. The Silhouette index showed homogeneity and cohesion, with greater homogeneity in cluster 4 with an index of 0.86. Clusters 1 and 2 show high heterogeneity. In this relationship, the variables that influenced the homogeneity of Clusters 1 were Chlorophyll-a values in

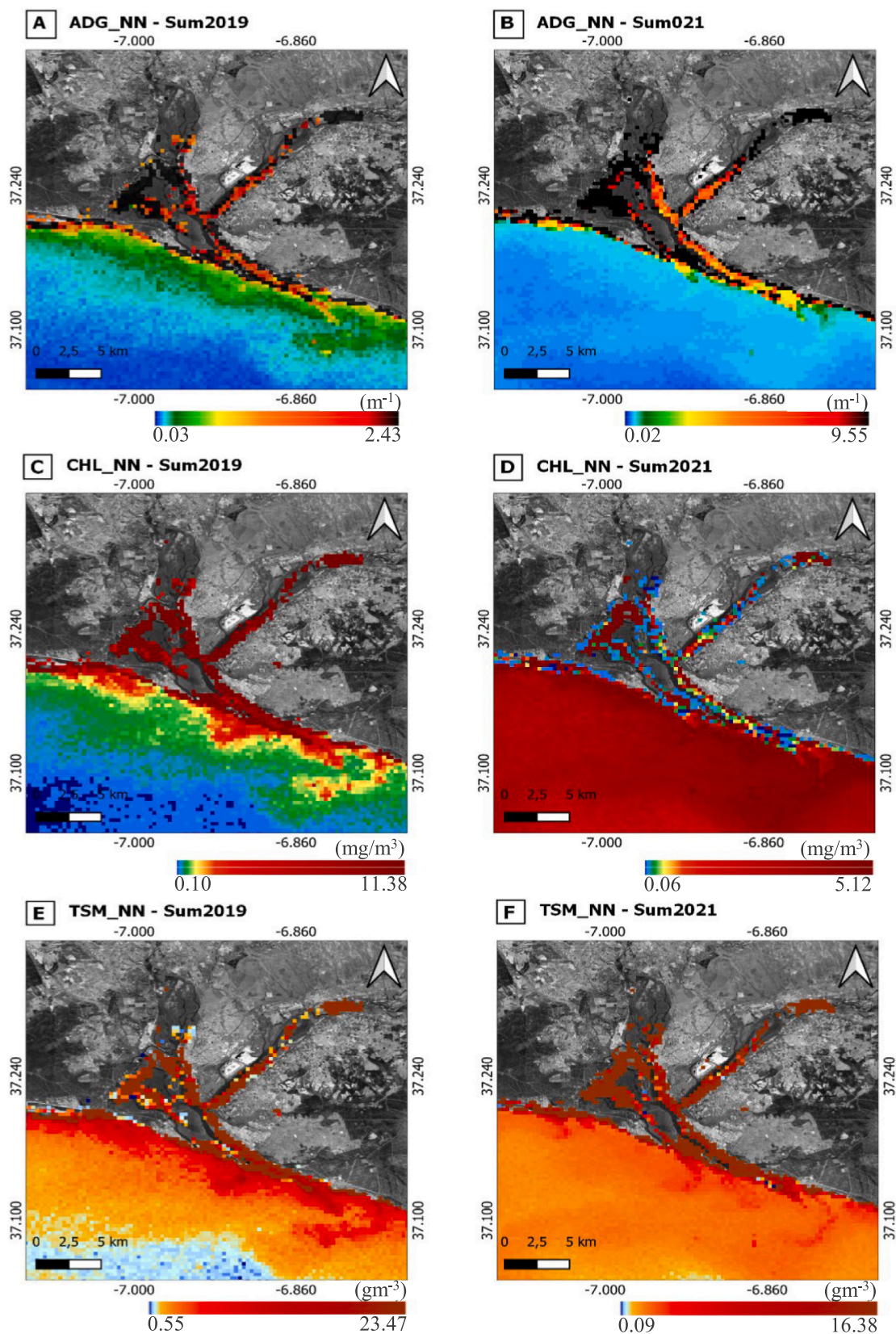


Fig. 11. Compositions of Sentinel-3B OLCI satellite images referring to the analysis period in the summer season: (A) surface dissolved material (ADG443_NN) from 2019; (B) surface dissolved material (ADG443_NN) from 2021; (C) 2019 chlorophyll-a (CHL_NN) concentrations; (D) 2021 chlorophyll-a (CHL_NN) concentrations; (E) 2019 Water Turbidity (TSM_NN); (F) Water Turbidity (TSM_NN) of 2021.

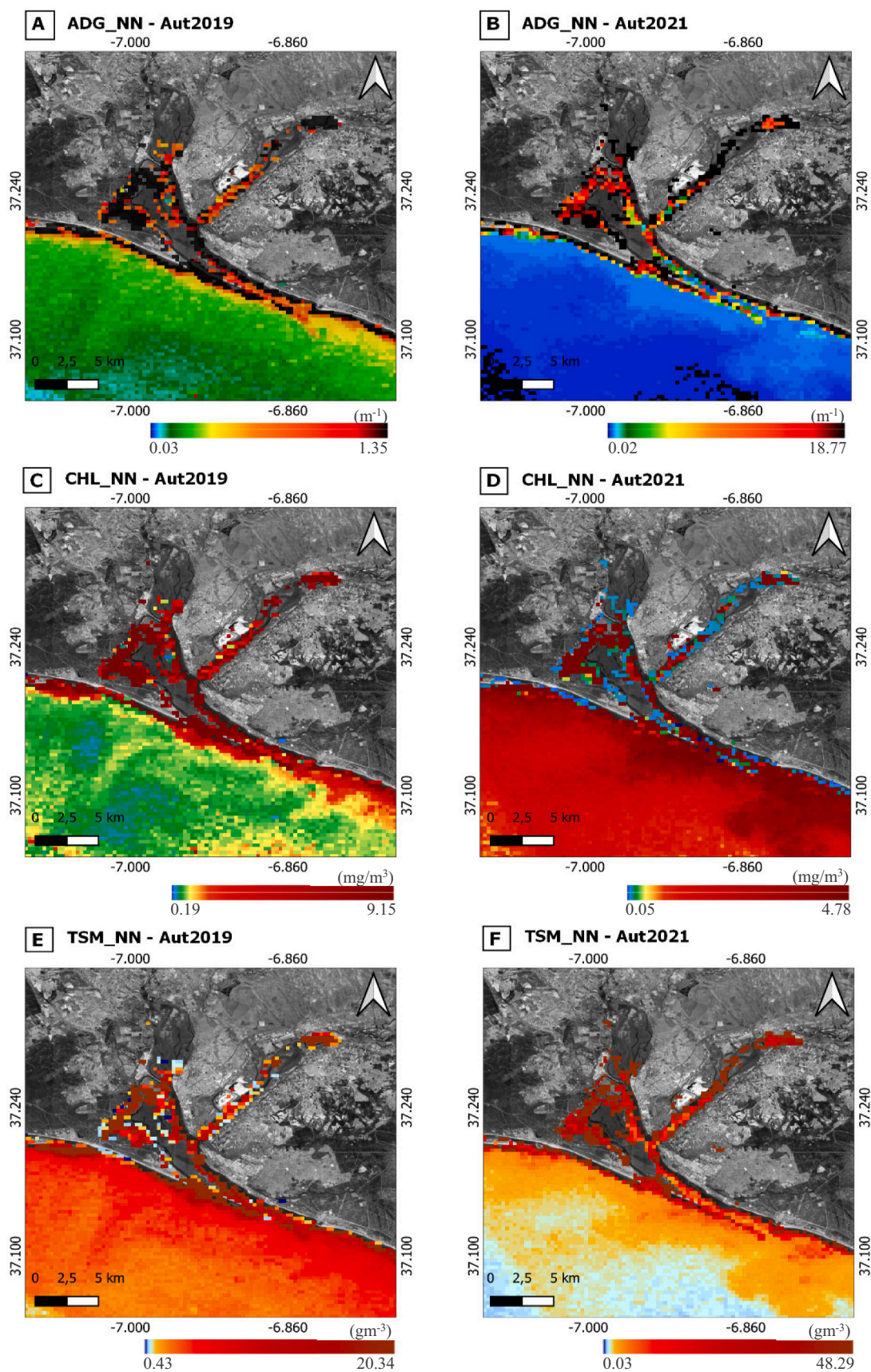


Fig. 12. Compositions of Sentinel-3B OLCI satellite images for the autumn season analysis period: (A) 2019 surface dissolved material (ADG443_NN); (B) surface dissolved material (ADG443_NN) from 2021; (C) 2019 chlorophyll-a (CHL_NN) concentrations; (D) 2021 chlorophyll-a (CHL_NN) concentrations; (E) 2019 Water Turbidity (TMS_NN); (F) Water Turbidity (TMS_NN) of 2021.

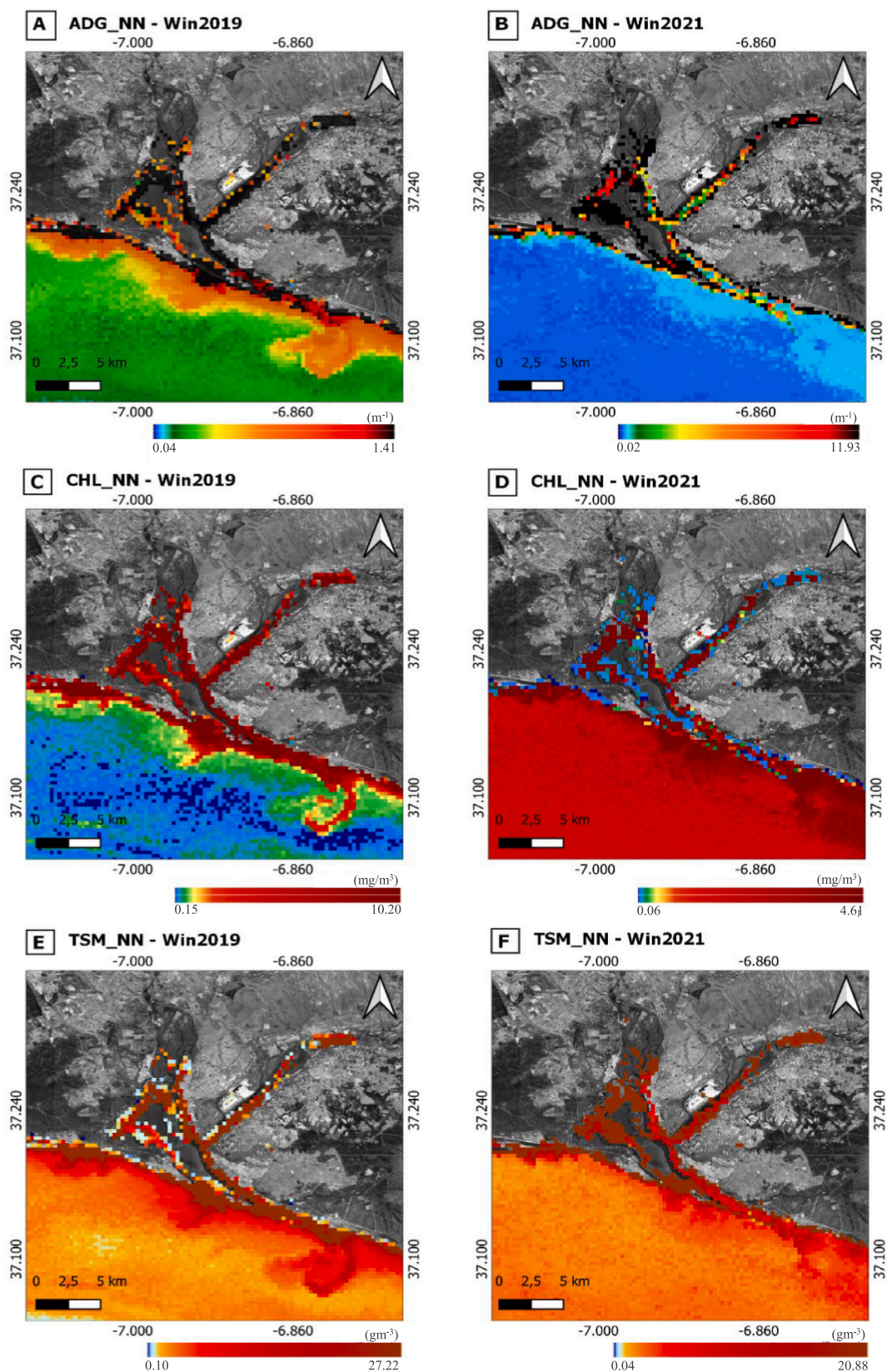


Fig. 13. Compositions of Sentinel-3B OLCI satellite images for the analysis period in the winter season: (A) surface dissolved material (ADG443_NN) of 2019; (B) surface dissolved material (ADG443_NN) from 2021; (C) 2019 chlorophyll-a (CHL_NN) concentrations; (D) 2021 chlorophyll-a (CHL_NN) concentrations; (E) 2019 Water Turbidity (TSM_NN); (F) Water Turbidity (TSM_NN) of 2021.

Table 3

Statistical representation of the analytical results of the Sentinel-3B OLCI images in the spring, summer, autumn and winter seasons (2019 & 2021).

Items	ADG_SPR_2019	ADG_SPR_2021	ADG_SUM_2019	ADG_SUM_2021	ADG_AUT_2019	ADG_AUT_2021	ADG_WIN_2019	ADG_WIN_2021
Valid	40	40	40	40	40	40	40	40
Missing	0	0	0	0	0	0	0	0
Mean	1.30	3.51	0.77	4.32	1.72	17.20	1.57	2.76
Std. deviation	1.36	7.24	0.91	11.80	1.67	22.95	1.32	6.87
Minimum	0.21	0.28	0.11	0.30	0.11	0.22	0.23	0.21
Maximum	4.38	30.77	4.38	69.58	4.38	63.55	4.00	36.89

Items	CHL_SPR_2019	CHL_SPR_2021	CHL_SUM_2019	CHL_SUM_2021	CHL_AUT_2019	CHL_AUT_2021	CHL_WIN_2019	CHL_WIN_2021
Valid	40	40	40	40	40	40	40	40
Missing	0	0	0	0	0	0	0	0
Mean	5.06	3.28	4.00	3.80	6.31	4.41	6.46	4.79
Std. deviation	4.63	3.06	4.50	2.59	5.16	5.52	6.55	4.51
Minimum	0.56	0.06	0.43	0.06	0.89	0.08	0.43	0.07
Maximum	14.11	18.19	13.61	12.20	15.17	27.10	20.28	22.61

Items	TSM_SPR_2019	TSM_SPR_2021	TSM_SUM_2019	TSM_SUM_2021	TSM_AUT_2019	TSM_AUT_2021	TSM_WIN_2019	TSM_WIN_2021
Valid	40	40	40	40	40	40	40	40
Missing	0	0	0	0	0	0	0	0
Mean	16.81	10.76	12.36	15.30	26.99	61.49	34.64	10.33
Std. deviation	25.45	22.68	18.14	41.68	36.67	83.13	37.66	16.09
Minimum	0.77	1.72	2.06	1.55	2.38	1.76	2.76	1.43
Maximum	100.00	100.00	100.00	232.55	100.00	213.93	100.00	92.87

Table 4

Cluster Information in relation to the collections carried out in the Sentinel-3B OLCI satellite images.

Cluster information				
Cluster	1	2	3	4
Size	15	3	2	20
Explained proportion within-cluster heterogeneity	0.64	0.25	0.07	0.02
Within sum of squares	224.49	89.73	27.45	8.79
Silhouette score	0.10	0.05	0.25	0.86

Note. The Between Sum of Squares of the 4 cluster model is 585.52.

Note. The Total Sum of Squares of the 4 cluster model is 936.

2019 and the turbidity of autumn and winter of 2019 (Table 5). Thus, it is possible to verify that environmental issues related to the Tinto River, such as rainfall regimes (Aemet, 2022) and ore extraction (Metdc, 2022) may have influenced the grouping of clusters.

Cluster 2 was mostly influenced by ADG_NN and TSM_NN. The points

that make up Cluster 2 are characterized by a high amount of material suspended in water, in practically all seasons of the year 2019. The turbidity of these points is also high for the year 2021, regardless of rainfall or levels of production. The composition of Cluster 3 is influenced by the first and summer seasons in both 2019 and 2021, demonstrating that in this analyzed period there is a tendency to have high concentrations of pollutants in the Tinto River estuary region. Cluster 4 shows greater homogeneity, as observed in the median values, when considering the variables of material concentration in these clusters.

Figs. 14, 15 and 16 present the density graphs of the analyzed clusters. Through Fig. 14, it is possible to observe in the ADG_NN variations, that in relation to the analyzed period, Cluster 4 presents a high concentration and homogeneity peak. This means that these locations are characterized by the presence of pollution on the water surface. In Fig. 15, represented by CHL_NN concentrations, it is noted that Cluster 2 reached peaks of concentration and homogeneity in spring (Fig. 15 (I and J)), summer (Fig. 15 (K and L)) and autumn (Fig. 15 (M and N)). Cluster 4 peaks were identified in the spring (Fig. 15 (I and J)) and

Table 5

Representation of Cluster Means in progress, 2019 & 2020.

Cluster means								
Clusters	ADG_SPR_2019	ADG_SPR_2021	ADG_SUM_2019	ADG_SUM_2021	ADG_AUT_2019	ADG_AUT_2021	ADG_WIN_2019	ADG_WIN_2021
1	0.59	-0.16	0.23	-0.15	0.88	0.58	0.45	-0.24
2	0.45	2.74	1.09	2.52	0.73	1.51	1.70	2.45
3	1.98	1.49	2.76	0.69	1.20	0.56	1.52	1.68
4	-0.71	-0.43	-0.61	-0.33	-0.89	-0.72	-0.74	-0.35
Clusters	CHL_SPR_2019	CHL_SPR_2021	CHL_SUM_2019	CHL_SUM_2021	CHL_AUT_2019	CHL_AUT_2021	CHL_WIN_2019	CHL_WIN_2021
1	0.83	-0.45	0.38	-0.40	0.89	0.21	0.85	0.32
2	-0.06	-0.90	1.27	-1.40	0.54	-0.76	0.38	0.13
3	1.84	3.18	1.97	3.07	1.56	0.53	0.92	1.72
4	-0.79	0.15	-0.68	0.20	-0.90	-0.10	-0.79	-0.43
Clusters	TSM_SPR_2019	TSM_SPR_2021	TSM_SUM_2019	TSM_SUM_2021	TSM_AUT_2019	TSM_AUT_2021	TSM_WIN_2019	TSM_WIN_2021
1	0.18	-0.18	0.21	-0.14	0.64	0.57	0.76	-0.01
2	-0.15	2.56	0.04	2.72	-0.47	1.32	0.40	2.26
3	3.26	1.27	3.07	0.16	1.99	0.61	0.83	1.21
4	-0.44	-0.37	-0.47	-0.31	-0.60	-0.69	-0.72	-0.44

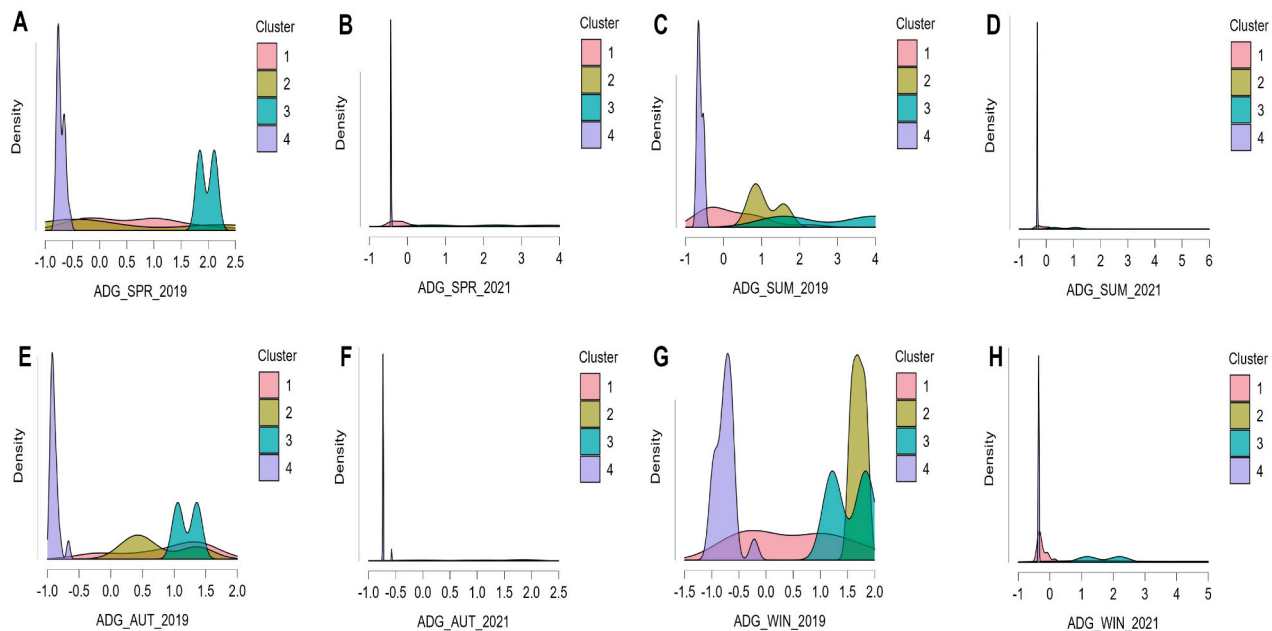


Fig. 14. Density graphs, referring to the compositions of the Sentinel-3B OLCI Satellite images, in relation to the dissolved material on the surface (ADG443_NN). (A) Spring 2019; (B) Spring 2021; (C) Summer 2019; (D) Summer 2021; (E) Autumn 2019; (F) Autumn 2021; (G) Winter 2019; and (H) Winter 2021.

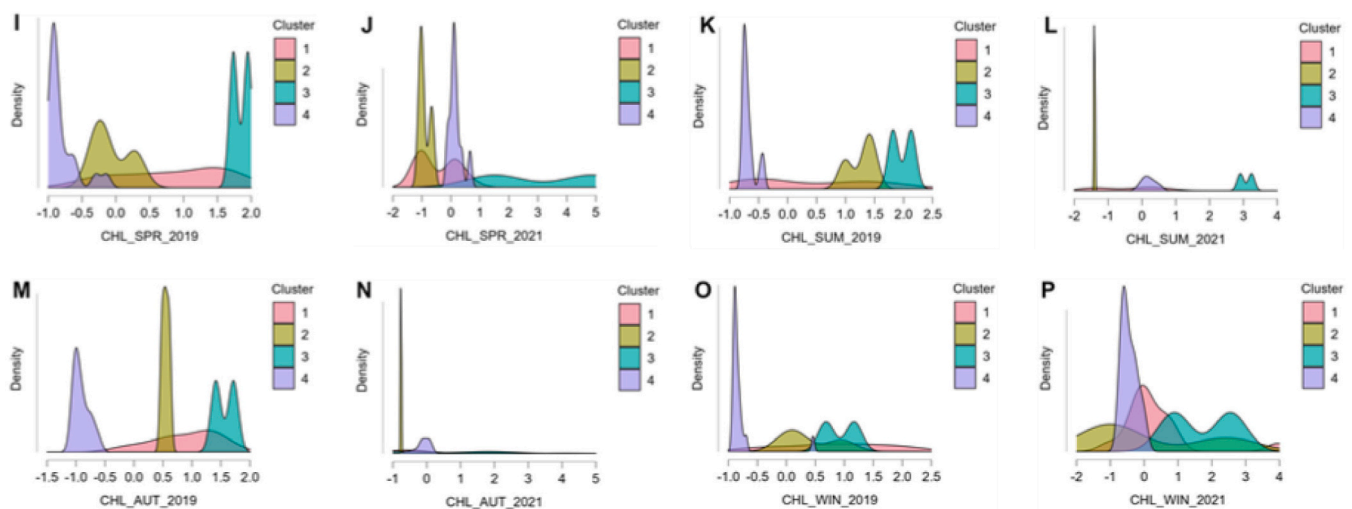


Fig. 15. Density graphs, referring to compositions of the Sentinel-3B OLCI Satellite images, in relation to concentrations of chlorophyll-a (CHL_NN): (I) Spring 2019; (J) Spring 2021; (K) Summer 2019; (L) Summer 2021; (M) Autumn 2019; (N) Autumn 2021; (O) Winter 2019; and (P) Winter 2021.

winter (Fig. 15 (O and P)) seasons. These peaks may be related to the rainfall regime, as the rains are more intense in winter and autumn. Consequently, in Fig. 16 that represents the TMS_NN, it is noted that Cluster 2 has a higher concentration of TMS during the summer (Fig. 16 (S)) and autumn (Fig. 16 (U)), as it has greater amplitude in the graphs, indicating a higher concentration of material in reaction to the analyzed points. Cluster 4 presents peaks of concentration and homogeneity in all periods studied, demonstrating that in the points that make up this cluster there are high levels of water pollution, reinforced by the analysis of SSs, where the FE-SEM/EDS detected the types of hazardous elements (As, Cd, Ni, V, Se, Mo, Pb, Sb and Sn), presenting a risk to both human health and the quality of the marine environment of the Tinto River estuary. According to Neckel et al. (2021), Nilin et al. (2021), Partescano et al. (2021) and Silva et al. (2021) the solution would be the creation of public policies for environmental preservation, aimed at

guaranteeing water quality, capable of justifying projects for the recovery of marine environments on a global scale.

4. Conclusion

The analysis of the SSs collected at the 40 points in the field, in addition to identifying chemical elements in the form of nanoparticles and ultra-fine particles by FE-SEM/EDS, such as: As, Cd, Ni, V, Se, Mo, Pb, Sb and Sn; together, detected the presence of hydroxides and sulfates, which, due to their low density, have a high capacity to absorb toxic pollutants. These were present in the sediments of the Tinto River estuary, which can negatively affect the marine ecosystem in addition to compromising human health. This highlights the need for continuity of future studies not only in the Tinto River estuary, but also other rivers in the world. Through the results of this study, it is possible to understand

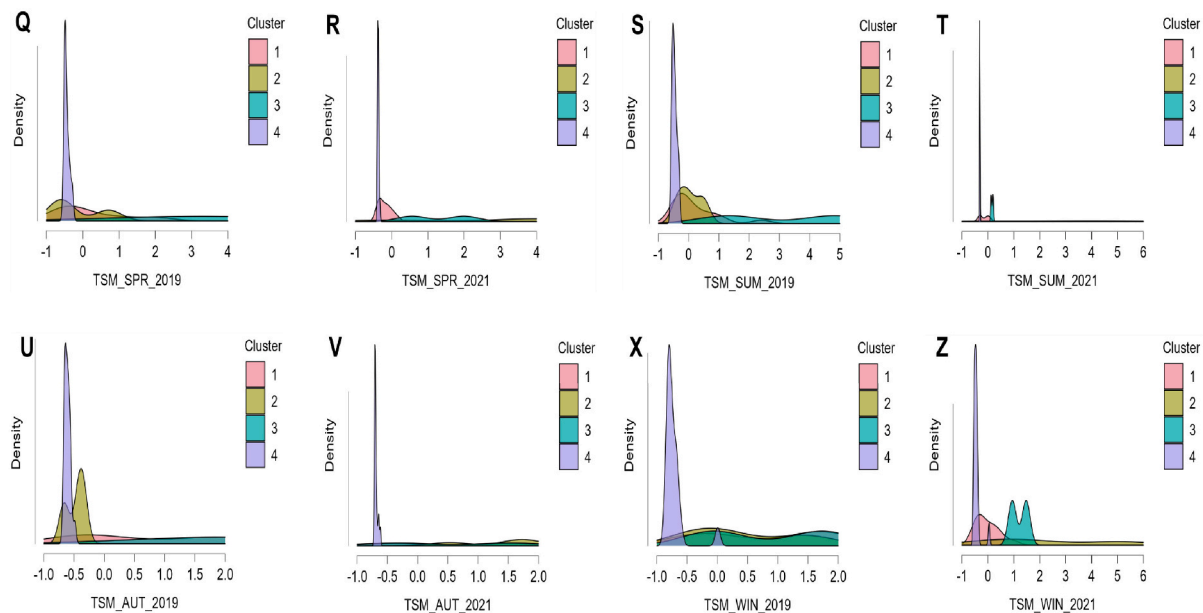


Fig. 16. Density graphs, referring to Sentinel-3B OLCI Satellite image compositions, in relation to Water Turbidity (TSM_NN): (Q) Spring 2019; (R) Spring 2021; (S) Summer 2019; (T) Summer 2021; (U) Autumn 2019; (V) Autumn 2021; (X) Winter 2019; and (Z) Winter 2021.

the very real threat these contaminants present, in addition to the very real way that they spread throughout a riverine ecosystem. The authors advocate for the creation of strong, future public policies and projects for the environmental protection of and recovery of marine environments.

The use of images from the Sentinel-3B OLCI satellite proved to be efficient at making it possible to obtain statistically reliable data, where the R^2 value was 0.62, to compare with real-world, on the ground sampling at 40 points. It is noteworthy that the TSM_NN value in 2019 was 23.47 g^{-3} , whereas for 2021 it was 16.38 g^{-3} , influencing, in the high presence of suspended solids (e.g.: clay, silt, colloids and silica), and inorganic and organic material in addition to the presence of algae and organisms of microscopic origin. This decrease occurred with changes in the concentration of TSM_NN and ADG_443_NN from 2019 to 2021, with the presence of CHL_NN. This was reflected in Cluster 2 mostly by ADG_NN whereas TSM_NN remains high. The authors suggest further studies investigating the use of logarithmic scales assigned to the data collected from ADG_443_NN, CHL_NN and TSM_NN by Sentinel-3B OLCI images, with particular focus paid to seasonal periods.

In addition, the authors suggest the following questions be examined in future studies. To what extent do humans have the potential to change a river's course? Over 2000 years there have been the same changes, are human interventions accelerating this geological process? Are Iberian Peninsula beaches contaminated, or is it just a process that only humans participate in? There remains a great deal to be understood, but real toxicological studies will be needed in the world.

CRediT authorship contribution statement

Alcindo Neckel: Conceptualization, Funding acquisition. **Marcos L. S. Oliveira:** Writing – original draft. **Laércio Stolfo Maculan:** Writing – original draft. **Bashir Adelodun:** Writing – original draft. **Brian William Bodah:** Conceptualization, Funding acquisition. **Leila Dal Moro:** Writing – review & editing. **Luis F.O. Silva:** Writing – review & editing.

Declaration of competing interest

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.

Data availability

The data that has been used is confidential.

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