HEAVY METAL CONCENTRATIONS IN THE SEA SURFACE MICROLAYER AND ASSOCIATED NEUSTON IN NW MEDITERRANEAN WATERS

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Abstract

Analyses of Barcelona and Banyuls-sur-mer coastal waters indicated that heavy metal concentrations were generally higher in the surface microlayer (SML) than in the underlying waters. The highest concentrations of many metals in the SML were noted in one sample from Barcelona that may have been influenced by the presence of oil slicks. The relatively elevated levels of metals such as Zn, Pb and Cu in neuston from Barcelona are likely a reflection of the high SML enrichment factors of these metals (Zn, 12X; Pb, 21X; Cu, 35X).

Key words: metals, surface microlayer, neuston

Introduction

The sea surface microlayer (SML) plays a key role in material transfers between the atmosphere and ocean (1). Furthermore, the SML (i.e. top few hundred microns) is often enriched in trace metals relative to the underlying waters, and therefore could lead to metal enrichments in biota living in this layer (2); however, a general understanding of the impact of anthropogenic activities on the sea surface ecosystem is far from clear. For the Mediterranean, very little information is available on trace element chemistry of the SML and even fewer data exist on trace element concentrations in the neustonic community inhabiting the SML. Therefore, within the EU-sponsored AIRWIN project, selected heavy metals were measured in the SML, subsurface waters (SSW) and associated neuston from two contrasting sites that were considered as relatively "polluted" (Barcelona) and "clean" (Banyuls sur Mer).

Material and Methods

Sampling

SML samples were collected from the upper 40-50 µm using glass plate and ultra clean techniques (2), and stored in acid-cleaned 250 ml Teflon bottles. For collecting SSW, bottles were capped, immersed ~0.5 m below the surface, opened and re-capped under water.

Neuston was collected by towing a pre-cleaned neuston net 15 m behind an inflatable rubber boat. Samples were carefully examined, subsequently cleaned of detritus, and freeze-dried.

Analyses

Water samples were diluted 20X with milli-Q water and the dilutions analysed directly for trace metals by high resolution ICP-MS using a microconcentric nebulizer and a standard double-pass condensing spray chamber (3). In addition to direct analysis, a modified preconcentration method employing hydrated Chelex-100 resins was also used (4). CASS-4 seawater reference material was analysed along with all samples as a check on the analytical accuracy.

Weighed neuston was placed in Teflon vessels and digested in concentrated HNO_3 - HF for ~40 minutes at 200 °C. The samples were brought to 50 mL volume with Milli-Q water and analysed by ICP-MS. Standard reference materials were also analysed with each run.

Results and discussion

In general, most metal concentrations in the SSW were quite uniform at both sites (Table 1) except for one of the samples taken off Barcelona that contained higher concentrations of nearly all the metals, possibly a reflection of the greater suspended particulate load observed that day. Metal concentrations in the SML were generally higher than in the SSW at both locations. Little variability was noted between concentrations in the SML samples from Banyuls except perhaps for Pb (4X). At Barcelona the variability among SML concentrations was much greater due to the significantly higher metal concentrations in one of the samples, possibly due to the presence of surface oil slicks noted during that time. If that sample is not considered, then metal concentrations in the SML from both locations are quite similar. At Banyuls metal enrichments were not marked except in the case of Pb and to some degree Cu. Likewise off Barcelona, some metals showed little enrichment, e.g. Cr, Ni and Cd. In contrast, the single SML sample associated with the slicks displayed the highest enrichment factors, particularly for Cu, Pb and Zn (Table 1).

Information on metal concentrations in the Mediterranean SML is extremely limited, therefore comparisons with other areas in the region are difficult to make. The only published data are derived from two SML samples collected with a nylon screen between mainland France and Corsica in 1983 (5). SML values were 4800 ng l^{-1} Cd and 2600 ng l^{-1} Pb and, compared with SSW from 10 m depth (87 and 140 ng l^{-1} of Cd and Pb), resulted in corresponding EFs of 55 and 19, respectively. These SML concentrations were considerably higher than those we measured except for Pb (4810 ng l^{-1}) in the single enriched sample from Barcelona.

Table 1. Trace element concentrations* (ng l^{-1}) in the surface microlayer (SML) and subsurface waters (SSW), resulting SML enrichment factors (EF), and mean trace element concentrations in neuston (µg g^{-1} dry) in the northwestern Mediterranean.**

	Cr	Co	Ni	Cu	Zn	Ag	Cd	Pb
SML								
Barcelona	26-160	20-100	450-730	525-4020	1810-13700	1.3-1.7	15-59	719-4810
Banyuls-sur-m	17-21	30-38	290-430	590-2060	1410-3400	1.1-2.8	17-35	401-1570
SSW								
Barcelona	23-32	9-25	230-610	116-273	907-1710	1.1-2.0	16-19	84-272
Banyuls-sur-m	17-34	19-20	250-300	198-384	870-3920	0.9-1.6	15-47	50-255
EF								
Barcelona	0.9-5.0	1.4-9.0	1.2-3.1	2.3-35	1.7-12	0.65-1.5	0.81-3.7	2.6-21
Banyuls-sur-m	0.5-1.2	1.2-2.0	1.1-1.5	1.5-6.5	0.65-2.3	0.73-1.8	0.36-2.3	1.6-19
Neuston								
Barcelona	31.9	2.1	20	110	494	0.23	3.8	117
Banyuls-sur-m	14.3	2.4	11	20.7	192	0.83	0.48	25

* Range of 3 samples taken over 3 days at Barcelona and 2 days at Banyuls.

** Average of 2 samples taken at Barcelona and 4 samples at Banyuls using a 90 µm mesh net.

Following the same trend noted for the SML, neuston sampled off Barcelona contained higher mean concentrations of Cr, Ni, Cu, Zn, Cd and Pb than those from Banyuls (Table 1). Although simultaneous sampling the subsurface plankton was not done, some insight into possible metal enrichment in neuston can be gained by comparisons with previously determined metal concentrations in subsurface microplankton from this region (6). Such comparisons suggest that neuston is enriched in Cr, Co, Ni and Pb whereas no clear trends in enrichment were suggested for Cu, Zn, Ag and Cd. Although not definitively tested here, it would appear there is a definite linkage between the metal enrichment in the SML and the high levels measured in neuston associated with it.

References

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