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Microplastics in the abyss: a first investigation into sediments at 2443-m depth (Toulon, France)

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Abstract :

Plastic and microplastic pollutions are known to be widespread across the planet in all types of environments. However, relatively little about microplastic quantities in the deeper areas of the oceans is known, due to the difficulty to reach these environments. In this work, we present an investigation of microplastic (<5 mm) distribution performed in the bottom sediments of the abyssal plain off the coast and the canyon of Toulon (France). Four samples of deep-sea sediment were collected at the depth of 2443 m during the sea operations carried out by the French oceanographic cruises for the KM3NeT project. The chemical and physical characterisation of the sediment was carried out, and items were extracted from sediments by density separation and analysed by optical microscope and µRaman spectroscopy. Results show microplastics in the deep-sea sediments with a concentration of about 80 particles L^{-1}, confirming the hypothesis of microplastics spread to abyssal sediments in the Mediterranean Sea.

Keywords : Microplastics, mu Raman, Deep sea, Sea currents, KM3NeT project, Toulon (France)

1. Introduction

It is known that plastic litter, and among these the microplastics (items with size between 1 µm and 5 mm), impact any environment, terrestrial (Dioses-Salinas et al. 2020; Hoffman and Hittinger 2017), aerial (Dris et al. 2016; Zhang et al. 2020) and marine (Alomar et al. 2016; Fossi et al. 2012; Ruiz-Orejon 2018). Since the 2000s, attention on microplastics has grown exponentially (Schmid et al. 2018) and there are many researchers and teams conducting studies on microplastic sampling and characterisation in environment (Gago et al. 2018; Yu et al. 2019), their effects on animals (Lusher et al. 2017) and humans (Campanale et al. 2020), and investigating their relationship with pollutants, such as metals, hydrocarbons etc. (Constant et al. 2019; Kutralam-Muniasamy et al. 2021; Pereao et al. 2020; Tesán Onrubia et al. 2021). In marine environment, microplastics are sought in the beach areas (Antunes et al. 2018; Bosker et al. 2017; Browne et al. 2011; Constant et al. 2019; Pieper et al. 2019) and at different depth from the sea surface along the water column (Andrady 2011; Bagaev et al. 2018; Baini et al. 2018; Pan et al. 2019; Zheng et al. 2019) and down to sediments (Anderson et. al. 2016; Andrady 2011; Bergmann et al. 2017; Zheng et al. 2017); their transport and behaviour related to dynamics is investigated as well as their degradation process due to seawater and microorganism action (Browne et al. 2011; Cutroneo et al. 2020a).

Concerning sediments, studies applied to their content in microplastics are mainly carried out in bottom sediments of coastal areas (Cutroneo et al. 2020a; Ruiz-Compean et al. 2017; Zobkov and Esiukova 2017) or on the continental shelf (Mu et al. 2019), while it is very difficult to have information on sediments at great depths due to the poor accessibility of deep environments and, consequently, the very high costs of such investigations. Despite difficulties, some recent studies have focused their attention on abyssal sediments, verifying the presence of macrolitter by video analysis (Bergmann and Klages 2012; Chiba et al. 2020) and testifying the presence of microplastics by sediment sampling and analysis even at high depths (Courtene-Jones et al. 2020; Gerigny et al. 2019; Van Cauwenberghe et al. 2013; Zhang et al. 2020).

In this context, the testimony of the presence of microplastics in deep sediments off the coast of Toulon (42°48.352' N – 006°01.613' E; France; **Fig. 1**) is presented here. Sediment sampling was carried out on 21 October 2019 during a sea campaign organised in the field of the French oceanographic cruises in the MEUST NUMerEnv deep sea infrastructure that hosts the project KM3NeT (Adrián-Martínez et al. 2016), a research infrastructure consisting of new generation neutrino telescopes in the deepest areas of the Mediterranean. In addition, the chemical and physical characterisation of sediments was carried out by analysing grain size, chemistry, mineralogy, and organic and inorganic matter content to frame the deep environment and gather as much information as possible on it.

2. KM3NeT infrastructure and study area

KM3NeT is a new Research Infrastructure consisting of a network of deep-sea neutrino telescopes in the Mediterranean Sea (KM3Net 2021). Its main objectives are (1) the discovery and subsequent observation of high-energy neutrino sources in the Universe and (2) the determination of the neutrino mass ordering and other fundamental physics searches, such as sterile neutrinos, neutrino non-standard interactions, dark matter, and quantum gravity effects. The KM3NeT infrastructure allows performing also deep-water biological studies, such as bioluminescence monitoring and acoustic detection of marine mammals.

Two deep-sea sites for the telescope deployment have been selected, namely Toulon (France) and Capo Passero (Italy). The selection was based on the optical properties of the water, distance to shore and local infrastructure. The samples analysed and presented in this paper come from the Toulon site (Fig. 1), at a depth of about 2443 m.

The study area is located in the abyssal plain 10 km off the coast of Toulon (south-eastern France) and at the base of the canyon that characterised the continental slope in front of Toulon. The abyssal plain is mainly composed of fine-grained sediments and characterised by scarcity in benthic macrofauna and flora (Cartes et al. 2004). From an oceanographic point of view, the study area lies on the border between the Ligurian-Provençal basin and the Gulf of Lion that is characterised by the presence of a surface cyclonic circulation 50 km wide, the Northern Current also known as the Liguro-Provençal-Catalan Current, which flows mainly counter-clockwise along the coast (Millot et al. 2005) (Fig. 1). The abyssal plain is an area of formation of the Western Mediterranean Deep Waters that flow towards Catalonia and Balearic Islands Cisneros et al.

2019). Due to the cyclonic gyre trapping water in the middle of the basin and to the significant winter heat losses due to the strong northern winds, the Gulf of Lion is affected by periodically massive events of dense shelf water cascading that impact on sediment dynamics and suspended particle transport on the slope and abyssal plain (Durrieu de Madron et al. 2017). These dense events erode the sediments along the slope and transport a large quantity of suspended particles into the lower layer; they are associated with strong mixing of the water down to the sea bottom and strong currents near the bottom in the horizontal diffusion phase of the newly formed deep waters (Durrieu de Madron et al. 2017).

The marine area hosts military activities, Toulon being a major French military harbour, and the site is subject to maritime traffic with ferry lines to Corsica. The fishing activity is very limited in the area.

3. Materials and Methods

On 21 October 2019, superficial bottom sediments were taken at the depth of 2443 m. Sediment sampling was performed during a dive of the HROV Ariane operated from the RV L'Europe of Ifremer (EMSO-KM3NET-LIGURE-OUEST 2019 EU)(**Fig. 2**). Originally, it was planned to use a standard corer device to perform the sampling. Unfortunately, the sediment was too smooth and did not stay in the corer after the sampling. We changed the sampling method and, therefore, we took sediment samples directly with the grab of the ROV and put the sediments in an open plastic container placed in the basket of the ROV. The container was previously coated with an aluminium foil to avoid plastic contamination of the sample. Since it was not possible to also coat the container lid with aluminium foil, knowing the composition of the lid in terms of plastic polymer, any finding of this polymer would have been subtracted from the results of the analysed samples. In **Online Resource 1**, it is possible to see how the robotic arm of the HROV Ariane picks up and stores the sample from the bottom; for short, the video playback speed is multiplied by 4 times. The robotic arm took 3 portions of surface sediment approximately 5 cm thick with the grab (Fig. 2) and collected them on the container. Once the ROV was recovered on the vessel, sediment was taken from the container using a metallic tool and divided in four samples stored in glass jars with aluminium-coated cap. From the moment of the sample recovery on board the ship until the moment of analysis, samples were stored at 4 °C.

A portion each of the four original sediment samples was placed in Petri dishes and dried in a thermostatic oven at 60 °C. Afterwards, each portion was divided in three for the grain-size, mineralogical and chemical analyses to characterise the sampled sediments. Dimensional, mineralogical, and chemical analyses were conducted following methodologies described in Cutroneo et al. (2017).

For grain-size characterisation, samples were firstly wet-sieved to divide the fine fraction (particle diameter (Ø) <63mm) from the coarse fraction (Ø>63 mm), and then the coarse fraction was dried and subsequently dry-sieved to determine grain-size classification considering the following size classes: Ø<63 µm, 63<Ø<125 µm, 125<Ø<250 µm, 250<Ø<500 µm, 500<Ø<1000 µm, 1000<Ø<2000 µm, Ø>2000 µm (Cutroneo et al. 2017).

For the mineralogical characterisation of sediments powder X–ray Diffraction (XRD) analysis was carried out on pre-grounded sediment with an agate pestle, with Co Kα radiation (current 20 mA, voltage 40 kV).

Quantification of minerals was performed according to the Reference Intensity Ratio (RIR) method (Zhout et al. 2018). Dimensional and mineralogical results were expressed in %.

Chemical analysis was carried out to quantify the metal and trace elements concentration of sediments (Al, Fe, Mg, As, Cd, Co, Cu, Cr, Mn, Ni, Pb, V, Zn, Ag, Hg). Inductively coupled plasma mass spectrometry (ICP-MS) analysis was applied to 0.5 g of dry and ground sediment sample after modified Aqua Regia digestion (ISO 15587) to determine trace elements, while major element concentrations were investigated with an inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on 1 g of sample digested in hot aqua regia. Chemical analyses were carried out by Bureau Veritas Mineral Laboratories (Canada; ISO9001 Quality Management Systems). Standard quality assurance procedures include analysis of blanks within each batch and a routine testing of certified reference material standards; duplicate samples included in each batch to ensure that reproducible results are being achieved (Consani et al. 2017).

To avoid sample contamination from external microplastics, different measures of prevention were taken. All the laboratory procedures described below were performed by operators wearing a white cotton coat; laboratory instruments used were only in glass or steel and thoroughly rinsed with previously micro-filtered water before their use; moreover, almost all the passages took place under the laboratory hood and in the presence of a control filter Cutroneo et al. (2020b).

Fifty millilitres of sediment were taken from each sample, placed inside a beaker, and covered with watch glass dish. Two hundred millilitres of Magnesium Chloride saturated solution (prepared with approximately 2400 g of $MgCl_2$ per L of filtered water to reach the density of 1.31 g cm^{-3}) were added to extract microlitters from sediment by density separation following this process:

- the mix was stirred with a glass stick for 5 minutes and then allows settling under a flow hood for 48 h (duration of the process time was chosen based on the fine nature of the sediment);
- afterwards, 10 mL of supernatant were taken and placed inside a glass jar. The separation process was carried out 3 times for each sample, obtaining 30 mL of supernatant for each sediment sample which was filtered on a GF/F glass fibre membrane (porosity 0.42 µm);
- the obtained filter was rinsed with 1 L of micro-filtered water to eliminate the eventual residual salts that could create difficulties during the following analysis;
- filters were treated with 30 mL of H_2O_2 overnight to dissolve organic matter and then subjected to additional washing with 1 L of micro-filtered water;
- filters were finally placed in glass Petri dishes.

Particles over the filters were observed with a Leica Z16 microscope and photographed with a Leica Application Suite software, then measured and classified according to shape, colour, and size. Shape identification classified microparticles into filaments, spheres, granules, fragments and other types (pellets, foam, film, other), while size classification divided microparticles into the following categories: Ø<63 µm, 63<Ø<125 µm, 125<Ø<250 µm, 250<Ø<500 µm, 500<Ø<1000 µm, 1000<Ø<2000 µm, 2000<Ø<5000 µm.

Once the observation under microscope was completed, 40% of microparticles for each sample were analysed with Raman spectroscopy (Galgany et al. 2013). Despite Galgani et al. (2013) indicate a percentage equal to 5-10% of the items observed under the optical microscope, we opted for analysing 40% of the items by µRaman spectroscopy to have a better detail of the plastic component observed and as compromise between time and cost of the analysis and the intended results. In our study, only µRaman analysis can assess with certainty that the particles identified in the samples are composed of plastic polymers, and therefore identified as microplastics. Only the resulting spectra with a correspondence of more than 70% to the reference spectra were considered acceptable and entered in the results.

Throughout the period in which the samples were exposed to air in laboratory, a control filter was placed on the work surface and then analysed by microscope and µRaman to remove particles from the results due to contamination of the sample by the laboratory environment (laboratory contamination was quantified as an average of 6% of the particles analysed, and consist of cellulose fibres, mineral particles and microplastics).

4. Results

The results of the sediment grain-size analysis (**Table 1**) show the general predominance of fine sediment (Ø<63 µm), while the most representative classes of the coarse fraction (Ø>63 µm) were very fine sand and fine sand.

Mean mineralogical results are reported in Table 1. The main minerals found in all the samples were quartz, calcite, plagioclase and pyroxenes, with muscovite and chlorite in minor percentage, and zircon and rutile in trace.

Metal concentrations are reported in **Table 2**.

From the optical results obtained from the four starting 50-mL samples, a total of 446 items was classified, with an average of 111 particles per sample. Among them, the main categories represented were fragments, filaments, granules, while only a few particles (< 10 %) were classified as 'other' (film, foam, other types) and spheres (**Fig. 3**). In addition, most of the items fell within the size class 63-125 µm (Fig. 3), followed by microparticles smaller than 63 µm and the size range 125-250 µm in accordance with sediment size results (Table 1). The remaining size classes were poorly represented (<7%) and the size class over 2000 µm was represented by only 3 fibres found in only one sample. Considering the colour (Fig. 3), most of the particles were white, grey, and black.

From the total of 446 items, 40% was analysed by µRaman spectroscopy and only 4% of the items analysed have been recognised as microplastics (polymers, additives, and industrial dyes; **Fig. 4**). Two per cent of the analysed particles has been identified as organic material (such as cellulose; Fig. 4A, C), whereas the majority of particles (94%) has mineral origin (such as carbon and quartz; Fig. 4D,E) and therefore are classified as inorganic material. Regarding these, the main minerals found are quartz (mean of 38.8%), muscovite (mean of 21.0%; Fig. 4G), and plagioclase (mean of 8.4%) which match the mineralogical composition of the sediments found through mineralogical analysis (Table 1). Plastic polymers found consist of polyurethane (PU) foam in the form of 2 grey particles of 50 µm of dimension (Fig. 4B), polyvinyl chloride (PVC) as 1 transparent particle of 183 µm (Fig. 4F), and copper-phthalocyanine ($C_{32}H_{16}CuN_8$) as 3 blue particles of 10-20 µm. Copper-phthalocyanine is a blue synthetic pigment with numerous applications in industrial coatings, textile and paper manufacturing, fine art pigments, organic and photovoltaic cells

(Ahmed Basha et al. 2013; Matoko-Ngouma et al. 2020). Although not a recognised microplastic, as we cannot determine the composition of the material making up the particle because the dye prevents it from being analysed with the µRaman, we have considered the blue particles to be part of the microplastic category as it is an artificial dye.

Starting from particles found in the samples, considering 446 microparticles found in 200 ml of total sediment analysed, a concentration of about 80 microplastics L^{-1} has been found in this study.

5. Discussion

Size characteristics of sediments were in accordance with the general low dynamism of abyssal environment (Cisneros et al. 2019) and to results found by Durrieu de Madron et al. (2017) in the abyssal plain of the Gulf of Lion where particles distribution is dominated by a principal mode around 8 µm and a secondary mode around 30 µm. Metal concentrations show generally low values like those found in lightly contaminated areas of the bay of Toulon by Tessier et al. (2011).

Regarding microplastic contamination of sediments, the sea bottom, especially at great depths, is the final site of arrival and deposition of MPs, as reported by da Courtene-Jones et al. (2020), but little is actually known about the deep environments because of their inaccessibility. This makes any information that can be gleaned from sediments taken in these remote environments valuable and useful for understanding deep circulation mechanisms. As regards the Mediterranean Sea, several studies have been carried out on surface waters (mainly by manta trawl sampling) (Suaria et al. 2014; Ruiz-Orrejon et al. 2016; Cincinelli et al. 2019; Akarsu et al. 2020; De Haan et al. 2019; Zayen et al. 2020) and on coastal sediments (Alomar et al. 2016; Cutroneo et al. 2020a; Missawi et al. 2020; Tata et al. 2020), but only one research article focused on deep sediments (Woodall et al. 2014). Thus, our results bring a new contribution to the lack of knowledge of microplastic pollution in deep marine environments.

Considering other studies at similar depths, Woodall et al. (2014) searched only microfibers in deep-sea sediments in different part of the world by analysing 50 mL of sample. They found 10 and 15 fibres in open slope in the North East Atlantic and in the subpolar region of the North Atlantic (2000 m depth), respectively, while in canyon in the western part of the Gulf of Lion they found 35 and 10 items at 300 and 1300 m of depth, respectively. Contrary to the findings of Woodall et al. (2014), no plastic fibres were found in our samples as all microfibers consisting of cellulose. In this case, our results seem to support the fact that most of the fibres are concentrated near the coast and especially near population centres, as indicated by Alomar et al. (2016), and in areas of accumulation. Our study area is far from the coast and from the city of Toulon, and the high depth may be a determining factor for the absence of this type of microplastics. Strong currents and winds, such as those affecting the Gulf of Lion, may transport microlitter, especially the most buoyant, far away from its source (van Sebille et al. 2020) and so fibres are perhaps not facilitated to deposit at the study site, but more to be transported along the water column by general circulation.

Bergmann et al. (2017), analysing sediments at 2340−5570 m depth in the Fram Strait in the western part of Svalbard (Norway), found concentrations (mean of 2264 microplastics L^{-1}) much higher than those found in Toulon deep sediments. Showing relatively low microplastics concentrations, our results are like what found by Courtene-Jones et al. (2020) in the deep-sediments of the Rockall Trough (North Atlantic Ocean), and by Van Cauwenberghe et al. (2013) in different part of the world (Polar front in the Southern Ocean, Porcupine Abyssal Plain in the North Atlantic Ocean, distal lobe of Congo Canyon in Gulf of Guinea, and the Nile Deep Sea Fan in the Mediterranean Sea).

Regarding the polymeric composition of the plastics found in deep sediments, due to the low variety of plastic polymers found (i.e. 3), only the following evidence can be highlighted. Polyvinyl chloride is a high-density polymer that is extensively present in sediments worldwide and was also found in deep sediments by Courtene-Jones et al. (2020). Copper-phthalocyanine, widely used pigment in multiple industrial processing, was also extracted from deep sediments by Van Cauwenberghe et al. (2013). Finally, polyurethane is a dense polymer that tends to settle quickly and becomes incorporated into sediment (Uddin et al. 2021).

Considerations about the origin of the microplastics found cannot be made due to the great depth of the sampling site and the great distance between the sampling site and the coast or the main anthropogenic activities in the area. In fact, Kane et al (2020), studying the complexity of mechanisms of the microplastic transport and diffusion on the sea bottom, highlighted that microplastics are not simply affected by vertical setting, but are subject to wind mixing, current transport along the water column, dense down-canyon flows and strongly near-bed thermohaline currents, as well as and biological interactions (biofouling, inclusion in the trophic chain, and inclusion in marine snow). Notwithstanding, microplastics found in our samples are all definable as secondary microplastics, i.e. resulting from the degradation and fragmentation of larger plastics. This, together with their small size (Ø < 200 µm), may be a clue as to the type of microplastics that, in relation to their site and time of origin, manage to reach great depths. Kooi et al. (2020) found that small fragments are more susceptible to wind mixing, because of their low buoyant terminal rise velocity, which strengthens the hypothesis that wind mixing causes a size selective loss of plastics from the surface and facilitate small particles transport along the water column. In addition, the study site is subject to the formation of very extensive nepheloid bottom layers events (Tessier et al. 2011) that can lead to the resuspension of the bottom sediment along the water column and thus to the dispersion and subsequent re-deposition of the particles even at great distances from the origin site. In a recent study conducted by Gerigny et al. (2019) on the presence of macro-debris on the sea bottom by ROV, the Toulon Canyon, located between the continental shelf and the abyssal plain off Toulon, does not appear to be strongly contaminated by plastic debris (1 item km^{-1}), but rather by metallic materials (about 3 item km^{-1}) due to the presence of the large naval base of Toulon and the metal materials that have been dumped regularly in the past. This may support the relatively low concentrations of microplastics found in the abyssal sediments.

Further considerations on the origin of the fragments found in the deep sediments in front of Toulon can be made based on previous findings in the Gulf of Lion by Lefebvre et al. (2019) and Schmidt et al. (2018). Lefebvre et al. (2019), analysing water column in the Gulf of Lion found microplastics in 93% of water column samples consisting only of fibres composed by polyethylene terephthalate (PET; 61%). This could support the hypothesis that the fibres are diffuse more along the water column and are unlikely to reach great depths. Schmidt et al. (2018) found that particles < 1 mm^2 clearly dominated water sampling stations in the

Northern Current, the Rhône River and its plume, suggesting a long exposure time in the environment, while items between 1 mm^2 and 5 mm^2 in size were the most abundant microplastics near the coast in the Marseille Bay, suggesting coastal pollution sources or the removal of smaller particles from surface waters by ballasting owing due to the presence of epibionts. This may support the hypothesis that the small particles found in the deep sediment have come a long way over a long period of time before depositing on the deep sediments.

Settled particles are likely to be affected by patterns of deep circulation, such as deep-sea currents acting as conveyor belts which can transport small plastic items across the seafloor, possibly creating microplastics hotspots on the sea bottom. Poor information still exists about the conditions of deep ocean across the world and small-scale deep circulation, in addition to the abundance of factors affecting microplastics settling, such as density, polymeric compositions, shape and interaction with organisms, making it difficult to predict microplastics transport from coastal environment to the sea bottom (Kane et al. 2020; Abel et al. 2021). However, considering the described morphology and characteristics of the study area and the local circulation in relation to the relative low number of microplastics found and the lack of fibres, it can be assumed that the seabed in front of the Toulon canyon is not to be considered as a microplastic hotspot due to the periodic strong resuspension phenomena present, which generate shear stress on the seabed, and resuspension and dispersion of microplastics.

5. Conclusions

Our study, although preliminary due to the small number of samples considered, confirms the ubiquity of microplastics in environment, finding them also in the deep-sea environment of the abyssal plain. Thanks to the KM3NeT infrastructure and the periodical project campaigns, further sampling and in-depth study of the number and morphology of microplastics present in this kind of environment are underway. This will allow us to broaden knowledge of the origins and diffusion of abyssal microplastics and study possible variations over the years, as well as have indirect information on sea-bottom circulation and the shear stress on the seabed.

Supplementary Information: Online Resource 1: HROV Ariane picks up and stores the sample from the bottom; for short, the video playback speed is multiplied by 4 times. In the video, it is possible to see the robotic metallic arm of the HROV Ariane that opens the lid of the sample storage container that was previously coated with an aluminium foil to avoid plastic contamination of the sample, picks up the sediment samples from the sea bottom, stores them in the container, and, finally, closes the lid of the container. The robotic arm takes 3 portions of surface sediment approximately 5 cm thick with the grab and collected them on the container.

Declarations

- Ethics approval and consent to participate: Not applicable
- Consent for publication: Not applicable

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Figure captions

Fig. 1 Localisation of the sampling point off the coast of Toulon (France) in the north-western Mediterranean. Blue arrows outline the cyclonic general circulation, black arrows the strong winds affecting the Gulf of Lion, and black circle the area of trapping water by the cyclonic gyre. Red point indicates the city of Toulon and the red triangle the sampling point

Fig. 2 HROV Ariane (left) and sediment sampling with the grab (right)

Fig. 3 Particle classification according to shape, size, and colour

Fig. 4 Combined results obtained from microscope and Raman analysis. Starting from the top, examples of fibres in cellulose, polyurethane foam, and particles of carbon, quartz, polyvinyl chloride, and muscovite. In the Raman spectrum box on the right, the reference molecule spectrum is shown in red, while the spectrum resulting from the analysis of the sample item is shown in black

Figure 1

Click here to access/download;Figure;Fig. 1.jpg

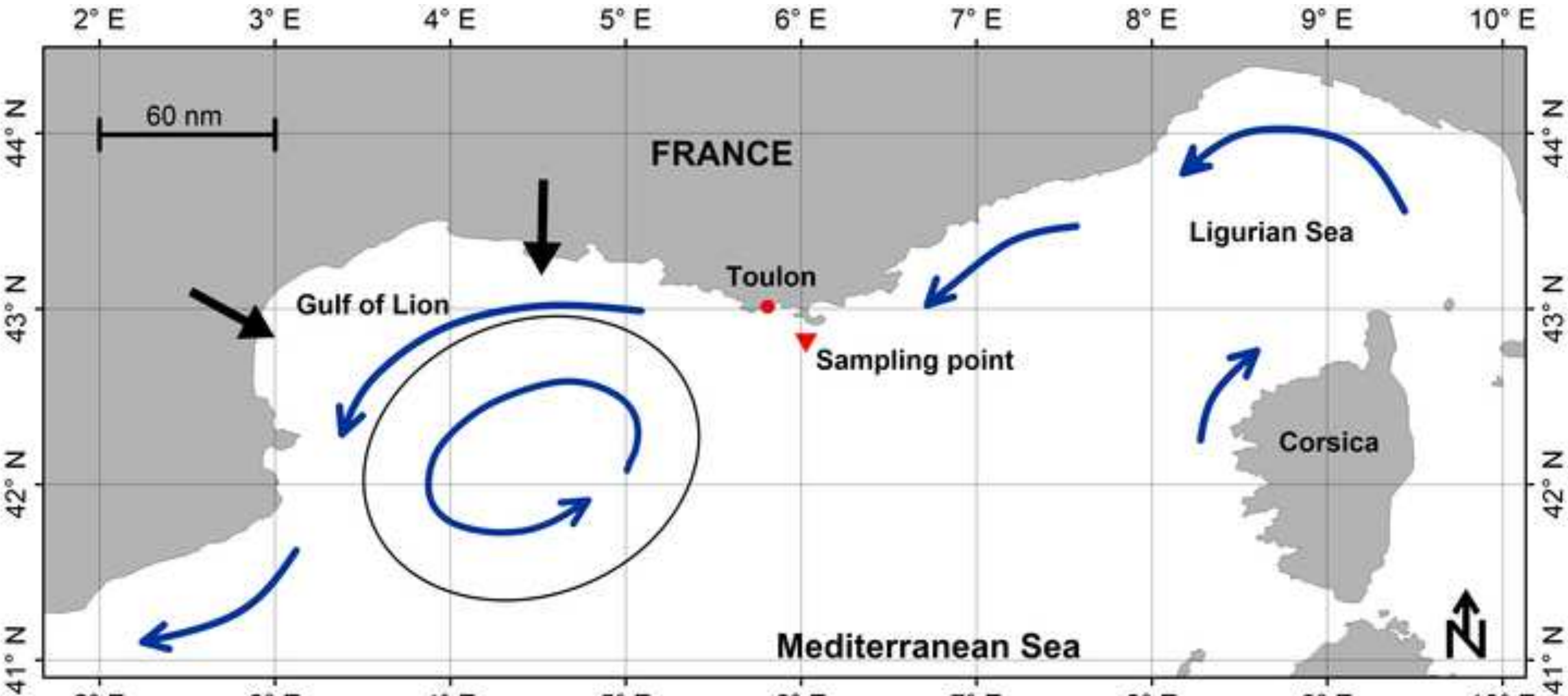

Figure 2

Figure 3

[Click here to access/download;Figure;Fig. 3.jpg]

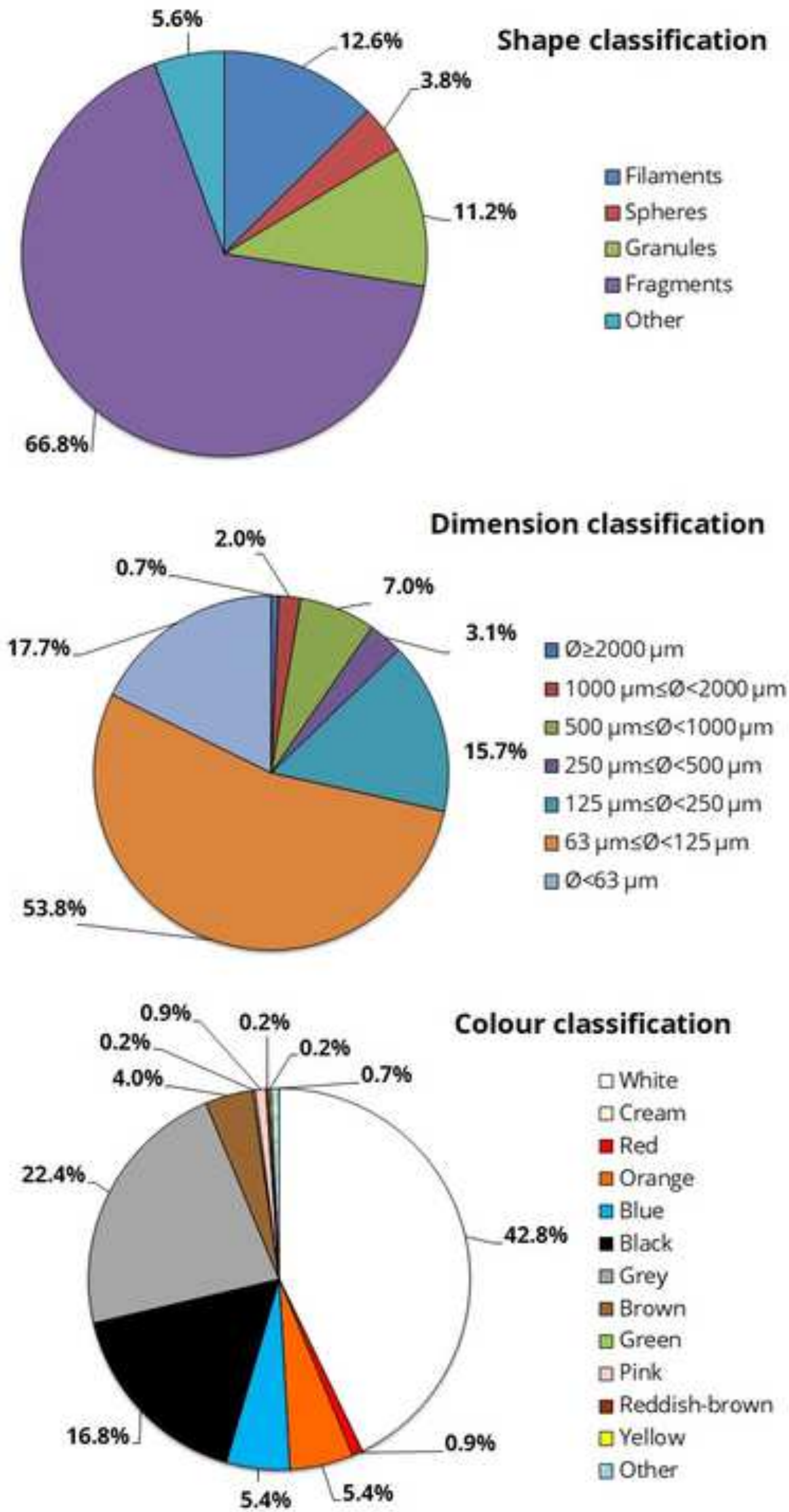

Figure 4 Click here to access/download;Figure;Fig. 4.jpg

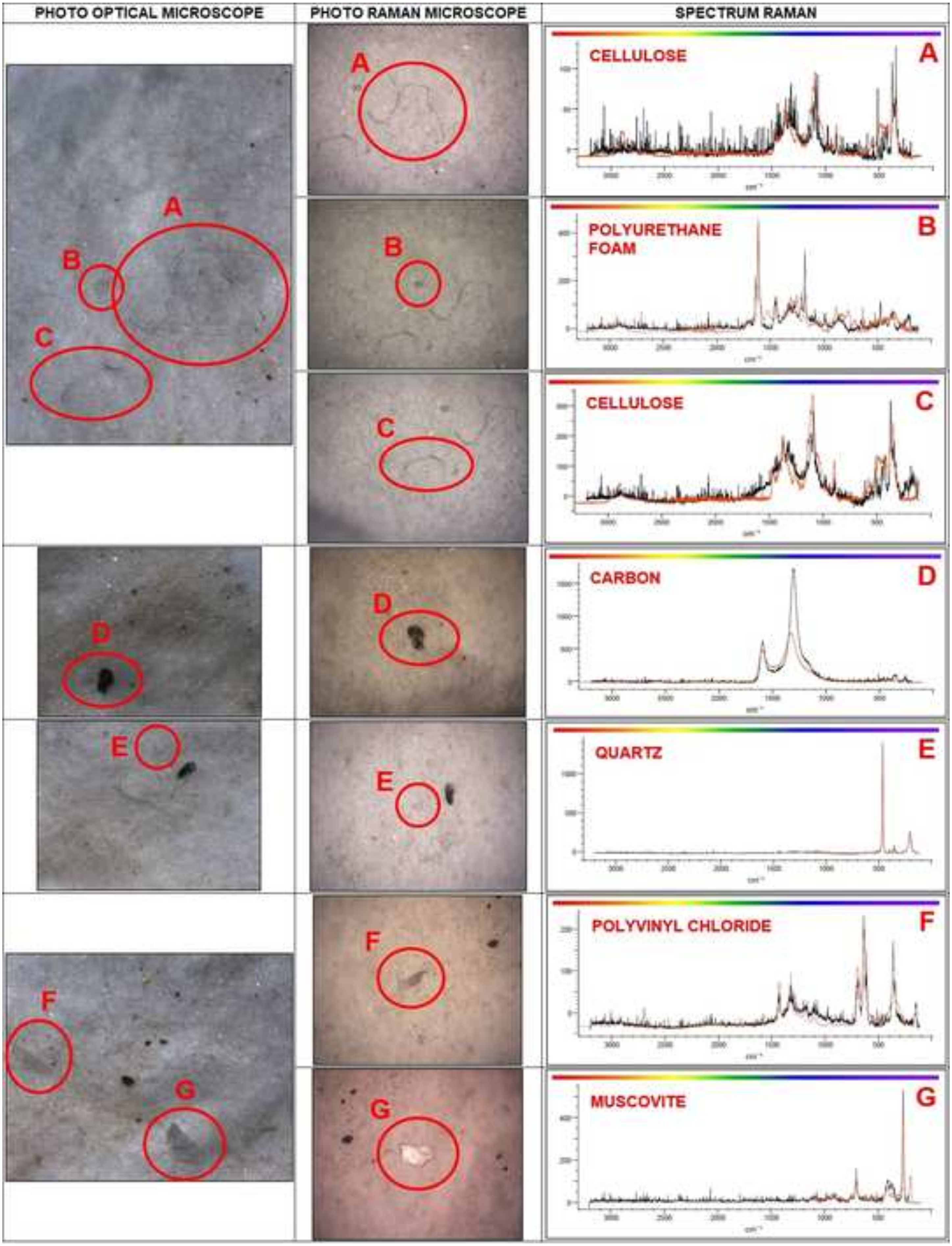

Table 1 Mean grain-size and mineralogical composition (in %) of sediments

Grain size	**Mean (%)**	**Standard Deviation (%)**
Fine material (Ø<63 μm)	53.7	3.2
Coarse material (Ø>63 μm)	46.3	3.2
Very fine sand (63<Ø<125 μm)	31.3	1.9
Fine sand (125<Ø<250 μm)	13.9	2.7
Mean sand (250<Ø<500 μm)	0.9	0.1
Coarse sand (500<Ø<1000 μm)	0.1	0.0
Minerals	**Mean value (%)**	**Standard Deviation (%)**
Zircon	0.8	1.6
Rutile	0.8	1.5
Muscovite	9.0	2.7
Plagioclase	14.8	3.1
Calcite	25.6	0.6
Quartz	29.0	2.3
Pyroxenes	12.8	2.6
Chlorite	7.2	2.7

Table 2 Detection limit, mean concentration, and standard deviation for selected metals to characterise the study area

Metal	**Detection limit**	**Mean concentration**	**Standard deviation**
Al (%)	0.01	0.89	0.13
Fe (%)	0.01	1.52	0.18
Mg (%)	0.01	0.95	0.06
As (ppm)	0.10	8.35	1.20
Cd (ppm)	0.01	0.08	0.01
Co (ppm)	0.10	7.75	0.90
Cu (ppm)	0.01	18.60	3.26
Cr (ppm)	0.50	31.08	4.30
Mn (ppm)	1.00	612.50	62.88
Ni (ppm)	0.10	31.33	4.29
Pb (ppm)	0.01	18.10	2.93
V (ppm)	1.00	23.25	3.10
Zn (ppm)	0.10	40.95	5.57
Ag (ppb)	2.00	46.75	21.62
Hg (ppb)	5.00	136.50	15.02