DYCOMED – Dynamics of chemical contaminants in the Mediterranean Sea: An integrated investigation from the atmosphere to the sea bed

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Abstract

Our PhD team deals with the chemical fingerprinting of trace metals (TM) and persistent organic pollutants (POPs) in the Ligurian Sea, a region of the Northwestern Mediterranean where the inputs of elements and chemicals are mainly controlled by atmospheric deposition. The chemical cycling of TM and POPs was studied for the first time in a holistic perspective, from the atmospheric input over exchange processes at the atmosphere-ocean interface, biological feedback, vertical transport, mineralisation and recycling to the final deposition on the marine sediments. Monthly sampling campaigns were carried out over a period of 2 years in order to study the water column distributions of dissolved and particulate TM and POPs. In addition, a mooring line with sediment traps allowed the bimonthly collection of sedimentary material. Sediment coring completes the sampling design. Trace-metals (Al, Ag, Cd, Co, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Zn) and POPs (PBDEs, PCBs and PFAs) were determined at a 2356 high resolution stations (DYFAMED site located between the French Riviera and Corsica) in order to explore their seasonal variation patterns and establish relationships between atmospheric inputs and the marine environment response. The DYFAMED site, the longest marine Mediterranean timeseries site, is sheltered from any fluvial inputs by the Ligurian current and therefore mainly influenced by atmospheric sources, including those of anthropogenic TM and POPs. Measurements of the aerosol content, wet and dry deposition at the Cap Ferrat reference site (in the French Riviera coastline), the oldest operational atmospheric sampling site in the Mediterranean region, give an estimation of atmospheric inputs to the Ligurian Sea. Focus was the definition of main sources, trends and evolution of TM and POPs. Seasonal variation of distributions, partitioning and fluxes of TM and POPs in the water column allow a better understanding of the impact of such atmospherically introduced trace elements and the role of the oligotrophic waters of the Northwestern Mediterranean and its ecosystems. Their cycling, biological interactions and atmospheric exchange processes were examined in relation with auxiliary parameters such as hydrological parameters, nutrients, oxygen and chloride. This work aims to establish a present state of the contamination (TM and POPs) of the open western Mediterranean and to provide pioneer data of environmentally dangerous species as methylated mercury and PBDEs.

Seasonality of methymercury distributions in relation with biological activity in an oceanic water column of the North-western Mediterranean

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We present here a time-series measurements of high-latitude vertical profiles of methylated mercury (MeHg) in surface waters of the North-Western Mediterranean Sea. MeHg concentrations in the surface waters during the stratification period (May–July) were higher than those at the downwelling waters, while the opposite trend was observed during the fall (October–November). The highest MeHg values were observed in the aphotic layer as a result of the activity of the microbial loop, recycling sinking organic matter. Atmospheric and biological inputs are the dominant pathways of MeHg to the marine system. This results from the interaction of the biological and chemical cycling of MeHg in the NW Mediterranean Sea. The MeHg inputs from the atmosphere to the sea bed were calculated from the atmospheric deposition of MeHg at the Cap Ferrat atmospheric sampling site.

Quantification of trace metal enrichments of Ligurian surface waters by atmospheric deposition

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Surface water samples were collected monthly at Cap Ferrat atmospheric sampling site (on the French Riviera coastline), the oldest operational atmospheric sampling site in the Mediterranean region, give an estimation of atmospheric inputs to the Ligurian Sea. Where Fe is the dissolved Fe content of a given TM, the enrichment factor (EF) is calculated as:

EF = (cFe - cFe0) / cFe0

where EF0 is the atmospheric ratio of Fe/Hg. The EF of Hg in the surface waters of the Ligurian Sea is 10-12 times higher than in the atmosphere.

Seasonal variations of trace elements in the water column of the Ligurian Sea, North-western Mediterranean

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Trace metal concentrations in the North-western Mediterranean and an atmospheric aerosol between 1986 and 2008: Seasonal patterns and trend trends

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Chronic and anthropogenic changes are always suspected to modulate the elemental composition and redox state of the surface waters of the Mediterranean Sea. The study of the temporal evolution of anthropogenic trace metals (Al, Ag, Cd, Co, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Zn) and Fe on a timescale of two decades from the North-Western Mediterranean case of Banyuls Cap Ferrat, during the four decades from 1986 and 2008. From seasonal averages (1986-2008) and decadal means (1986-1995), 1996-2005 and 2006-2008, the concentrations of Fe and Al were found to be significantly higher (50-90%) in the decadal means compared to the seasonal averages. Elemental concentrations of Cu, Cr, Mn, Ni, Pb and Zn were not significantly different between the seasonal and 20-year averages. Fe and Al are not significantly different in the seasonal averages of the last two decades, while Cr, Cu, Cd, Mn, Ni, Pb and Zn are significantly higher in the 20-year averages of the last two decades. The seasonal concentrations of anthropogenic TM decreased remarkably over the last two decades, while crustal trace metals did not show any evolution. The Fe/Al ratio is an important diagnostic of the deep marine reservoir. Some TMs (Fe, Hg, Pb, Zn) have a scavenged-like profile (35-130 pM) which suggests interactions with planktonic microorganisms (interactions with planktonic microorganisms) are discussed according to interactions with planktonic microorganisms. Cu (1.4 ± 2.0 µM) and Ni (0.9 ± 1.0 µM) have a characteristic which is consistent with their scavenged-like profile. Cr and Mn depict a scavenged-like profile (35-130 pM) which suggests interactions with planktonic microorganisms. Mn/Fe and Ni/Fe c/c ratios may reach values as high as several hundred per cent (Al, Cu, Ni). Biogeochemical cycling of these elements (Al, Cu, Ni, Cu, Cr, Mn, Fe, Hg, Pb, Zn) or may be less than 30% (Cd, Cr, Ni). High ratios of Fe/Al c/c can be explained by the quasi-complete sorption and removal of trace metals by plankton, which leads to surface-depleted profiles. Atmospheric and biological inputs are the dominant pathways of MeHg to the marine system. This results from the interaction of the biological and chemical cycling of MeHg in the NW Mediterranean Sea. The MeHg inputs from the atmosphere to the sea bed were calculated from the atmospheric deposition of MeHg at the Cap Ferrat atmospheric sampling site.

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