DISSOLVED ORGANIC MATTER IN THE WATERS OF THE GULF OF TRIESTE (NORTHERN ADRIATIC)

J. FAGANELI° and G. HERNDL°

Marine Research Centre, Piran (Yugoslavia)
Institute for Zoology, University of Vienna, Vienna (Austria)

Dissolved organic compounds play an important role in the cycling of matter and energy in the marine environment. The dissolved organic matter (DOM) pool of the coastal marine environment can be divided into three major pools: (1) an autochtonous pool derived mainly from in situ biological production, (2) an allochtonous pool derived mainly from fresh water drainage and (3) an anthropogenic pool derived from human activities. DOM represents the largest pool of organic matter in the sea. DOM in sea water is poorly chemically characterised. Only about 10 per cent of the total DOM present in the sea has so far been assigned to definite compounds - amino acids, urea, carbohydrates, lipids etc. The remaining 90 per cent is still chemically undetermined, but it is assumed that it consists of complex macromolecular compounds (humates, complexes, chelates).

The purpose of this contribution is to present recent results on DOM composition in terms of organic carbon (DOC), nitrogen (DON) and phosphorus (DOP) contents, and of urea and dissolved free amino acids (DFAA) in the waters of the Gulf of Trieste in relation to some chemical and biological processes. Special attention was paid to seasonal and vertical differences in relation to phyto- and bacterioplankton densities.

Distribution of DOC contents for the whole sea water column showed distinct seasona variations, ranging from 125-154 μ mol C l $^{-1}$ during the late autumn and winter to up to 500 $\mu mol \mbox{Cl}^{-1}$ during the summer. Concentrations of DON also showed seasonal variations. Lower concentrations, averaged over the whole sea water column, were found in the late summer with maximal values of approx. 58.2 μ mol DON 1⁻¹. The seasonal dynamics are similar to that found during the 3-year long study of DON variations at the sampling points K-1 and MA. Maximum DON values were regularly observed in the bottom layers and supernatant waters. The distribution pattern of DOP differed somewhat trom that of DOC and DON. The DOP concentrations decreased from summer, ranging from $5.2-9.2 \,\mu$ mol DOP l⁻¹, towards the winter period, with a minimum value of about 0.5 μ mol DOP 1⁻¹. Vertical distribution showed little depth variation with slightly higher DOP concentrations in the bottom water layers and supernatant waters. Urea contents varied at sampling points K-1 and MA in the range between 0 - 9.16 μ mol 1⁻¹, with a mean value for the whole sea water column of 0.60 $\mu mol~l^{-1}$. The percentage of DON analysed by the UV combustion technique, bonded in urea, averaged about 4.5 %, while that of DOC was about 0.2 %. Total DFAA concentrations, analysed as OPA reactive substances, ranged between 0.01 and 8.25 $_{\rm J}$ umol l⁻¹, with a mean value for the whole water column of 2.10 µmol l⁻¹. The percentages of DON and DOC bonded in DFAA averaged about 7.8 % and 2.1 %. respectively. Analyses of individual DFAA, analysed at sampling point MA, showed high concentrations in the surface layer, in parallel with high inorganic nitrogen centent and lower salinity, originating from fresh water inflows. The dominant DFAA were Ser, Glu and Ala throughout the sea water column. Considerably higher basic DFAA content was found above the pycnocline. Deeper layers (5, 10, 15 m) were characterised by a higher basic amino acid content with higher Lys and/or Orn contents.

Our results indicate the spatial uniformity of DOM content in the waters of the Gulf of Trieste, despite pronounced anthropogenic influences on some near-shore areas in the Gulf, i.e. the Bay of Koper. From the present study it appears that intense DOM variations are principally biologically controlled, probably through phytoplankton decomposition and phytobenthos excretion and decomposition. The significant relationship between DON and bacterial biomass suggested that DON has an dominant role as the growth-limiting source for bacterioplankton in the Gulf. Our results also indicate the sea water bottom layer and sediment-water interface as the site of the most intense DOM microbial transformation.

THREE ITALIAN HOT SPRINGS AS POSSIBLE MERCURY SOURCES FOR ATMOSPHERE AND SEAWATER

Romano FERRARA and Biancaelena MASERTI

CNR, Istituto di Biofisica, Via S. Lorenzo 26, Pisa (Italia)

INTRODUCTION

The exchange processes at the air/sea interface between atmospheric mercury (particulate and gaseous forms) and surface sea layer represent one of the most important links in the Biogeochemical cycling of the metal in the aquatic environment (1). In fact, gases and aerosol of natural and anthropogenic origins are injected into the marine environment often in such amounts as to constitute one of the major sources of the metal (2).

In this context, measurements of mercury levels in the atmosphere of three particular mediterranean zones characterized by the presence of hot vapour springs were carried out. The areas studied are located in the Central and Southern parts of Italy and differ from each other for these mineralogical features: Mt. Amiata is rich in cinnabar deposits, Larderello originates from sedimentary rocks, and Pozzuoli is characterized by the volcanic nature of the soil.

EXPERIMENTAL

Separation of gaseous mercury from the aerosol was achieved by pre-treated Sartorius membrane filters. Air was sucked for 2 hours at a constant flow rate of 1.5 1/min by means of a membrane pump, and gaseous mercury was collected on gold absorbers. Collection of particulate matter in air was performed by filtration of 6 - 10 m³ of sample. Filters were digested with 3.4 ml of a mixture of $H_2SO_{\rm h}/$ HNO₃ H₂SO₄/HNO₃/HCl (2:1:0.⁴) at 20 C for 10 hours and then photo-oxidized by a U.V. immersion lamp for 15 min. The determination of the gaseous mercury and of the metal associated to the aerosol was performed by Atomic Fluorescence Spectroscopy as reported elsewhere (3).

RESULTS

In fig. 1 the studied areas are reported. A common characteristic of these areas is the presence of hot vapour springs spurting from the earth. These steam jets, because of their elevated temperature, could transport a large amount of

mercury, in both gaseous and particulate phase, from the subsoil to the atmosphere. Vapour springs at Larderello and Mt. Amiata are exploited for geothermal hydroelectric power, while those at Pozzuoli are comparable rather to fumarole and are not useful for practical application.

In tab.1 the levels of gaseous mercury are reported. High values of the metal asured near the individual point sources; however, these levels decrease with distance from the springs, and the background concentration of the area is rapidly reached.

Concentration values of atmosoheric mercury in the mineralized region of Mt. Amiata are about three times larger than those found in other mediterranean rural areas (3).



Hg air

gaseous form

15

18.2

6.9

Location

1 Mt. Amiata

2 Larderello

Tab.1 Mercury concentra-

tion(ng/m3) of the gaseous form in the air of

the examined areas.

3 Pozzuoli

Mt. Amiata: this is an unexpected finding on account of the completely different nature of the soil. Mercury concentration in the air of Pozzuoli is a little higher than the background values for rural areas. The concentration values measured in the three areas are, however, much higher than those observed over the open sea (~ 2 ng/m³). This fact clearly indicates that the sources of atmospheric mercury are mainly located over the land and that the aerial transport of the metal from the continent to the sea is an important pathway for the enrichment of the surface sea layer of the marine environment.

Values from Larderello are comparable with those of

Active and passive scavenging by suspended particles and the subsequent settling is probably the most important mechanism for the transfer of mercury from the atmosphere to the deeper part of the sea. In fact, our recent observation (4) indicate that for mercury the scavenging efficiency of the gas phase by rain is much smaller than that of the aerosol phase.

Although volcanic activity is the major natural source of suspended particles it is also true that in fumarole area of Pozzuoli high levels were measured (0.37 ng/m^3) . Results of direct measurements of dry and wet deposition in the three areas are not, at the moment, satisfactory because of the inherent sampling difficulties and the

strong dependence on meteorological conditions. At the present state of our research, additional observations seem necessary to establish the magnitude of the atmospherically - transported mercury from this type of sources to the sea.

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