

## Evaluating the influence of river discharge on marine benthic ecosystems using benthic foraminifera and lithology as the main tools

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### Introduction

River discharge has a significant impact on marine environment through its effect on the salt balance of the thermohaline structure and convection circulation of the water masses. Being enriched in the various organic and inorganic compounds, river flow is actively involved in biological processes and sedimentation, affecting the equilibrium state of the benthic ecosystems. Spatial distribution of river flow in the marine environment depends on meteorological and hydrological conditions that are characterized by inter-annual variability and varying proximity to the source. Coastal areas located in the confluence of major rivers experience the strongest impact of freshwater discharge. The northwestern shelf of the Black Sea—where the second largest river in Europe, the Danube, discharges annually 190.7 knf and 51.7 million tonnes of liquid and solid waste, respectively (Bondar et al., 1991; Panin, 1996), is a good example of such areas. Tracing the spatial distribution of river water into the sea and assessing its impact on benthic ecosystems have important theoretical and practical significance, both for understanding the causes affecting their balance, and for the development of methods and approaches to maintain their stability. Therefore, the choice of a reliable group of organisms as indicators of river discharge into the sea has primary significance. Such organisms should be benthic, small in size, and abundant (for population statistics), have a short life cycle, and be well preserved after death.

Benthic foraminifera perfectly fit these requirements. They play a significant role in global biogeochemical cycles of inorganic and organic compounds, making them one of the most important animal groups on earth. They are ubiquitous in marine environments. Their tremendous taxonomic diversity gives them the potential for diverse biological responses to various pollutants, which in turn adds to their potential as an index species for monitoring pollution from diverse sources. Their tests are readily preserved and can record evidence of environmental stresses through time, thus providing historical baseline data even in the absence of background studies. They are small and abundant compared to other larger hard-shelled taxa (such as mollusks, which are often used for pollution monitoring), and this makes them particularly easy to recover in statistically significant numbers. They have very short reproductive cycles (six months to one year) and rapid growth making their community structure particularly responsive to environmental change. They often show species-specific responses to ecological conditions. They have biological defense mechanisms which protect them from unfavorable environmental factors, thus providing detectable biological evidence of the pollution effect. All these characteristics make them powerful tools for continuous *in situ*, biological monitoring of marine environments (Yanko et al., 1999).

This paper focuses on tracing the Danube River discharge into the Black Sea and its influence on bottom ecosystems using complex analysis of benthic foraminifera and lithological properties of the

sediments as the main tool. The study was conducted recently within the framework of the international project BS-ERA.NET 076 “Water Pollution Prevention Options for Coastal Zones and Tourist Areas: Application to the Danube Delta Front Area,” WAPCOAST (2010–2012).

### Study area

The study area includes the southern (Romanian) part of the northwestern corner of the Black Sea located between the Danube delta and Cape Kaliakra (Fig. 1).



Figure 1. Study area and location of sampling stations.

The study area includes the seaside (water depth >5 m), submerged part of the delta (5-25 m), prodelta located on the inner and partially outer shelf (25-50 m), and the outer shelf.

The seaside of the Danube Delta is located parallel to the shore, has an 8-10 km width, and is characterized by a strong mixture of marine and fresh water. The width of the seaside varies significantly depending on the amount of Danube solid runoff being closer to the shore or moving away from it. The distribution of sedimentary material here is under the strong influence of longshore currents that form a series of bars and spits in the wave-cut zone.

The seabed of the submerged part of the delta has a relatively steep slope. The relief is formed mainly by the deposition-removal processes of sediment runoff. Despite the fact that the Danube discharges annually into the Black Sea 25-35 million tons of solid material, the bulk of it is carried away by longshore currents to the south, being exposed to erosion south of the Sulina mouth. Therefore, the sedimentation rate here is low and does not exceed 5-10 cm/1000 years (Panin and Jipa, 2002).

The prodelta is characterized by deposition of sedimentary material. Due to the weak impact of wave processes and active accumulation of sediments, the delta grows fast. There is a zone of geochemical barrier at the boundary between river and sea water. In this zone, an intensive abiogenic flocculation develops leading to the formation of vast areas of pelites.

### Material and methods

Seventeen stations have been sampled using the Romanian R/V “Mare Nigrum” during the period from 3 to 7 May 2012. Sampling was performed by 0.1 m<sup>2</sup> van Veen grab and multicorer (Mark 11-400 with four tubes, each 60 cm long and 10 cm in diameter) that enabled the recovery of up to a 40 cm sediment column.

The hydrological parameters were obtained by Neil Brown Instalments Systems (CTD), equipped with 11 samplers and electronic sensors. They include water depth (D), dissolved oxygen (DO), saturation index of oxygen (SI), salinity (S), electrical conductivity (U), temperature (T°C), pH, and Eh (subsequently normalized to a standard pH = 7 and indicated as Eh'). Transparency (Tr) was measured using a Secchi disk. The content of PO<sub>4</sub> and SiO<sub>2</sub> is determined using the Molybdovanadate Method with Acid Persulfate Digestion (HASH equipment) on board.

The CaCO<sub>3</sub> content is determined by titration. Carbon (C), organic carbon (C<sub>org</sub>), and nitrogen (N) in the sediments are determined by gas chromatography using a Carlo Erba NA 1500 with an accuracy of 0.01%, 0.02%, and 0.002%, respectively. The <sup>15</sup>N/<sup>14</sup>N ratio was expressed as δ<sup>15</sup>N and determined by the mass spectrometer Finnigan MAT 252, after processing the samples at 1100°C in a gas chromatograph at the Institute of Biogeochemistry and Marine Chemistry, University of Hamburg in Germany.

Grain-size distribution (sieve and elutriation) together with determination of Median Diameter (Md) and coefficient of sorting (So) as well as foraminiferal analysis performed for the uppermost 0-2 cm layer of sediments as described in Logvinenko and Sergeeva (1986) and Yanko and Troitskaya (1987), respectively, at the laboratory of Micropaleontology, Odessa LI. Mechnikov National University, Ukraine (Yanko-Hombach et al., 2013).

According to their ecological preferences, foraminifera are divided into oligohaline (1-5 psu), strictoeryhaline (11-26 psu), polyhaline (18-26 psu), holoeuryhaline (1-26 psu), shallow (0-30 m), relatively deep (31-70 m), and deep (71-220 m) species (Yanko-Hombach, 2007).

All measured parameters were treated statistically (cluster, correlation, factor analyses, and multidimensional scaling) using the Statistics-7 package in order to find out the main factor/s responsible for taxonomic and spatial distribution of foraminifera. Correlation in this study was considered strong and meaningful if  $r < 0.52$  ( $P < 0.05000$ ), at greater than the 95% confidence level. If  $r = 0.5-0.4$  ( $P < 0.0500$ ), we would consider such correlation to be a trend.

## Results and Discussion

No planktonic species were discovered. Benthic foraminifera are represented by 15 species (14 calcareous and one agglutinated) from 3 orders, 7 families, and 14 genera. The orders Rotaliida, Lagenida, Ataxophragmiida were represented by 8, 5, and 1 species, respectively. Among the Rotaliida, the dominant species of the genus *Ammonia* were *A. tepida*, *A. compacta*, *A. Ammoniformis*; among the Lagenida, it was *Fissurina lucida*. The rest of the species belong to an accessorial group.

Results of the Q-mode cluster analysis revealed three clusters of stations similar with regard to foraminiferal parameters: shallow, relatively deep, and deep (Fig. 2; Yanko-Hombach et al., 2013).

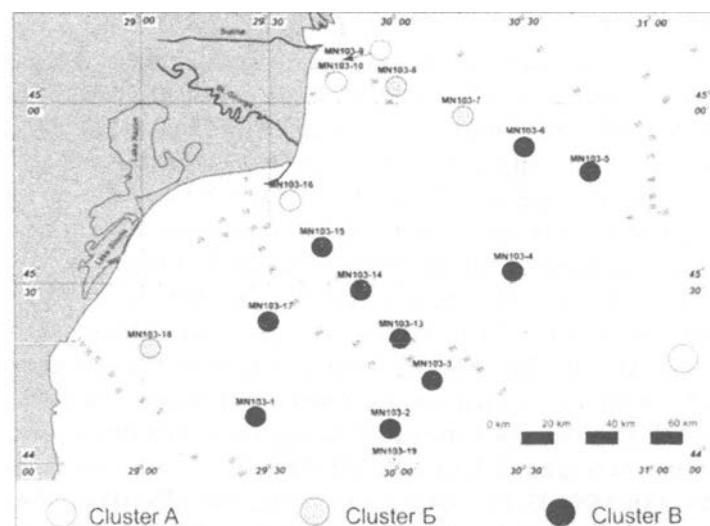


Figure 2. Map showing the spatial distribution of sample localities falling within the three clusters obtained by cluster analysis and multidimensional scaling: A - shallow (17.5-24.6 m, salinity 17.8-18 psu), B - relatively deep (33.6-46 m, 18.2-18.3 psu), and deep (50.4-80.0 m, 18.2-18.9 psu), with the dominant species *Ammonia tepida*, *A. compacta*, and *A. ammoniformis*, respectively.

The distribution of grain-size fractions in surface sediments is extremely uneven (Fig. 3).

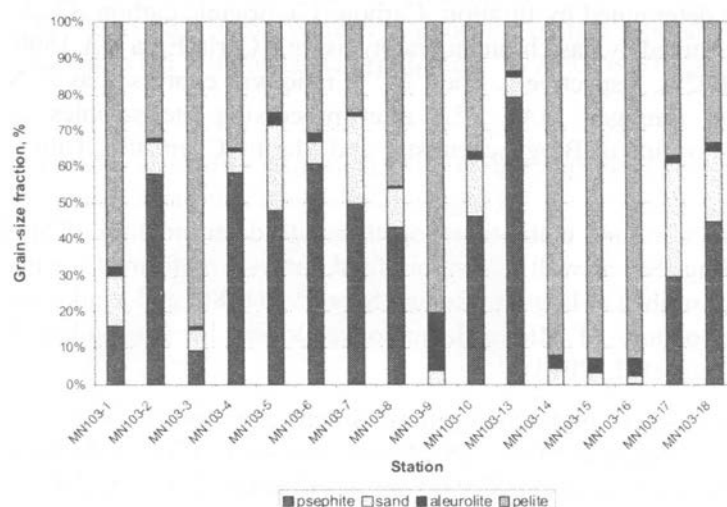


Figure 3. Distribution of grain-size fractions in the uppermost layer (0-2 cm) of bottom sediments.

Psephites are present at most of the stations and make up to 79% of the sediments. They are represented mainly by shells and detritus of *Mytilus galloprovincialis* and *Modiolus phaseolinus* that form coquina in the east and southeast of the study area at water depths of 40-80 m.

Sand content does not exceed 31%. A submerged band of deposited sand in the form of a tongue extends southeastward from the mouth of the St. George arm as far as isobath -75 m, and a solitary underwater accumulation of sand was laid down at a depth of about 20 m just off the coast of the Sulina arm. Under the microscope, the sands are composed primarily of grains of quartz, feldspar, mica, heavy minerals, and a small admixture of biogenic material (detritus, shells of foraminifera and ostracods).

The same areas are confined by silty and pelitic sediments. While silt dominates in front of the Sulina mouth, pelites are localized in front of the St. George mouth with a content of 89% and 70%, respectively. Almost everywhere in front of the Danube delta, the surface of the sediment is covered by secondary warp representing the result of geochemical flocculation.

Environmental parameters were measured as follows: In the bottom water, Tr ranged between 2 m (St. MN103-9, -17.5 m) and 12.5 m (St. MN103-3, -80.5 m); S – between 17.8 psu (St. MN103-9, -17.5 m) and 18.9 psu (St. MN103-3, -80.5 m); U – between 29.6 mSm/cm (St. MN103-9, -17.5 m) and 31.1 mSm/cm (St. MN103-3, -80.5 m); T°C – between -6.9°C (St. MN103-9, -17.5 m) and 10.9°C (St. MN103-3, -80.5 m) [the increase in temperature with depth but not vice versa is due to the fact that sampling was performed in early spring when the shallow water did not heat up enough and was cooler compared with water at depth -80.0 m]; DO – between 4.05 mg/l (St. MN103-3, -80.5 m) and 9.21 mg/l (St. MN103-6, -54.7 m); SI – between 36.5% (St. MN103-3, -80.5 m) and 78.7% (St. MN103-6, -54.7 m); pH – between 8.1 (St. MN103-18, -34.5 m) and 8.65 (St. MN103-4, -78.0 m); Eh – between 93.0 mV (St. MN103-14, -61.5 m, located in front of the St. George discharge point) to 258 mV (St. MN103-2, -67.0 m, located on the outer shelf beside the river discharge);  $\text{PO}_4^{3-}$  – between 0.01 mg/l (St. MN103-18, -34.5 m) and 0.22 mg/l (St. MN103-1, -58 m);  $\text{SiO}_2$  – between 0.43 mg/l (St. MN103-16, -24.6 m) and 1.13 mg/l (St. MN103-3, -80.5 m). In the bottom sediments,  $C_{\text{org}}$  ranged from 2.034% (St. MN103-16, -24.6 m) to 4.39% (St. MN103-6, -54.7 m);  $\text{CaCO}_3$  – from 9.126% (St. MN103-9, -17.5 m) to 44.38% (St. MN103-7, -46.0 m); C/N ratio – from 8.311 (St. MN103-8, -33.6 m) to 11.43 (St. MN103-3, -80.5 m);  $\delta^{15}\text{N}$  – from 4.936 (St. MN103-8, -33.6 m) to 6.35 (St. MN103-1, -58 m).

Factor analysis of environmental parameters revealed three main factors F-1, F-2, and F-3, with total dispersion of eigenvalues of 89%. This shows that the obtained results are statistically significant. The contribution of each factor to the total dispersion of data was 48.2%, 25.8%, and 14.6%, respectively. Their position of the three factors in the plane of Factor 1 x Factor 2 is shown in Fig. 4.

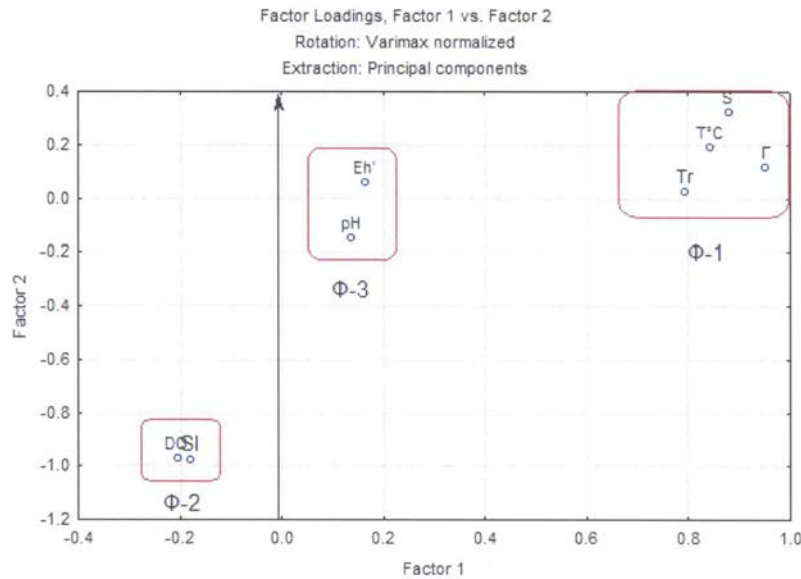


Figure 4. 2D diagram of factor analysis showing position of the three factors in the plane of Factor 1 x Factor 2.

The most powerful is F-1. It is positively correlated with D, Tr, S, U, T, SiO<sub>2</sub>, CaCO<sub>3</sub>, C/N and negatively with the aleurolite fraction. F-2 is positively correlated with DO, SI, and negatively with SiO<sub>2</sub>. The least powerful factor is F-3, which is positively correlated with Eh and SO.

Factor 1 is a distance from the shore or water depth—the farther from the shore, the deeper and the higher the salinity and the more closely related electrical conductivity, and hence the weaker freshening influence of the Danube.

Positive correlation of F-1 with SiO<sub>2</sub> shows more intensive accumulation of SiO<sub>2</sub> on the outer shelf. This is in a good agreement with analytical measurements of SiO<sub>2</sub> in the water column, which also increases toward the sea bottom. The C/N ratio indicates processes that take place with organic matter on its way from the surface to the bottom and further burial. Values of C/N between 4 and 10 indicate a marine genesis of organic matter (Meyers, 1994) as in our study where C/N varies between 8.3 and 11.5. The main source of SiO<sub>2</sub> is diatoms, frustules of which are much more abundant in bottom sediments of the outer shelf compared to the inner one.

Positive correlation of F-1 with CaCO<sub>3</sub> ( $r = 0.52$ ) indicates an increase in the amount of carbonate material with water depth. The positive correlation of CaCO<sub>3</sub> with psephite fraction ( $r = 0.57$ ) speaks in favor of a biogenic origin for the psephites (by mollusk shells). Areas of distribution for the psephites identify the most favorable conditions for mollusk survival, and these are located alongside the Danube river discharge.

Negative correlation between F-1 and the aleurolite fraction ( $r = -0.62$ ) indicates distance from the shore or water depth. The latter plays an opposing role in the accumulation of fine-grained material. This contradicts the classical model of sedimentation. According to that model, accumulation of fine-grained material increases, not decreases, with depth and/or low hydrodynamic activity. In our case, the main source of fine-grained material is the Danube. Therefore, the areas of fine-grained accumulation are located in front of the Sulina and St George mouths (Fig. 5).

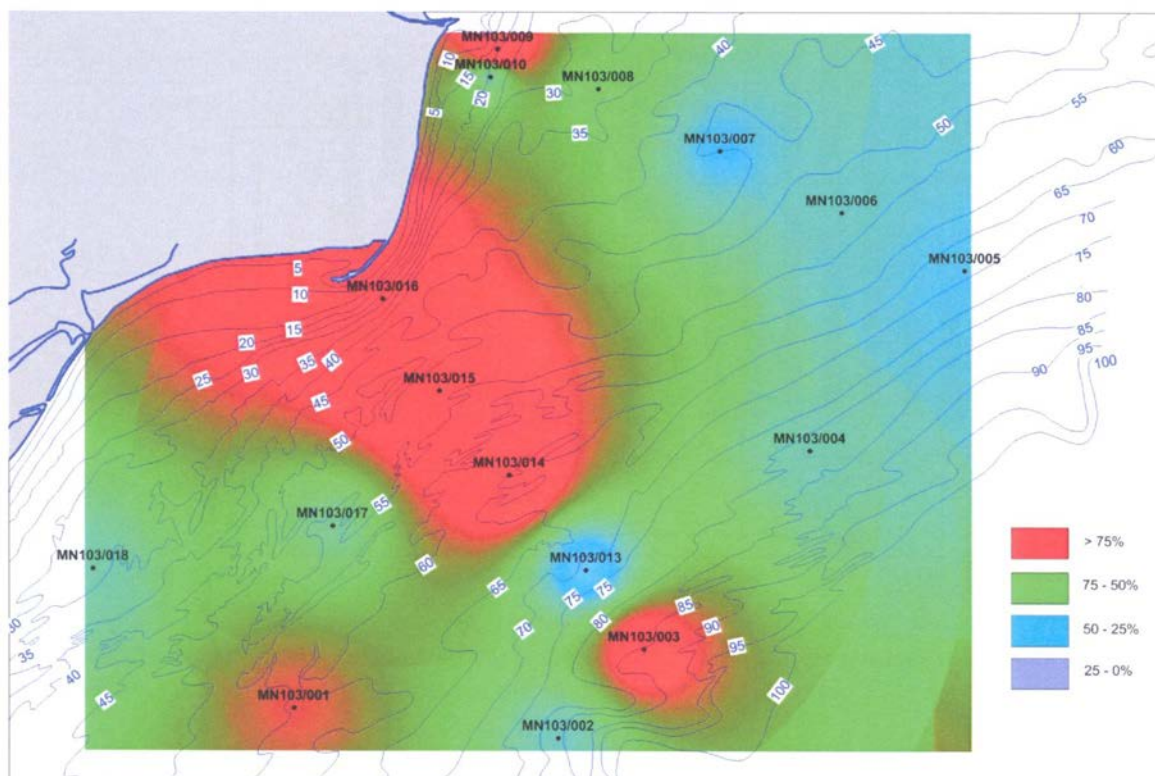


Figure 5. Spatial distribution of the pelite fraction in bottom sediments of the Black Sea Romanian shelf.

Negative correlation of  $\text{CaCO}_3$  with the pelite fraction ( $r = -0.51$ ) shows that carbonate material does not participate in the accumulation of this fraction. Together with the dominance of pelites in the prodelta, it speaks in favor of the formation of a geochemical barrier with intensive development of the processes of abiogenic flocculation leading to the accumulation of pelites.

Factor 2 most likely relates to eutrophication of the water column. Its effect increases towards the bottom. It can be seen from the negative correlation of  $\text{SiCF}$  with  $\text{DO}$  and  $\text{SI}$  ( $r = -0.65$ ;  $-0.68$ , respectively) and the positive correlation with  $\text{C/N}$  ( $r = 0.61$ ). Decrease in  $\text{DO}$  can be explained by its utilization by decaying diatom algae—the more algae, the lower the oxygen content and the higher the content of organic matter, and consequently eutrophication of the water column. Judging by the uneven distribution of  $\text{DO}$  and  $\text{SiO}_2$  in the bottom water, the eutrophication has a spotty pattern.

Factor 3 seems to represent anthropogenic contamination of bottom water by organic matter discharged by the Danube. This is supported by closely related values of  $\text{Eh}$  and  $\text{pH}$ , which characterize the state of the water. Fresh water lowers the  $\text{pH}$  values of seawater while anthropogenic pollution enriches it with organic matter.

Correlation of the frequency of occurrence of the main species of foraminifera with F-1, F-2, and F-3 shows that each species or group of species can be used as an indicator of a certain state of benthic ecosystems of the Romanian part of the Black Sea.

## Conclusions

Fifteen species are indicated. Their quantitative characteristics and the restructuring of their assemblages was found to correlate with hydrological and geochemical parameters of the bottom water and sediments as well as grain-size data, and it enabled the identification of three main factors influencing the environmental state of bottom ecosystems. They are as follows: (1) distance from the shore and related parameters (salinity, transparency, water temperature); (2) eutrophication of the bottom water, and (3) pollution of the bottom water by organic matter discharged from the continent. Benthic foraminifera along with lithology of the bottom sediments permitted an evaluation of the degree of influence from environmental parameters on the state of bottom ecosystems, and they facilitate the tracing of the spatial distribution of Danube freshwater discharge near the sea bottom.

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