OceanoScientific Mediterranean Contaminants Expedition 2020

Scientific report

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In charge of Sampling:	**Linn Sekund** - OceanoScientific France assisted by **Marc Archer** - AMAALA
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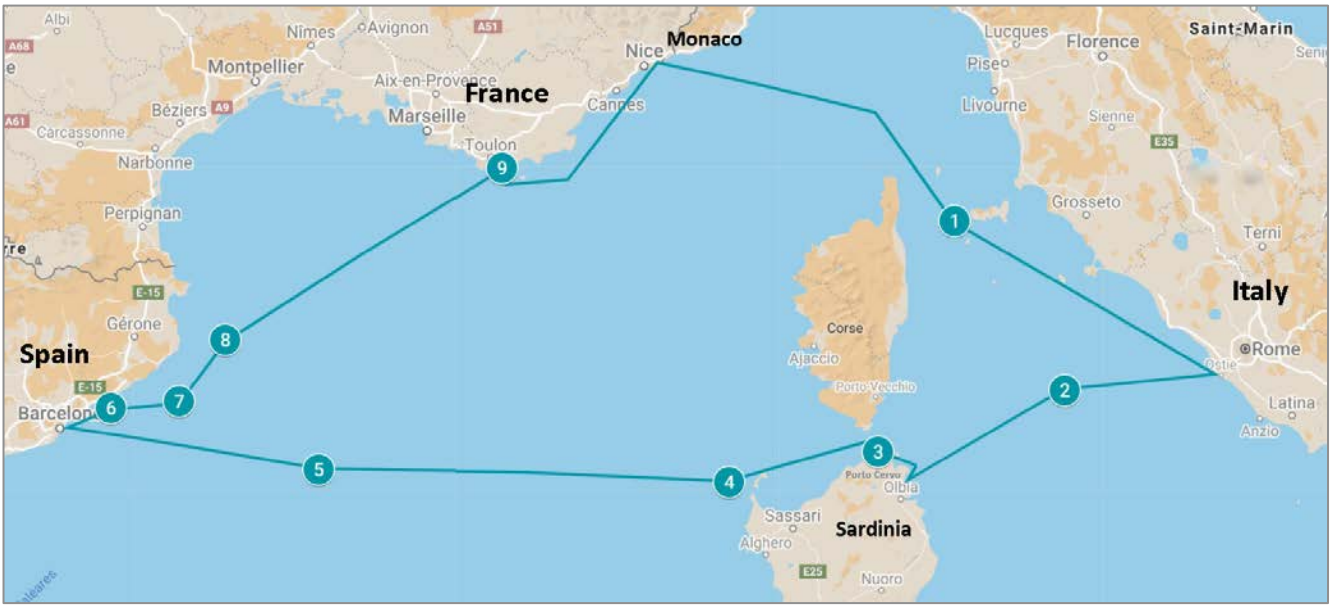
Scientific objective

The *OceanoScientific Mediterranean Contaminants Expedition 2020* was carried out under sail without CO2 emissions or waste on the initiative and under the direction of Yvan Griboval (OceanoScientific France / OceanoScientific Monaco / SailingOne - LOVE THE OCEAN) with the maxi-catamaran (33,50 m) *AMAALA EXPLORER* ex-*CLUB MED* - the largest ocean racing catamaran in the world - from Monaco to Monaco, from the 15th to the 29th of October 2020 with a crew of nine people towards the mouth of the Tiber River (Fiumicino near Rome - Italy), with port calls in Porto Cervo (Sardinia - Italy), Barcelona (Spain) and La Seyne-sur-Mer (France), on a course of 1,000 nautical miles.

The scientific objective of the *OceanoScientific Mediterranean Contaminants Expedition 2020* was to study the nature and density of organic chemical compounds that affect the marine environment and poison phytoplankton, at nine sampling stations (Map 1).



Map 1: Nine sampling stations

The protocols were implemented according to the recommendations of the Institut Français de Recherche pour l'Exploitation de la Mer (Ifremer), principally the Ifremer site located in Toulon - La Seyne-sur-Mer, which scientifically supervised this *OceanoScientific Mediterranean Contaminants Expedition 2020*.

Organic contaminants: **Polychlorinated biphenyls** (PCBs), **Polycyclic aromatic hydrocarbons** (PAHs), **Tributyltins** (TBTs) have been introduced into Nature largely due to human activities (urban, agricultural, and industrial activities). They have a high bioaccumulation capacity and a tendency to biomagnify in the food chain, which is reflected in the food we eat.

Since the 1930s, **Polychlorinated biphenyls** (PCBs) have been used in industry for their electrical insulating, lubricative, and non-flammability properties. They were used as insulators in electrical transformers and capacitors; as lubricants in turbines and pumps or as components of oils, adhesives and paints.

The production and use of PCBs have been banned since 1987. They have been recognised as "persistent organic pollutants" and classified as "carcinogenic" to humans. Due to their fat-soluble nature, PCBs tend to accumulate in the lipid tissues of living organisms (Marchand et al. 1990).

Most **Polycyclic aromatic hydrocarbons** (PAHs) are natural constituents of coal and oil. They also come from the incomplete combustion of organic materials such as fuels, wood and tobacco. They are present everywhere: air, water, food. PAHs can result from natural origins (forest fires, volcanic eruptions, etc.), and from anthropogenic combustion sources (emissions from chimneys, household waste incinerators, petrol and diesel engine exhausts, etc.).

It is worth noting that Benzopyrene is present in a good number of PAH mixtures, often in a relatively constant proportion (about 10%). However, it is mutagenic (the ability to modify the genome) and is a proven carcinogen.

PAHs play a major role in genotoxicity, which can damage DNA and cause tumour-causing mutations in fish (Cachot et al., 2006). Disturbances in development and neuromuscular function have also been observed in the copepod *Eurytemora affinis* (Forget et al., 2003 - Cailleaud et al., 2004).

Tributyltin (TBT) has been used in antifouling paints on ships and yachts because it is a powerful biocide, toxic to plants and to many organisms exposed to it, starting with humans. Its use in paints was banned in the late 1980s, as was the use of lead. However, TBT was definitively banned under the Rotterdam Convention, signed on the 10th of September 1998 in the Netherlands, but only applied since the 24th of February 2004. Today, TBT is on the list of persistent organic pollutants, classified as a "priority substance" by the Water Framework Directive 2000/60/EC (WFD).

TBT, a lipophilic compound, tends to bioaccumulate in marine organisms and sediments. In gastropods, TBT causes hormonal problems resulting in the appearance of male sexual characteristics in females (imposex). It is therefore a threat to the proper propagation of the species (Hagger et al., 2006). Abnormal shell development in oysters due to TBT has also been observed (Gibbs & Bryan, 1994).

Materials & Methods

Linn Sekund, assisted by Marc Archer, took nine water samples over the 1,000 nautical mile course of the maxi-catamaran *AMAALA EXPLORER*, at stations determined together with Jean-Louis Gonzalez from the Institut Français de Recherche pour l'Exploitation de la Mer (Ifremer).

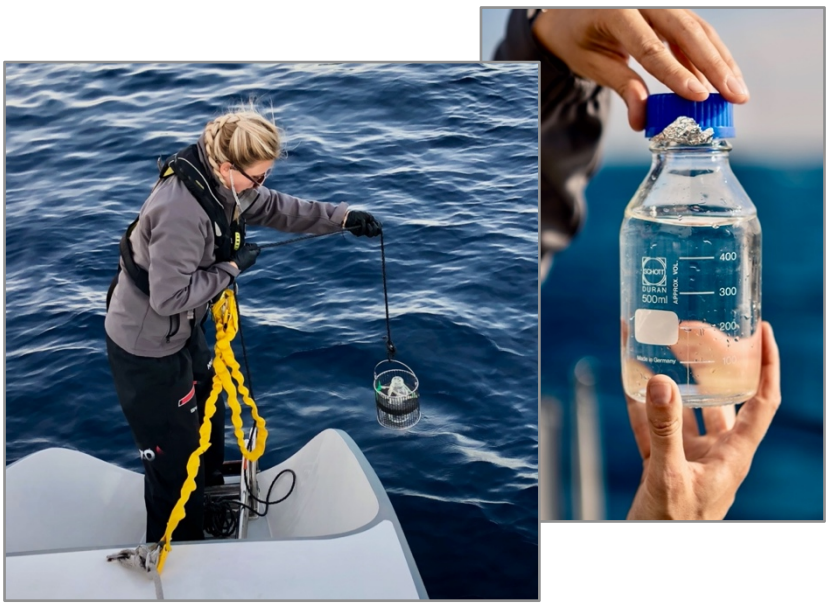
All the samples were taken at the subsurface, i.e. between one and two metres deep. The physicochemical parameters Temperature & Salinity were measured at each sampling site.

The samples were immediately frozen onboard (-20°C), then handed over to scientists at the Ifremer site in Toulon - La Seyne-sur-Mer (France). The Cedre laboratory, located in Brest (Brittany - France), specialised in accidental pollution, conducted the analyses.

The Stir Bar Sorptive Extraction (SBSE) technique was used to collect and analyse the presence of organic compounds (PCBs - PAHs - TBT). This technique allows the extraction and concentration of hydrophobic organic compounds. The SBSE technique combines sensitivity and ease of use.

The SBSE technique is based on the extraction by sorption of hydrophobic molecules dissolved on a polymer: polydimethylsiloxane (PDMS). This 0.5 to 1 mm thick polymer covers a 20 mm long magnetic stirring bar, which is immersed in the water sample to be analysed.

After an extraction phase lasting a few hours in a sample volume of 100 ml, the analysis of the compounds is carried out "live" from the bar, by thermo-desorption, with gas chromatographic-mass spectrometry (GC-MS) analysis (Gonzalez et al. 2009).



Results

Station 1

West of the island of Elba (Italy): 42°43.446' N - 9°57.682' E
Depth: 139 m / Seawater: 20°C - 38.57 PSU (Practical Salinity Unit)

The presence of Polycyclic aromatic hydrocarbons (PAHs) was detected. Among the 24 PAHs of interest, the presence of three PAHs including Fluoranthene, Benzoahantracene and Benzo(g,h,i)perylene were identified, but in concentrations below the limit of quantification: LOQ = 1-5 ng/L. Despite the sensitivity of the sampling method, no traces of Tributyltin (TBT) or Polychlorinated biphenyls (PCB) were observed based on the limit of detection of: LOD = 0.15 ng/L.

Station 2

Off the coast of Fiumicino (Italy): 41°37.889' N - 10°55.197' E
Depth: 1 380 m / Seawater: 18.2°C - 38.91 PSU (Practical Salinity Unit)

In a marine area where the seafloor exceeds a depth of 1,000 metres, no traces of Tributyltin (TBT) or Polychlorinated biphenyls (PCB) were observed at the surface. This means that the levels present are below the limit of detection (LOD = 0.15 ng/L). On the other hand, the presence of Polycyclic aromatic hydrocarbons (PAH) was detected. Among the 24 PAHs of interest, the presence of Naphthalene was observed, but in concentration below the limit of quantification (LOQ = 1-5 ng/L).

Station 3

The Maddalena Archipelago (Sardinia - Italy): 41°13.713' N - 9°17.434' E
Depth: 47 m / Seawater: 18.6°C - 37.02 PSU (Practical Salinity Unit)

The concentration of Tributyltin (TBT) was 2.03 ng/L. It should be noted that the Environmental Quality Standard (EQS) for TBT is set at: EQS = 1.5 ng/L. Polycyclic aromatic hydrocarbons (PAHs) such as Naphthalene and Methylnaphthalene were detected, but in concentrations below the limit of quantification (LOQ = 1-5 ng/L). Polychlorinated biphenyls (PCBs) were not detected at this station.

Station 4

At the North-Western tip of Sardinia (Italy): 41°1'.914' N - 7°59.943' E
Depth: 2 500 m / Seawater: 19.4°C - 39.20 PSU (Practical Salinity Unit)

The concentration of Tributyltin (TBT) was 2.37 ng/L, higher than the Environmental Quality Standard (EQS) set at 1.5ng/L. No traces of Polycyclic aromatic hydrocarbons (PAHs) or Polychlorinated biphenyls (PCBs) were found in the analyses.

Station 5

At 100 miles East of Barcelona (Spain): 41°06'.848' N - 4°25.940' E
Depth: 2 621m / Seawater: 19.1°C - 39.02 PSU (Practical Salinity Unit)

The concentration of Tributyltin (TBT) was 2.16 ng/L. The analysis of the sample taken at this station did not reveal any traces of Polycyclic aromatic hydrocarbons (PAHs) or Polychlorinated biphenyls (PCBs). Among the 29 pesticides of interest, 4-4ddt was detected at this location, but at a concentration below the limit of quantification (LOQ = 0.5 ng/L).

Station 6

Close to Mataró (Spain): 41°30.908' N - 2°37.155' E
Depth: 65 m / Seawater: 20.7°C - 39.30 PSU (Practical Salinity Unit)

Out of the nine stations of the *OceanoScientific Mediterranean Contaminants Expedition* 2020, the highest concentration of Tributyltin (TBT) was measured at Station 6 (Map 6). The observed level was 6.12 ng/L, which is four times higher than the Environmental Quality Standard (EQS) of 1.5 ng/L. Despite the sensitivity of the sampling method used, no traces of Polycyclic aromatic hydrocarbons (PAHs) or Polychlorinated biphenyls (PCBs) were detected at this station near the Spanish coast.

Station 7

North West of Lloret de Mar (Spain): 41°33.499' N - 3°12.290'
Depth: 256 m / Seawater: 18.7°C - 39.17 PSU (Practical Salinity Unit)

The concentration of Tributyltin (TBT) was 2.41 ng/L. Naphthalene, a Polycyclic aromatic hydrocarbon (PAH), was detected, but in concentration below the limit of quantification (LOQ = 1-5 ng/L). Polychlorinated biphenyls (PCBs) were also absent.

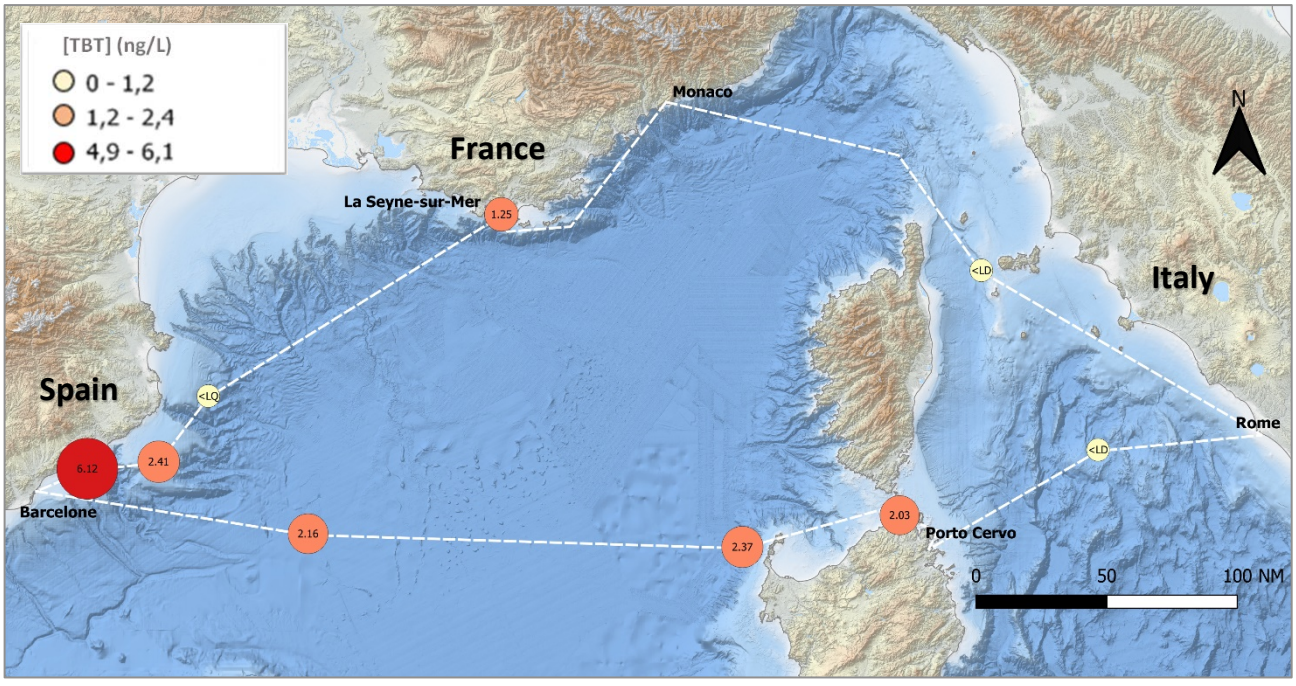
Station 8 — Off the coast of Palafrugell (Spain): 41°57.655' N - 3°36.761' E
Depth: 700 m / Seawater: 16.6°C - 39.39 PSU (Practical Salinity Unit)

The presence of Tributyltin (TBT) was observed, but in concentration below the limit of quantification (LOQ = 1ng/L). We also noted the absence of Polycyclic aromatic hydrocarbons (PAHs) and Polychlorinated biphenyls (PCBs) at the time of sampling at this station.

Station 9 — At the entrance of the Bay of Toulon (France): 43°03.688' N - 6°01.175' E
Depth: 60 m / Seawater: 18.7°C - 39.35 PSU (Practical Salinity Unit)

The concentration of Tributyltin (TBT) at the entrance of the Bay of Toulon was 1.25 ng/L, i.e. a value lower than the Environmental Quality Standard (EQS) set at 1.5 ng/L. The presence of Polycyclic aromatic hydrocarbons (PAHs), Naphthalene and Methylnaphthalene was detected, but in concentrations below the limit of quantification (LOQ = 1-5 ng/L). Polychlorinated biphenyls (PCBs) were also absent.

The TBT concentration is comparable to those measured by Gonzalez and Guyomarch in 2020 using SBSE (0.30 < **[TBT] Station 9** < 5.8ng/L) and to those measured by Michel and Averty in 1999 using other analytical methods (0.44 < **[TBT] Station 9** < 14.6ng/L)



Map 2: TBT concentrations (ng/L) measured at each sampling station using SBSE

Summary table

Summary of sampling stations SBSE (Stir Bar Sorptive Extraction)

SBSE Station	Location	Date	Time	Latitude	Longitude	Depth (m)	Temp. (°C)	Salinity (PSU)	[TBT] (ng/L)	[HAP] (ng/L)	[PCB] (ng/L)	[Pesticides 4-4ddt] (ng/L)
1	West of the island of Elba	16/10/20	08:56	42°43.446'	9°57.682'	139	20.0	38.57	< LOD	> LOQ	> LOD	
2	Off the coast of Fiumicino	17/10/20	09:53	41°37.889'	10°55.197'	1 380	18.2	38.91	< LOD	> LOQ	> LOD	
3	The Maddalena Archipelago	18/10/20	09:00	41°13.713'	9°17.434'	47	18.6	37.02	2.03	> LOQ	> LOD	
4	At the NW tip of Sardinia	19/10/20	18:00	41°1'.914'	7°59.943'	2 500	19.4	39.20	2.37		> LOD	
5	100 MN East of Barcelona	20/10/20	11:00	41°06'.848'	4°25.940'	2 621	19.1	39.02	2.16		> LOD	> LOQ
6	Close to Mataró	23/10/20	11:30	41°30.908'	2°37.155'	65	20.7	39.30	6.12		> LOD	
7	NW of Lloret de Mar	23/10/20	15:00	41°33.499'	3°12.290'	256	18.7	39.17	2.41	> LOQ	> LOD	
8	Off the coast of Palafrugell	23/10/20	19:00	41°57.655'	3°36.761'	700	16.6	39.39	< LOQ		> LOD	
9	At the entrance of the Bay of Toulon	24/10/20	06:00	43°03.688'	6°01.175'	60	18.7	39.35	1.25	> LOQ	> LOD	

LOQ: Limit of quantification
LOD: Limit of detection

Conclusion

This *OceanoScientific Mediterranean Contaminants Expedition 2020* highlighted important levels of Tributyltin (TBT) within five miles from the shoreline, at depths ranging from 47 to 65 metres, with a higher peak in the North-East of Barcelona where a concentration of 6.12 ng/L was measured, i.e. a value four times higher than the Environmental Quality Standard (EQS) set at 1.5 ng/L. These high concentrations can be explained by the important port and maritime commercial activity (cargo ships, tankers, ferries, liners, etc.) and by the persistence of TBT in the sediments, even after its gradual ban in the late 1980s.

The further away from the coast and the greater the depth, the lower the traces of Tributyltin (TBT). Moreover, traces of contaminants are particularly low around the Isle of Elba, between Corsica and Italy, far from any large commercial harbour.

Nevertheless, in the North of Sardinia (Italy), not far from the Southern tip of Corsica (France), within the Bonifacio Strait International Marine Park (PMIBB - France/Italy), the levels of Tributyltin (TBT) significantly exceeded the Environmental Quality Standard (EQS), highlighting the fact that marine pollution is taking place in Marine Protected Areas (MPA).

Conversely, it would not have been surprising to find a high concentration of Tributyltin (TBT) in the Bay of Toulon (France), Europe's largest military port and a major maintenance site for super yachts. However, the TBT level there is significantly lower than the Environmental Quality Standard (EQS).

This expedition made it possible to test the use of the SBSE (Stir Bar Sorptive Extraction) sampling technique on board a sailing boat with real technical and energy constraints. It offers significant advantages in terms of sensitivity and ease of use. The SBSE technique is therefore validated for the next *OceanoScientific Expeditions*.

The quality partnership implemented for more than twelve years with the Institut Français de Recherche pour l'Exploitation de la Mer (Ifremer) within the framework of the *OceanoScientific Programme* has once again confirmed its relevance and effectiveness for the benefit of the scientific community.

Ifremer scientists, experts in contaminants, were highly involved in the project and were present alongside the OceanoScientific team, both for the training in the collection of samples and the implementation of protocols. Ifremer also provided dedicated equipment for controlled efficiency.

Further studies about chemical and organic contaminants are fundamental to better understand their fate in the marine environment, their impact on marine organisms and, potentially, on human health. Carrying out this work under sail without any CO2 emissions, in particular thanks to an *OceanoScientific Explorer*, such as the *AMAALA EXPLORER* chartered for the occasion, is an additional asset for the international oceanographic community.

Delivery of samples

From left to right: Yvan Griboval - Vincent Rigaud (Director Ifremer Toulon / La Seyne-sur-Mer) Linn Sekund - Brendan Jack (Chief Sustainability Officer AMAALA).

Acknowledgements

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