Chemical contamination of coastal Mediterranean waters, the Mytilos/Mytimed projects

Contamination chimique des eaux côtières méditerranéennes, les projets Mytilos/Mytimed

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Abstract

The MYTILOS and MYTIMED project were launched to draw up a preliminary report on coastal chemical contamination on a Western Mediterranean scale (continental coasts of the Balearic Islands, Sicily, Sardinia, Corsica and Maghreb) and a part of the Eastern basin (Southern Italian and Sicilian coasts, Greece), based on a standard methodology developed on the French Mediterranean coast by Ifremer and Rhone Mediterranean & Corsica water board since 1996. From 2004 to 2007, 174 mussel stations were installed and recovered 3 months later along the Mediterranean shores.

The analysis of 40 chemical substances has been carried out on mussel samples. The results show that the most highly impacted areas are urban and industrial centres and the mouth of major rivers. When going from the coast towards open sea a far higher dilution effect is observed for organic compounds than for heavy metals. For metals, levels measured offshore are generally found to be similar to those in natural shellfish populations living along the coast.

Résumé

Les projets MYTILOS et MYTIMED ont été initiés pour établir un état préliminaire de la contamination chimique des eaux côtières à l'échelle de la Méditerranée occidentale (côtes continentales européennes et du Maghreb, îles Baléares, Sicile, Sardaigne, Corse) et d'une partie de l'Est du bassin (du sud de l'Italie et la Sicile côtes, de la Grèce), sur la base d'une méthodologie standardisée développée sur la façade française par l'Ifremer et l'Agence de l'Eau Rhône Méditerranée et Corse depuis 1996. De 2004 à 2007, 174 stations de moules ont été installées sur les côtes méditerranéennes et récupérées 3 mois plus tard.

L'analyse d'une quarantaine de substances chimiques a été effectuée sur les échantillons de moules. Les résultats montrent que les sites les plus contaminés sont les zones urbaines, les centres industriels et l'embouchure des grands fleuves.

Quand on s'éloigne de la côte vers le large, un effet de dilution nettement plus important est observé pour les composés organiques (par rapport aux métaux lourds). Pour les métaux, les niveaux mesurés en mer sont généralement similaires à ceux trouvés dans les populations naturelles de coquillages vivant le long des côtes.

INTRODUCTION

Most monitoring programmes now include the use of biological indicators. This is based on the assumption that levels of trace contaminants accumulated in biological tissues represent the time and space integrated value of these contaminants in the surrounding waters. High concentrations resulting from bioaccumulation of many chemicals in bio-indicator organisms make the measurement of contaminant concentrations technically simpler. Variations of contaminant levels in tissues may reflect the variations in dissolved and particulate contaminant concentrations, although biological variability can also affect tissue concentrations.

In the Mediterranean Sea, the species *Mytilus galloprovincialis* is widespread, but in some locations natural populations are rare or absent. The transplantation method compensated for this scarcity. It also allows controlling the source, age, and stage of sexual maturity of the samples. However, implementing it on a large geographic scale introduces factors such as variations in physiochemical characteristics and food availability in the stations. Although the measured concentrations in the tissue are a function of bioavailable pollutant levels, the bioaccumulation factor depends on mussel growth in relation to the primary food production, or trophic capacity, of the environment. Comparison of raw data on tissue concentration between sectors of different trophic potential may be misleading. A biometric parameter representing growth must be used to correct initial data and to produce reliable comparison at a large spatial scale.

The Condition Index (CI) is an efficient indicator of physiological state and growth resulting from the environmental effect. The results acquired by the RINBIO network show robust condition index / contaminant concentration correlations in all geographical zones for certain contaminants. It is therefore possible to determine a correction model for these contaminant families and obtain a concentration, notwithstanding the environmental effect, which is representative of bioavailable contaminant concentrations in the environment. At a large spatial scale, this model enables the adjustment of results to get "standard individual" normalized data, and result comparison notwithstanding the physiochemical and trophic heterogeneity of the target zones.

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[1] ICRAM: Instituto Centrale per la Ricerca Scientifica e Tecnologica Applicata al Mare
[2] IEO: Instituto Español de Oceanografia
[3] PSTS: Parco Scientifico e Tecnologico della Sicilia

(Balearic Islands), CSIC[5] (Catalonia), the Agencia Catalana del Agua, INSTM[6] (Tunisia), ISMAL[7] (Algeria), INRH[8] and University of Agadir (Morocco), ANEM- Tourist autorithy of Magnesia, HCMR[9] (Greece), HIMR[10] (Syria), CNRS[11] (Lebanon). MYTILOS and MYTIMED are also backed by the PNUE/PAM - MEDPOL and the Rhone Mediterranean & Corsica water board.

Materials and methods

Transplantation

The species used is *Mytilus galloprovincialis*. The batch is made up of adult mussels 18 to 24 months old, measuring about 50 mm long, sorted twice according to the height of the shell through 19-mm mesh. The 3-kilogram samples are stored in conchylicultural pouches mounted on PVC tubing. Subsurface moorings include a mussel bag attached to a 30 kg weight. Mussels are maintained in open water with an 11-litre float. The stations are installed with an oceanographic vessel at various depths and distances from the coast. Globally speaking, depth is around 20 to 50 meters according to coastal configuration, and the bags are attached at a depth of 8-10 meters. The aim is to install each station in an equivalent continental input dilution volume to avoid it being under the direct influence of one contamination source and then get good station relative representativity.

Recovery

After 3 months, retrieval of the samples at sea is carried out using an oceanographic vessel which provides vital logistics support (diving logistics, sample processing, vial preparation), including a zodiac equipped with detection instruments (sweep sonar, vertical echo sounder) for station retrieval operations.

On site, the mussels are separated and rinsed with seawater. Mortality and height of the shell are recorded. At each station, the samples are pre-processed according to standardized procedures. The mussels are opened raw and the flesh is scraped out of the shell with a stainless steel scalpel. Shells are dried at 60 °C in the oven for 48 hours, then weighed. Flesh is weighed after freeze-drying. The ratio of dry flesh weight to dry shell weight (FW/SW) is used to determine a condition index (CI) for each sample.

Mytilos I (2004) sampled a coastline stretching from Cartagena (Spain) to Orbelleto (Italy). Mytilos II (2005) covered southern Italy and part of southern Spain, with sampling along the coast of the Balearic Islands, Sardinia and Sicily. Mytilos III (2006) covered Corsica, the southernmost coasts of Spain and the Maghreb coasts (Morocco, Algeria, Tunisia), Mytimed (2007) covered the southern part of Italy, Sicily and the Greek coast.

[4] IMEDEA: Instituto Mediterraneo de Estudios Avanzados
[5] CSIC: Consejo Superior de Investigaciones Científicas
[6] INSTM: Institut National des Sciences et Technologies de la Mer
[7] ISMAL: Institut National des Sciences de la Mer et de l'Aménagement du Littoral
[8] INRH: Institut National de Recherche Halieutique
[9] HCMR: Hellenic Center for Marine Research
[10] HIMR: High Institute for Marine Research
[11] CNRS: Conseil National de la Recherche Scientifique du Liban

Analysis

The following contaminants were analysed: Lead, Cadmium, Nickel Mercury,DDT+DDD+DDE, Hexachlorocyclohexane, Polychlorobiphenyles (PCBs), Polycyclical Aromatic Hydrocarbons (PAHs), non-ionic detergents such as nonylphenols (4-(para)-nonylphenol) and octylphenols (para-tert-octylphenol), Dioxins, Brominated diphenyl ethers. All of the above compounds were analysed in mussel flesh in each station, excepted dioxins, brominated diphenyl ethers and non-ionic detergents, which were measured at around one 1 in 5 stations.

RESULTS

A total of 174 stations were retrieved out of the 207 stations deployed (84 %).

Contaminants

The raw concentration results show that growth has a major impact on contamination level distribution, in particular with regards to heavy metals. Some trace metals (Cd, Hg, Ni) showed systematically higher levels in the most highly oligotrophic areas, which are correlated with the mussel condition index. Concentrations of the vast majority of PCB congeners were lower than the limits of detection set at the study outset. CB 153 and 138 were the most reliable markers and were present in all samples; their distribution is similar to that of the sum of the 10 analysed congeners. Regarding PAHs, out of the 16 analysed compounds, a large majority did not exceed the analytical limit of detection. Compound distribution between stations was widely heterogeneous in comparison, for example, to that of PCBs. α HCH and γ HCH did not in any case exceed the limit of detection in coastal zones. Lastly, metabolites of DDT were the most commonly-found organic contaminants. Analyses of brominated diphenyl ethers and non-ionic detergents all showed results below the analytical limit of detection.

Models

For each contaminant, adjustment parameters have been calculated on the basis of the raw data collected from theses campaigns.

Models were significant (p-values < 0.05) for most contaminants, excepted for PAHs. The highest growth effect was observed for cadmium, mercury and nickel, with a variation of more than 50 % in results explained by sample growth.

Data adjustment

The value of the reference condition index is 0.11, which corresponds to the mean of the condition indices obtained from each sample. Raw data was adjusted using this value and the model parameters computed for every contaminant. However, data on PAH was not processed according to this method. For every contaminant, descriptive statistics were calculated and presented in table 1 among regional sub basins.

At the scale of the study, the distribution of lead adjusted data was relatively homogenous, with a median level of 1.49 mg/kg. However, two sites were

pinpointed as being particularly impacted by lead: the Portoscuso industrial site (South Western sub-basin), with a maximum of 8.25 mg/kg and the zone spanning Portman to El Portus (Alboran sub-basin) from 5.3 to 6.25 mg/kg, which was home to a thriving mining industry with the dumping of 50·106 tons of waste-mining resulting from the intensive extractive activities carried out during the 1960-1990 period. The maximum levels observed in the North Western sub-basin are in the area of Barcelona (2.79 mg/ kg), in the Tyrrhenian sub-basin in Porto Ferrario at Elba island (3.05 mg/ kg) and in the Ionian sub-basin in Corinthos (2,69 mg/kg). For this heavy metal we can observe that the background in the Eastern basin is more elevated than in the Western basin.

Adjusted levels of cadmium were globally homogenous throughout stations, with an average of 1.32 mg /kg and a median of 1.32 mg /kg. A few stations showed relative peaks of around 2 mg/kg : Filicudi and Ustica stations in Tyrrhenian sub-basin (Sicily), Aguilas and Adra in Spain (Alboran sub-basin) and 4 mg/kg in Athens (Aegean sub basin). Nevertheless the background levels are similar in all the sub-basins.

Several sites were found to be impacted by mercury (Fig. 1): first and foremost the Portoscuso site in Sardinia (South Western sub-basin), with a maximum level of 0.31 mg/kg, witnessing significant contamination generated by a large industrial complex. To a slightly lesser degree, high levels are recorded in the South Western sub-basin in Skida (0.19 mg /kg), in the Tyrrhenian sub-basin especially in Palermo (0.22 mg /kg) and in the Ionian sub-basin in Augusta (0.20 mg/kg). For this metal we cannot observe differences between the Eastern basin and the Western basin for background levels.

Figure 1. Mercury in mussels (∑PCBi ng.g^{-1} dry weight)

Average adjusted concentrations of nickel were around 1.3 mg / kg, Extreme values were found in some sampling sites in the South Western sub basin especially in Tabarka (3.18 mg/kg), Oued Zhor (2.89 mg /kg), Oran (2.47 mg/kg),

Nador (2.72 mg/kg), in the south of Spain in Fuengirola (2.44 mg/kg) and in the south of Aegean sea in Rhodos (4 mg/kg). For this metal the background in more elevated in the eastern part of the basin especially in the Aegean Sea.

The median value of the sum of DDTs compounds was 2.52 µg/kg at the scale of the study. Significant peaks were recorded in the North Western and Tyrrhenian sub-basin especially in front of Marseille (15.47 µg/ kg), Barcelone (15.17 µg/ kg) and Napoli (15.34 µg/ kg). In the South Western sub-basin Algiers also showed a high level (10.23 µg/ kg). The level recorded at the Algiers station was equivalent to the overall levels recorded at stations off the coast of the following rivers and streams: Ebro, Rhône and, to a lesser degree, Tet, Aude, Herault (North Western sub-basin) and Tevere (Tyrrhenian sub-basin). In the Eastern part of the basin the higher levels are observed in Thessaloniki (7 µg/ kg). For this contaminant's family we can observe that the background is more elevated in the North Western and Tyrrhenian sub-basins.

Regarding the sum of the 10 congeners of PCBs (Fig. 2) and the CB153, the distribution shows a similar profile. The median value of the sum of PCBs compounds was 7.76 µg/kg. The results show some sites are significantly contaminated by PCBs : in the North Western sub basin (Barcelona [63.87 µg / kg], Marseille [103.52 µg / kg]) ; in the Tyrrhenian sea (Naples [91.48 µg / kg]) and on South Western coast (Algiers [51.13 µg / kg]). If there is a characteristic presence of PCBs in the vicinity of major urban centres, high values are also observed in the Tyrrhenian Sea at La Maddalena (58.49 µg / kg), at a station located close to a major naval base. To a lesser degree, we can also pinpoint inputs by the Ebro (20.37 µg / kg) and Rhône rivers (37.80 µg / kg). In comparison the higher concentration observed in the Eastern Mediterranean was 11.25 µg/kg in Thessaloniki. If the background levels are similar at the scale of this study, the maximum levels are always observed in the Western Mediterranean.

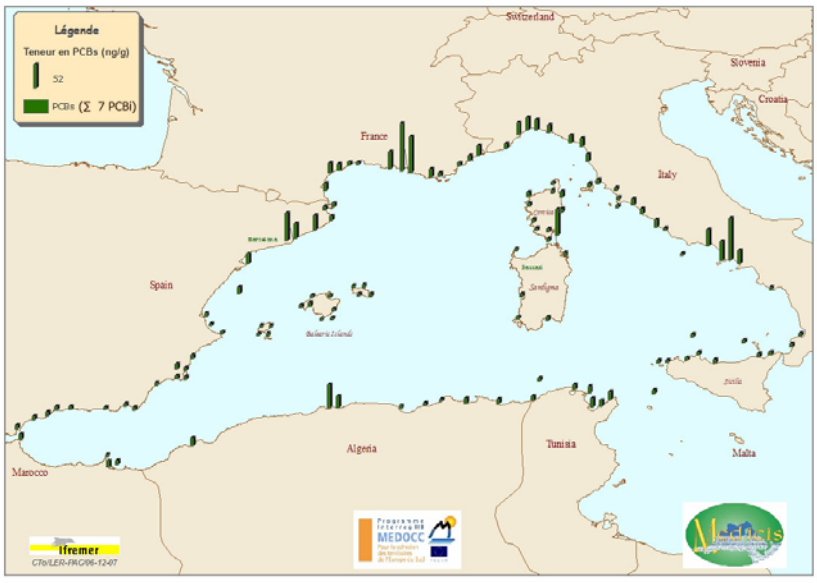

Figure 2. PCB in mussels (∑PCBi ng.g^{-1} dry weight)

Results related to the sum of the 16 analysed molecules for PAH are expressed in raw values. Wide data heterogeneity was observed at the scale of the study with a median value of 39.7 µg/kg. Two peaks have been identified in the North Western and Tyrrhenian sub-basins close to Marseille (105.5 µg/kg) and Piombino in Italy (80.8 µg/kg). Both are coastal cities associated with a large industrial complex. As for PCBs, the levels for these compounds are globally lower in the Eastern Mediterranean.

For dioxins, the median value is around 0.7 ng/kg (TEQ: Toxic Equivalent Quantity). One peak recorded in the Marseille area reveals the existence of significant inputs of these compounds (2.66 ng/kg). Moreover, it confirms the peak measured for PCBs, which belongs to the same organic halogenous compound family. On the project scale, the distribution observed for dioxins is similar to the one of PCBs, with highest values at Barcelone, La Maddalena, Napoli and Algiers.

DISCUSSION

The Mytilos-Mytimed projects confirmed the operational viability of the RINBIO methodology. The project's logistics, mooring structures and deployment / retrieval techniques enabled cost minimization, plus a highly satisfactory retrieval rate taking into account the shape and diversity of the studied coasts.

The condition index range is indicative of the trophic heterogeneity of the Mediterranean coastlines. Overall, the waters are richer in the North Western sub-basin, due to the high loads of nutrients brought by the Rhône (Minas, 1989) and Ebro rivers, and in the Alboran sub-basin. The condition index spread also provides some clues as to the levels of chemical contamination (excepted for PAH), especially in the case of trace metals. Regarding cadmium concentration, the raw values measured in Balearic Islands were two to three times higher than those measured at the mouth of the Ebro river and along the Spanish coast.

In a more general way, the significant connection between the condition index and levels of contaminants in mussel tissue allows to adjust the findings and get comparable data, to identify background levels in the different sub-basin and then to point out contaminated areas. The most highly-impacted zones were mainly located in front of urban and industrial centres and near the outlets of major rivers.

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