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The Role of Sedimentary Organic Carbon and Nitrogen in the Distribution of Mercury in the Gulf of Trieste (Northern Adriatic Sea)

Nives Ogrinc[1], Milena Horvat[1], Stefano Covelli[2], Vesna Fajon[1] and Jadran Faganeli*[3]

[1]*Department of Environmental Sciences, "J Stefan" Institute, Jamova 39, 1000 Ljubljana, Slovenia*

[2]*Department of Geoscience, University of Trieste, Via E. Weiss 2, 34127 Trieste, Italy*

[3]*Marine Biological Station, National Institute of Biology, Fornace 41, 6330 Piran, Slovenia*

Abstract

Biogeochemical processes involving mercury compounds in aquatic environments are of great importance especially in areas where mercury inputs are particularly high, as in the case in the Gulf of Trieste (northern Adriatic Sea). In this study, stable isotope data were used in order to determine the role of sedimentary organic carbon and total nitrogen in the distribution of Hg species. The results show that the major source of inorganic mercury is the river Isonzo, from which mercury is transported into the Gulf, and adsorbed onto particles, while the major source of methylmercury is the bottom sediment of the Gulf itself. Terrigenous nitrogen seems to be involved in the transformation processes of methylmercury in sediments.

Keywords: Mercury; Carbon; Nitrogen; Sediments; Coastal waters; Northern Adriatic Sea

Introduction

During the last two decades, the global biogeochemical cycles of many elements have been investigated in considerable detail. Much effort has been invested into the mercury (Hg) cycle because of the toxicity of methylmercury (MeHg), the accumulation of MeHg in biota and its biomagnification in the aquatic food chain [1-3]. Hg toxicity often poses a serious threat to wildlife and the human population. The interest in this cycle and others, like those of carbon and nitrogen, has been heightened by problems associated with global, regional and local environmental changes. In addition, different element cycles are often interconnected requiring a more holistic research approach to fully understand the underlying mechanistic processes.

It is well known that the Gulf of Trieste is one of the most Hg-contaminated areas in the Mediterranean Sea [4] and worldwide [5], and is therefore suitable for studying the processes affecting the Hg cycle in the coastal marine environment. The Gulf is characterized by high Hg inputs from the river Isonzo [6] which carries the waste cinnabar deposits of the Idrija mercury mine [7]. Nearly twenty years after the final closure of the mine (1995), the Hg levels in seafood still exceed the value of 0.5 mg/kg, which is considered the maximum permissible level according to WHO criteria [8]. Estimates of the Hg balance in the Gulf of Trieste have shown that the annual input through the Isonzo discharge is about one and a half tons [9]. This area is subjected to summer water temperature stratification and hypoxic conditions in the bottom layer [10]. Such conditions generally favour the microbial transformation of inorganic Hg to more toxic MeHg, leading to elevated Hg values in marine organisms [11].

In the present study, stable isotope data of sedimentary organic carbon and total nitrogen were used in order to determine the association of sedimentary Hg species introduced through the Isonzo River mouth into the central part of the Gulf of Trieste.

Methods

Surface (0-1 cm) sediment samples from the Gulf of Trieste, collected using a gravity core sampler, were freeze-dried and ground to a fine powder for analysis. At two locations, the analyses were also performed in different sediment fractions (>50, 50-16, 16-2, <2 μm) separated by wet-sieving [12].

Total Hg and Methylmercury (MeHg) analyses

Total Hg in sediment was analyzed by CV AAS after acid digestion [13]. MeHg in sediments was determined by solvent extraction, aqueous phase ethylation, gas chromatographic separation, pyrolysis and CV AFS detection [14]. All analytical methods were regularly validated and performed within a quality control system.

Stable isotope analysis

Isotopic analysis of organic carbon (OC) in sediment was determined after treatment with 3M HCl, while for nitrogen (TN), bulk powdered samples were analysed. $\delta^{13}C$ and $\delta^{15}N$ were determined after Dumas combustion of samples at 1800°C using a Europa 20-20 continuous-flow stable isotope analyser with ANCA-SL preparation module. Following the standard procedure, the isotopic ratios are expressed in δ-notation in parts per mil (%):

$$\delta R = \left[\frac{(R_{sample} - R_{s\,tan\,dard})}{R_{s\,tan\,dard}} \right] x\ 1000$$

For carbon, R is $^{13}C/^{12}C$ and the standard is the V-PDB carbonate, while for nitrogen R is $^{15}N/^{14}N$ and the standard is atmospheric (air) nitrogen. The measurement uncertainties of the $\delta^{13}C$ the $\delta^{15}N$ values were ±0.2% and ±0.3%, respectively.

Analyses of total and organic C (OC) and total N (TN)

In sediment samples were performed using a Carlo Erba elemental

***Corresponding author:** Jadran Faganeli, Marine Biological Station, National Institute of Biology, Fornace 41, 6330 Piran, Slovenia, Tel: 386-05-9232911; E-mail: faganeli@mbss.org

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analyzer (mod. EA 1108) after acidification of the samples with 1M HCl [15]. The precision of measurements was ±3%.

Results and Discussion

The $\delta^{13}C$ and $\delta^{15}N$ values were used to study the origin of sedimentary organic matter in the Gulf of Trieste. Using the binary mixing equation for $\delta^{13}C$ and $\delta^{15}N$ values of terrigenous ($\delta^{13}C_t$= -26%, $\delta^{15}N_t$= +1.7%) and marine organic matter ($\delta^{13}C_m$= -21%, $\delta^{15}N_m$= +7.3% - average value determined in phytoplankton) [16,17] in the form

$$\delta R = F_m \delta R_m + F_t \delta R_t$$

$$F_m + F_t = 1$$

The percentage of the terrigenous fraction (F_t) of OC and TN in surficial sediments was established (Table 1). Sediments at the mouth of the river Isonzo were calculated to contain about 63% of OC and 84% of terrigenous nitrogen material, while in the central part of the Gulf of Trieste the sediments are assumed to contain less terrigenous material (8% of OC and 28% of TN). The deposition of almost entirely marine (phytoplanktonic and microphytobenthic) organic matter is restricted to a rather narrow strip in the central part of the Gulf located between two areas affected by increasing contribution of terrigenous organic matter [17] (Figure 1).

Results for total Hg in surface sediments show that the highest concentrations are found at the river mouth ranging from 23.3 µg/g up to 40 µg/g [12]. The concentration gradient from the river mouth towards the SE near-shore area of the Gulf shows over a hundredfold decrease of Hg, reflecting the decline of riverine particulate matter sedimentation rates with distance from the river mouth. The ratio of MeHg to total Hg in sediments increases with distance from the river mouth, and is in positive correlation with the percentage of the clayey fraction [18].

As is shown in (Figure 2a), total Hg is in significant correlation with the percentage of terrigenous organic carbon, confirming a strong association with riverine born particulate organic matter [1]. On the other hand, no correlation was found for MeHg vs. terrigenous organic C, however a positive correlation was observed between MeHg and organic C of marine origin (Figure 2b). This confirms our previous conclusion that the river input is a minor source of MeHg to the Gulf of Trieste [7,9], and that the MeHg is formed in the gulf sediments [18]. Interestingly, the correlation between terrigenous N and MeHg was found to be significant (Figure 2b), while no correlation was observed for total Hg vs. terrigenous N. At the present time, we are not in a position to explain this finding; however, the terrigenous N seems to be involved in the transformation processes of mercury in marine sediment. Further studies will address this issue in more detail.

	$\delta^{13}C$		$\delta^{15}N$	
Sample location	**F_t**	**% (Weight) OC**	**F_t**	**% (Weight) TN**
MA	0	0	0.44	0.05
C3	0.19	0.25	0.28	0.03
K0	0.09	0.11	0.43	0.05
F0	0.31	0.25	0.59	0.04
F1	0.09	0.04	-	-
F2	0.14	0.01	0.29	0.02
E3	0.61	0.65	-	-
D6	0.64	0.52	0.81	0.09
CZ	0.10	0.13	.54	0.09
35	0.11	0.13	0.28	0.03
A4	0.16	0.16	0.46	0.03
OL3	0.69	0.71	0.72	0.05
AA1	0.07	0.09	0.46	0.08
A20	0.39	0.42	0.40	0.01
SIS	0.23	0.25	0.44	0.02
A30	0.19	0.03	0.35	0.02
A28	0.14	0.19	0.59	0.02
A3	-	-	0.37	0.02

Table 1: $\delta^{13}C_{org.}$ and $\delta^{15}N$ values and terrigenous fraction (F_t) of organic carbon (OC) and total nitrogen (TN) in surface sediments of the Gulf of Trieste.

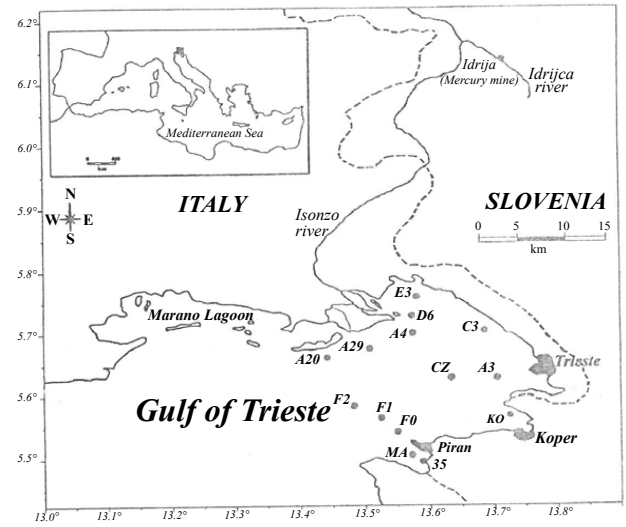

Figure 1: Location of sampling sites in the Gulf of Trieste (northern Adriatic Sea) with Idrija mercury mine and river Isonzo.

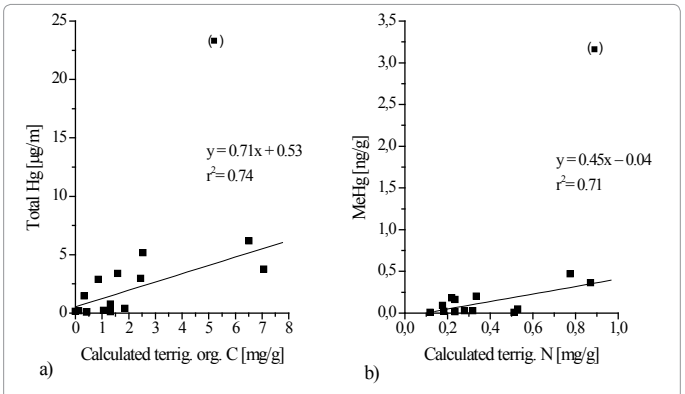

Figure 2: a) Correlation between total Hg and calculated terrigenous organic carbon and b) correlation between MeHg and calculated terrigenous nitrogen in the surficial sediment of the Gulf of Trieste. In the bracket is the point at the Isonzo River mouth.

Analyses of different sediment fractions showed that larger particles (>50 µm), characterized by low organic C and total N contents and low $\delta^{13}C$ values, are deposited at the mouth of the river Isonzo. In this fraction, the total Hg concentrations are the highest. Therefore, the large-size fraction play an important role in mercury transport probably mostly composed of cinnabar particles [19] originating from the Idrija mining district. Particles deposited in the central part of the Gulf of Trieste contain higher OC and TN values and higher $\delta^{13}C_{org.}$ values. This indicates that a minor part of riverine organic matter, associated with silt (16-2 µm), is transported throughout the Gulf. This fraction

can be used as a tracer of terrigenous (riverine) organic deposition since the low C and N isotopic compositions in this fraction indicate the presence of more terrigenous organic material. Corroborating our previous studies, a negative correlation between MeHg vs.% of sand and a positive correlation with the% of clay (<2 μm) was observed [12].

Conclusion

In conclusion, a combination of stable isotope data of sedimentary organic carbon and nitrogen with total Hg data suggests a strong association of total Hg with terrigenous organic C while MeHg is positively correlated with organic C of marine origin confirming the *in situ* origin of MeHg from the bottom sediment. Further studies are in progress in order to understand the role of terrigenous nitrogen in the transformation processes of MeHg in coastal marine sediments.

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