The origin of organic matter in Holocene sediments in the Bay of Koper (Gulf of Trieste, northern Adriatic Sea)

Izvor organske snovi v holocenskem sedimentu Koprskega zaliva

Nives OGRINC¹, Jadran FAGANELI², Bojan OGORELEC³ & Branko ČERMELJ²
¹Department of Environmental Sciences, "J. Stefan" Institute, Jamova 39, 1000 Ljubljana, Slovenia, nives.ogrinc@ijs.si
²Marine Biological Station, National Institute of Biology, Fornače 41, 6330 Piran, Slovenia, faganeli@mbss.org; cermelj@mbss.org
³Geological Survey of Slovenia, Dimičeva ul. 14, 1000 Ljubljana, Slovenia, bojan.ogorelec@geo-zs.si

Key words: marine sediments, organic matter, carbon, nitrogen, stable isotopes, northern Adriatic
Ključne besede: morski sedimenti, organska snov, ogljik, dušik, stabilni izotopi, severni Jadran

Abstract

Three cores, V-3, V-5 and MK-6, drilled in the inner part of the Bay of Koper were used to reconstruct the paleoenvironmental conditions occurring during the Holocene. Based on stable isotope results two depositing environments can be distinguished in the cores: the upper, marine and lower, brackish sedimentation. Marine sedimentation prevailed over fluviatile sedimentation at depths of 15 m, 19 m and 10 m in the V-3, MK-6 and V-5 cores respectively. The marine part of the core V-3 was influenced by varying amounts of land-derived organic carbon transported by the River Rižana, while in MK-6 and V-5 cores the marine algae and/or microphytes constituted the main source of sedimentary organic carbon. The fluvial sedimentation has typically lower $\delta^{13}$C$_{org}$ and higher C/N ratios, $\sim$ – 26 ‰ and > 12 respectively and based on stable carbon isotope mass balance the terrestrial organic carbon present up to 70 to 100 % of the sedimentary organic carbon. On the other hand, the higher $\delta^{15}$N values observed at some depths in the fluvial sedimentation indicated that nitrogen could be of marine origin. The observed data in parallel with previous studies are in good agreement with the simultaneous rise of the sea level in the Northern Adriatic.

Izvleček

Jedra vrtin V-3, V-5 in MK-6, izvrtanih v notranjem delu Koprskega zaliva smo uporabili za rekonstrukcijo paleoookoljskih razmer v času holocena. Na osnovi rezultatov izotopskih meritev $^{13}$C in $^{15}$N v organski snovi lahko v njih določimo dve sedimentacijski okolji – zgornje morsko in spodnje brakično. Morsko sedimentacijo prevladujejo do globine 15 m v vrtini V-3, 19 m v MK-6 in 10 m v vrtini V-5. Morska sedimentacija je bila pod variabilnim vplivom vnosa kopenske organske snovi z reko Rižano, medtem ko opazujemo, da izvira organska snov v vrtinah MK-6 in V-5 pretežno iz morskih mikroalgi in makrofitov. Okolje rečne sedimentacije karakterizirata nižja vrednost $\delta^{13}$C$_{org}$ $\sim$ – 26 ‰ in višje razmerje C/N > 12. Delež kopenskega organskega ogljika v teh delih sedimenta, določen na osnovi masne bilance, znaša 70–100 %. Povišane vrednosti $\delta^{15}$N ugotovljene v nekaterih globinah reče sedanjega sekvence kažejo, da je N tudi morskega izvora. Naše ugotovitve, vzporedno s predhodnimi raziskavami, so ujemajo z dvigovanjem morja v severnem Jadranu v holocenu.
Introduction

A large source of the uncertainty in present understanding of the global carbon cycle is the distribution and dynamics of the coastal sediment organic carbon (OC) reservoir, where total organic carbon (TOC) is composed of material derived from both marine and terrestrial sources. Identification of environmental factors, especially those related to degradation and preservation of OC, allow reconstruction of paleo-productivity, terrigenous OC input and anthropogenic impact in relation to global environmental and climate changes. The organic matter (OM) in marine sediments typically accumulates at slower rates and over longer periods of time and consequently has the potential ability to record longer paleoceanographic histories and to reveal the effects of slow-acting diagenetic alteration. A variety of geochemical approaches have been employed to define the marine to terrestrial ratio of OC buried in sediments. On the basis of elemental and isotopic values it is possible to distinguish two end-members: land-derived OM, with $\delta^{13}C_{\text{org}} \sim -26$‰, $\delta^{15}N \sim 0.4$‰, C/N $\sim 18$, and marine OM, with $\delta^{13}C_{\text{org}} = -20$‰ to $-22$‰, $\delta^{15}N \sim 8.6$‰, C/N $\sim 8$ (Meyers, 1994, 1997).

Despite the extensive early diagenetic processes which have influenced the OM, the C/N ratio and especially $\delta^{13}C$ values are not significantly influenced by sediment grain size making them useful in reconstructing past sources of OM. The $\delta^{15}N$ values can give additional information to distinguish the source of OM and to reconstruct past productivity rates. The dynamics of nitrogen in sediments are more complicated than those of carbon and make interpretation of sedimentary $\delta^{15}N$ records more difficult. The isotopic signature depends on the source of the nitrogen, the rates of primary production and respiration, and the nitrification-denitrification processes (Macko et al., 1993; de Lange et al., 1994; Prahl et al., 1997; Sigman et al., 1999; Brenner et al., 1999). However, $\delta^{15}N$ values of sedimentary organic matter are widely used to complement $\delta^{13}C$ values in paleoproductivity studies (Brenner et al., 1999; Meyers & Teranes, 2001; Huon et al., 2002).

The study of boreholes drilled in the Bay of Koper, inner part of the Gulf of Trieste (Fig. 1) has enabled us to reconstruct the sedimentation environment through the Holocene. The changes observed in the sediment are also closely related to the global rise of sea levels. Analyses at a depth of 26 m showed that, during the most intensive sea transgression marine sedimentation prevailed over fluvial sedimentation (Faganeli et al., 1987; Ogorelec et al., 1997), as illustrated in the lithology of cores V-3 and MK-6 presented in Figure 2. In addition, it can be seen that the V-3 core fluvial sedimentation is replaced by marine sedimentation and, in parallel a brackish environment changes into a marine environment in the MK-6 core.

The aim of the present study was to determine stable carbon and nitrogen isotopic composition in three deep cores, V-3, V-5 and MK-6, drilled in the inner part of the Bay of Koper in order to better understand the paleoenvironmental conditions obtaining during the Holocene in this area.

Materials and methods

Site description – The Bay of Koper covers an area of about 35 km². At present it is a wide submarine plateau up to 20 m deep
with restricted sea water circulation. In the west, i.e. along the Izola–Debeli rtič line, the Bay slopes downwards towards the open part of the Gulf of Trieste, while in the east it slopes upwards towards the inflow of the River Rižana. The Bay of Koper has a fairly steep coast which, at depths 5 and 10 metres, quickly grades into a sloping underwater plain. The coast is composed of Eocene flysch layers with alternating solid sandstone and soft marl. The flysch coast gives the Bay its characteristic form, particularly between Izola and Koper, at Cape Ronek and between Valdoltra and Debeli rtič. The surficial sediment of the Bay of Koper can be divided into three distinct zones according to grain size distribution, mineral composition and carbonate content: a) coastal sediment b) sediment of the inner part and c) sediment of the open part of the Bay (Ogorelec et al., 1987). All three cores are located in the coastal part of the Bay. In this zone the sediment is composed of dark grey-green silt and sandy silt with up to 40 % of sand and with less than 15 % of clay (grain size < 2 µm). The most abundant minerals in the recent sediments of the Bay of Koper are quartz and calcite. Quartz is present in all fractions originating from flysch sandstones and marl and its content ranges from 20 to 35 %. The carbonate content composed of calcite, dolomite and skeletal of various organisms molluscs, foraminifers and echinoids ranges from 20 to 30 %. Calcite is mainly of terrigenous origin, however a rather large proportion is associated with organic skeletons. Dolomite, as the second most abundant carbonate mineral, is present at only about 5 %. The clay is composed of illite, chlorite and illite/montmorillonite, the last as a mineral with mixed composition. The OC content in the surficial 5 cm sediment layer ranges from 0.44 to 2.72 % with an average value of 1.38 ± 0.50 %. The total nitrogen content (TN) ranges from 0.05 to 0.46 %, with an average value of 0.18 ± 0.13 %. Higher OC and TN contents are found in the fine clayey silt fraction, while the coarse sediment along the shore, influenced by tides and sediment resuspension, contains less.

**Samples and analyses** – A coring platform was set up in the sea to take the cores from the boreholes located in the cargo port of Koper – V-3, 200 m off Koper – V-5 and 200 m off Žusterna – MK-6 (Fig. 1). The V-3 core was 41 m deep, taken at a sea water depth.
of 4.5 m, while V-5 and MK-6 cores were 43 m deep, taken at a sea water depths of 5 and 7 m, respectively. The sediments was subsequently divided into several subsamples, which were freeze-dried and homogenized to a fine powder with a mortar. These samples were analysed for OC and TN contents and for stable isotopic composition of OC (\(\delta^{13}C_{\text{org}}\)) and TN (\(\delta^{15}N\)).

OC contents were determined using a Carlo Erba elemental analyzer (model EA 1108) after acidification with 1M HCl (Hedges & Stern, 1984). Weight percentages of TN and total C were determined similarly, but without acidification. The precision of measurements was ± 3 %.

The isotopic composition of sedimentary OC was determined after treatment with 1M HCl to remove carbonate material. Sample were treated on a sand plate at 70 °C at least twice, until no further gas bubbling was observed. A washing step was used prior to sample analysis to remove dissolved salts (Schubert & Nielsen, 2000; Ogrinc et al., 2005). \(\delta^{15}N\) of TN was determined directly on bulk powdered samples. The \(\delta^{13}C\) and \(\delta^{15}N\) of OC and TN fractions were determined by a Europa 20–20 continuous-flow isotope ratio mass spectrometer with ANCA-SL preparation module for solid and liquid samples. Isotopic ratios were expressed in the usual \(\delta\)-notation in parts per mil (%). For carbon, the standard is the V-PDB carbonate, while for nitrogen the standard is atmospheric (air) nitrogen. Data quality control was controlled by running a reference standard after every 8 samples: IAEA-CH-7 polyethylene and NBS22 were used for carbon, and IAEA-N-1 and IAEA-NO-3 were used for nitrogen. The overall analytical precision was ± 0.2 %o and ± 0.3 %o for \(\delta^{13}C\) and \(\delta^{15}N\) values respectively.

**Results and discussion**

The results from core V-3 are presented in Figure 3. The borehole reached the flysch basement at a depth of approximately 40 m. The core can be divided into two parts. The bottom section of the sediment starting at the depth of 25 m comprised alluvial deposit from the River Rižana with alternating layers of sand, silt and gravel. The sediment in the top 25 m of the core is mainly of marine origin and consists of dark grey silt with uniform grain size and mineral composition.

In this upper part, many foraminifers, gastropods, molluscs and fragments of sea urchin remains are present. The mineral composition consists of quartz, calcite, illite, chlorite, illite/montmorillonite, feldspars, dolomite and pyrite, while the last is absent in the fluvial deposit (Ogorelec et al., 1984, 1997). The carbonate content ranged from 20 to 30 % except below the depth of 26 m where only 5 to 6 % of carbonate is present due to the higher influence of land derived terrestrial material.

The OC content varied from 0.23 to 1.62 % in the upper marine part of the core, while in the lower fluvial part it ranged from 0.2 to 1.1 %. The vertical distribution of total nitrogen follows the distribution of OC contents. The TN concentrations ranged from 0.10 to 0.30 % in the marine part and from 0.01 to 0.07 % in the fluvial part of the core. A plot of % TN vs. % OC showed a rather good correlation (% TN = 0.13 (± 0.03) * % OC + 0.013 (± 0.03); r = 0.77), suggesting that there is close relationship between these two parameters. The intercept value indicates that some inorganic N may be present in these sediments. Previous estimates of exchangeable ammonium, nitrite and nitrate comprised up to 15 % of TN, while fixed ammonium comprised up to 56 % of TN in the sediments (Faganeli et al., 1987, 1991).

The \(\delta^{13}C_{\text{org}}\) values ranged from −21.5 to −26.2 %o, and from 1.7 to 7.8 %o for \(\delta^{15}N\) values. Higher variability in \(\delta^{13}C_{\text{org}}\) and \(\delta^{15}N\) values was found in the upper 12 m of the core and they do not follow the OC pattern. These variations correspond to different proportions of terrestrial OC discharged by the River Rižana to sediments. The highest \(\delta^{13}C_{\text{org}}\) of −21.5 %o, a value typical for marine microalgae, was determined at a depth of 10 m, but the \(\delta^{15}N\) value of 4.5 %o was lower than the expected value of 7.3 %o, probably due to selective degradation of organic N. Higher \(\delta^{15}N\) values of 7.8 %o and 6.0 %o were found at depths of 15 and 25 m, respectively. At these depths a prevalent terrestrial \(\delta^{13}C_{\text{org}}\) signature of −25.7 % was observed, but the higher \(\delta^{15}N\) contents in the sediment suggest that N is mainly of microalgal origin. Isotopic analysis below 15 m from the top of the core gave values of \(\delta^{13}C_{\text{org}}\sim −25 %o, \delta^{15}N\sim 2 %o\) and C/N ≈ 12 which, together with lithostratigraphic evidence, reflects sediments of mainly terrestrial origin.
A plot of $\delta^{15}N$ vs. $\delta^{13}C_{\text{org}}$ values were constructed, since the linear relationship is usually interpreted as a mixing trend between terrestrial and marine source of OM (Thornton & McManus, 1994; Muzuka & Hillarie-Marcel, 1999; Huon et al., 2002; Ogrinc et al., 2005). However, a low correlation ($r = 0.05$) and considerable spread in the distribution of values determined in the core V-3 suggests that other factors influence $\delta^{15}N$ to a greater extent than $\delta^{13}C_{\text{org}}$. Since the $\delta^{13}C_{\text{org}}$ values provide a better indication of the potential sources of OC than $\delta^{15}N$ values, a semi-quantitative estimate of the proportion of terrestrially derived OC of the cores was based on the stable carbon isotope mass balance:

$$\delta^{13}C_{\text{org,s}} = F_m \cdot \delta^{13}C_{\text{org,m}} + F_t \cdot \delta^{13}C_{\text{org,t}}$$  \hspace{1cm} (1)$$

$$1 = F_m + F_t$$  \hspace{1cm} (2)$$

where $\delta^{13}C_{\text{org,s}}$, $\delta^{13}C_{\text{org,m}}$ and $\delta^{13}C_{\text{org,t}}$ are the $\delta^{13}C_{\text{org}}$ values for the sample, marine and...
terrestrial source materials, respectively, and $F_t$ and $F_m$ are the respective terrigenous and marine OC fractions in the sample. For this calculation we assumed constant $\delta^{13}\text{C}_{\text{org}}$ end-member values for terrestrial and marine OC supply, since the effect of selective diagenesis of OC fractions that are isotopically heavy or light appears to be small, usually less than 2‰ (Meyers, 1997). A $\delta^{13}\text{C}_{\text{org}}$ value of $-26$‰ was used as the terrestrial end-member, while for the marine end-member the value of $-21$‰ was applied. The $\delta^{13}\text{C}_{\text{org}}$ for terrestrial end-member was based on the $\delta^{13}\text{C}_{\text{org}}$ determined in the sediments of the River Rižana outflow. This value is similar to terrestrial end-members identified in other studies (Wada et al., 1987; Thornton & McManus, 1994; Middelburg & Nieuwenhuize, 1998). Further, the average $\delta^{13}\text{C}_{\text{org}}$ value of $-20.7 \pm 1.6$‰ for marine derived OC is well-established for the Gulf of Trieste (Faganeli et al., 1994). According to our estimates, between 10 and 92 % of OC in sediments is of terrestrial origin in the upper 10 m of the cores, while in the lower part the terrestrial OC comprises more than 70 %.

The results from the core MK-6, drilled in the location of the planned Koper marina (Žusterna), are shown in Figure 4. In this core no fluvial deposit was observed. The sediment is homogeneous, being composed of grey clayey silt with mean grain size less than 10 µm, similar to the composition of surface sediment in the central part of the Bay of Koper. Several fossil remains are present such as foraminifers, molluscs and ostracods. The mineral composition is rather uniform and consists of quartz, calcite, illite, chlorite, illite/montmorillonite, feldspars, dolomite and pyrite. The carbonate content was around 20 % in the upper 20 m of the core, but lower content (approx. 10%) deeper in the core. The OC content varied from 0.58 to 2.59 %, while nitrogen content varied from 0.07 to 0.13%.

The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values ranged from $-19.0$ to $-27.0$‰ and from 2.3 to 6.3‰, respectively. The highest $\delta^{13}\text{C}$ value of 6.3‰ was found at a depth of 34 m together with the $\delta^{13}\text{C}_{\text{org}}$ of $-25.0$‰, similar to the core V-3 at the depths of 17 m and 25 m. Again, the source of N is different from that of C and appears to be of marine origin. The highest $\delta^{13}\text{C}_{\text{org}}$ value of $-19$‰ indicates that benthic macrophytes could represent an additional source of OC at a depth of 4 m. The $\delta^{13}\text{C}_{\text{org}}$ values of some microphytes were found to be higher than those of phytoplanktonic and microphytobenthic OC: Ulva rigida: $\delta^{13}\text{C} = -17.9$‰; Fucus virsoides: $^{13}\text{C} = -15.6$‰; Cymodocea nodosa: $\delta^{13}\text{C} = -9.6$‰ and $\delta^{15}\text{N} = 4.8$‰ (Ogrinc et al., 2005).

The depth distribution of the two parameters is not so variable as it is in the V-3 core. Using $\delta^{13}\text{C}_{\text{org}}$ values, we can clearly distinguish two depositing environments with two different sources of OC. The OC is mainly of marine origin in the upper 17 m of the core, with only 40 % of terrestrial OC. Like the V-3 core, more than 70 % of OC is of terrestrial origin in the lower brackish part.

The depth distributions of OC, $\delta^{13}\text{C}_{\text{org}}$, TN, $\delta^{15}\text{N}$ and C/N ratios, together with the lithology of the core V-5 are presented in Figure 5 which also shows the changes between marine and brackish environments during the Holocene deposition. OC and concentrations ranged from 0.54 to 1.85 wt. % and TN from 0.04 to 0.12 wt. %. The highest OC content was usually associated with the lowest $\delta^{13}\text{C}_{\text{org}}$ values, but not necessarily with the highest TN concentration. The C/N ratios ranged from 11.6 to 31.0, the highest found at a depth of 13 m. The $\delta^{13}\text{C}_{\text{org}}$ values varied by over 11.0‰, from $-27.2$ to $-17.1$‰, the highest being found at the depth of 2.5 m. The $\delta^{15}\text{N}$ values were less variable, ranging from 3.7 to 6.5‰. A good correlation between OC and TN contents in core sediments (% TN = 0.036 (± 0.01) * % OC + 0.033 (± 0.013); r = 0.59) suggests that there was a close relationship between OC and TN, while the intercept value of 0.033 indicates that there was more inorganic N present in the sediment than in the core V-3. This is also the reason why a slope-derived C/N value could not be representative of the bulk OC in these samples. Larger variations in $\delta^{13}\text{C}_{\text{org}}$ values were present in the upper 4 m of the core. These variations reflect a different cause of the changes of OC between marine algae and microphyte derived OC. In addition to a higher $\delta^{13}\text{C}_{\text{org}}$ values, the microphyte derived OC also had higher C/N ratios (> 20). Deeper in the core the terrestrial signature, with more than 70 % of OC, was first observed at depths of 5 and 6 m, then at 8 m, and in all samples below 10 m.

Changes in the marine and brackish environments during the Holocene deposition were also reflected in the downcore profile of the V-6 core drilled in the salt marsh Sečovlje near the inflow of River Dragonja.
The origin of organic matter in Holocene sediments in the Bay of Koper (Gulf of Trieste, ...

This was characterized by the changing of the carbon and nitrogen isotopic compositions of OC at depth intervals of 6–8 m, 8–14 m, 16–24 m (Ogrinc et al., 2005). However, the presence of terrestrial OC in the upper part of core V-3 is more abundant than in sediments of the core V-6, indicating that the River Rižana has a greater influence on sediments than the River Dragonja with lower mean discharge. In addition, the changes in δ¹³Corg and δ¹⁵N values observed in the upper part of the core V-6 are comparable to those obtained in the core V-5, but the C/N ratios are different. The data indicate changing variations in organic δ¹³C values affected by marine algae production and/or microphyte presence in the sediments. On the other hand, in the core GT2, collected near the River Soča/Isonzo outflow, variations of terrestrial OC are similar to those in the upper part of the V-3 core, indicating variable inputs of allochthonous material to sediment relative to in situ production (Ogrinc et al., 2005).

Conclusions

Due to their tight isotope-environment relation, carbon and nitrogen stable isotopes were used to draw a more detailed picture of the changes occurring in the sediments of the Bay of Koper during the Holocene. The considerable spread in the distribution of δ¹⁵N vs. δ¹³Corg values suggests that C and N were of
different origin and that additional processes influence $\delta^{15}$N values to a greater extent than $\delta^{13}$C$_{org}$. Variations in parameters determined in the depth profiles of the V-3, MK-6 and V-5 cores show variable inputs of allochthonous material relative to *in situ* biological production in the upper, marine part of the core. The marine sediments in core V-3 were additionally influenced by transport of terrestrial OC by River Rižana and OC originating mainly from algal production was observed only at the depth of 9 and 10 m. The MK-6 and V-5 sedimentary OC showed a different pattern. The isotopic composition of carbon and nitrogen indicate that most of the sediment OC was from marine algae, while at some depths the influence of OC derived from microphytes was observed, as is evident from $\delta^{13}$C$_{org}$ values ranging from $-17.9$ to $-19.8$ ‰ and high C/N ratios of $>20$. There are significant changes in the source of OC at depths of 15 m, 19 m and 10 m in V-3, MK-6 and V-5 cores respectively, indicating fluvial depositional environment. According to stable isotope mass balance the terrestrial supply was estimated to contribute up to 70 to 100 % of the OC. In the fluvial sedimentation the highest $\delta^{15}$N values

Figure 5. Vertical profiles of lithology, organic carbon (C$_{org}$), $\delta^{13}$C$_{org}$, total nitrogen (TN), $\delta^{15}$N values and C/N ratios in the sediment core V-5.
(6.0 %, 6.3 %, 6.5 % and 7.8 %) were found, together with a δ13Corg of ~ −25.0 % at depths of 17 m and 25 m in V-3, 34 m in MK-6 and 18 m in V-5 core. These results suggest that N was probably originating from marine algae and was thus of different origin from C.

Acknowledgments

We acknowledge the financed support of the Slovenian Research Agency (ARRS). Authors thank Prof. Roger H. Pain for linguistic corrections.

References


