Chapter 22

Organic Matter Sources and Dynamics in northern Adriatic Coastal Waters

M. Pettine · L. Patrolecco · S. Capri

22.1 Introduction

Organic matter in marine environments results from both autochthonous and allochthonous sources. Phytoplanktonic production is responsible for the internal production of organic matter, which according to dominant biological processes, distributes between the particulate and dissolved phases. Photosynthetic activity transforms, in the presence of inorganic nutrients and light, inorganic carbon into particulate organic matter (*POM*), of which more than 30% consists of carbon (*POC*) according to the Redfield stoichiometry and its revisitation by Morel and Hudson (1985). During photosynthetic processes, a variable percentage of photosynthates is released in the surrounding water as dissolved substances (*DOM*), consisting of monomeric and low molecular weight polymeric compounds. Other than being directly released by phytoplankton, *DOM* may be indirectly produced through sloppy feeding (i.e. the release of dissolved compounds following the breaking of large preyed cells that cannot be ingested whole by the zooplankton), dissolution of faecal pellets and marine snow, and virus-induced bacteria cell lysis.

Dissolved organic carbon (*DOC*) is by far the major carbon pool in oceans, outweighing any other marine source of organic carbon by at least a factor of 10 (Kepkay 1994). Furthermore, although algal biomass in oceans is only 0.2% of that of terrestrial plants, annual phytoplankton photosynthesis is roughly equivalent to that of plants, since algae have duplication rates on the order of days compared to month to years for plants (Chisholm 1992). Therefore, the fate of carbon in oceans not only influences the trophic food chain but also affects the exchange of carbon at the sea water-atmosphere interface.

In addition to the autochthonous sources, external inputs may further supply organic matter for marine ecosystems. On a world scale, terrestrial sources contribute about 10% to the total sea water *DOM*, while on a local scale their contribution may be much more important. Riverine inputs either directly discharge organic matter into sea water or indirectly provide new organic matter through the discharge of nutrients that feed primary production.

External inputs have markedly increased the productivity of the shallow and small northern Adriatic over the oligotrophic features of the Mediterranean. External annual contributions of nutrients in this basin have been estimated to be of the same order of magnitude as the regeneration rate, thus giving similar contributions to primary production from new and regenerated material (Degobbis and Gilmartin 1990). This evaluation strengthens the vulnerability of the northern Adriatic to external inputs and therefore to water management of rivers that discharge into this basin. An-

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nual loads of organic matter directly discharged into northern Adriatic waters account for more than 30% of the annual phytoplankton production in its most productive region along the western side (Pettine et al. 1998).

Responses of plankton biomass and productivity to riverine discharged nutrients and organic matter have been studied in many coastal ecosystems including the Hudson River, Narragansett Bay, northern Gulf of Mexico, Chesapeake Bay, Columbia River estuary, and the Baltic Sea (Benner et al. 1992; Maske 1994; Malone 1994; Cloern 1996; Harding et al. 1999; Kemp et al. 1999; Malone et al. 1999; Klinkhammer et al. 2000).

River-induced eutrophication is a general observed phenomenon involving a number of negative consequences such as excess phytoplankton growth, increased frequency of blooms, seasonal decline of oxygen in bottom waters, and changes in the trophic structure (Harding et al. 1999). However, the severity of these problems and in particular the fate of *DOM* resulting from both autochthonous and allochthonous sources may be strongly dependent on seasonal variations of freshwater flow, the geomorphology of the receiving systems and the dominant circulation pattern.

This was clearly disclosed by a recent thorough comparison (Malone et al. 1999) between the Chesapeake Bay (CB) and northern Adriatic (NA). Both of these systems are dominated by a single river, the Susquehanna in CB and the Po in NA; however, despite some similarities in terms of freshwater and nutrient loading, they exhibit significantly different trophic status. CB waters appear to be much more efficient in sequestering nutrients and retaining and recycling phytoplankton biomass than NA waters (Harding et al. 1999); in this latter system the export of nutrients due to water mass exchanges between the northern and middle basins, favoured by the counterclockwise circulation pattern during most of the year, and the confinement of regenerated nutrients, due to the strong vertical stratification during summer, reduce its capacity to retain nutrients on time and scale that promote primary and secondary productivity (Harding et al. 1999).

NA waters exhibit markedly lower average productivity levels than CB waters, although they experience large trophic gradients from coastal eutrophic to off-shore oligotrophic waters. However, the dynamics of *DOM* in this basin has resulted in the formation of a large quantity of sticky mucilaginous masses with serious problems for tourists and fishery activities; in 1989, the damages amounted to billion of dollars according to Italian authorities' estimations. This phenomenon is not reported for CB waters (Malone et al. 1999), while both the CB and NA systems experiment seasonal oxygen decline; anoxic problems are, however, much more severe in the former compared to the latter system.

There is now wide consensus that mucilaginous aggregates consist of organic and inorganic material entrapped in a gelatinous polysaccharides matrix (Degobbis et al. 1995), although timing and evolution of mucilaginous aggregates, trigger mechanisms, and biological species possibly involved in the formation of aggregates are still largely unknown (Funari et al. 1999). The mean percent values and related standard deviation ($\pm x$) of organic carbon, nitrogen, phosphorus, silicon and sulphur in aggregates collected in the summer of 1991 from surface and deep northern Adriatic waters were 24.0 ±7.2, 2.9 ±1.1, 0.26 ±0.12, 6.4 ±4.5 and 1.1 ±0.5, respectively (Pettine et al. 1995).

The scarce information available on the distribution and variability of dissolved organic matter and its important components in the northern Adriatic is one of the restrictions on the understanding of the mucilage occurrences.

In an attempt to improve our knowledge on sources, concentrations and variability of organic matter in coastal waters, we have determined organic matter loads discharged by the Po River in the dissolved and particulate phases, and the concentrations of dissolved (*DOC*) and colloidal (*COC*) organic carbon, together with those of total dissolved carbohydrates (*TDCHO*), free (*DFAA*) and total dissolved (*TDAA*) amino acids in two frontal regions of the northern Adriatic system (see Fig. 22.2). Polymeric organic compounds that are included in the colloidal fraction and in the *TDCHO* and *TDAA* variables are of particular interest in northern Adriatic waters for their involvement in the formation of micro- and macroaggregates.

This paper summarizes the results obtained in previous investigations (Pettine et al. 1998, 1999, 2001) highlighting an interannual variability in seasonal changes of *DOC* concentrations, which is strongly dependent on the hydrological regime of the Po River. Experimental findings also point out contrasting behaviours of mucilage and seasonal changes in *DOC*, *COC* and *TDCHO* concentrations, which strengthen the importance of the qualitative character of *DOM*, rather than its quantitative concentrations in triggering the formation of large mucilaginous aggregates.

22.2 Analytical Methodologies

Dissolved Organic Carbon. Samples were filtered through precombusted (4 hours at 480 °C) and preweighed Whatman GF/F glass fibre filters (0.7 μm nominal pore size). For freshwater samples, filtration was performed in a laboratory within a few hours from collection: in this case about 1 l samples were filtered under negative pressure and the filters, washed with 20 ml milli Q water, were stored at −20 °C for the analysis of *POC*. Filtered freshwater samples for *DOC* analysis were stored in high density polyethylene (HDPE) bottles as in the case of filtered sea water samples (see after) while the filtration procedure was different. For sea water samples, the filtration was performed aboard, and we were not interested in the analysis of *POC*: about 100 ml were filtered in this case by using a disposable polycarbonate syringe and a polypropylene filter holder (Nucleopore). Filtered samples were stored in duplicate into 25 ml HDPE-bottles (previously treated with HNO_3 1.2 M at 50 °C for 1 h), which were quickly frozen in an aluminum block at −20 °C. The suitability of HDPE containers for the storage of *DOC* samples was proved by recent findings (Norrman 1993; Tupas et al. 1994; Yoro et al. 1999), and confirmed by our preliminary tests. For *DOC* analysis, filtered samples were thawed in the laboratory, acidified to pH 2 with ultrapure HCl and purged with N_2 for about 10 minutes to remove inorganic carbon. Dissolved organic carbon (*DOC*) was assayed by high temperature catalytic oxidation (HTCO) and infrared detection using a Shimadzu TOC-5000 A analyser. Carbon concentrations were determined against potassium hydrogen phthalate standards after correction for total blank. This value, which is the analytical system blank plus a Milli Q water blank, was approximately 10–15 μM C under our experimental conditions and was mostly due to the

experimental system. Samples were measured in triplicate with a fixed c.v. of 2%; otherwise, further replicates were automatically carried by the instrument.

Particulate Organic Carbon. For *POC* analysis, the filters were dried at 60 °C overnight, re-weighed to determine particle loading and homogenized in an agate mortar mill. Blank filters were processed the same way. Powered, homogenized samples (10–15 mg) were accurately weighed (±0.01 mg) into tin or silver cups (9 × 5 mm) to determine particulate nitrogen (*PN*), total particulate carbon (*PC*) or particulate organic carbon (*POC*). Samples in silver cups were acidified with 20 µl 5 M ultrapure HCl and kept at 50–60 °C for 30 min to remove inorganic carbon. Care was taken to ensure complete saturation of the sample with HCl and to avoid sample loss. Acid treatment was repeated until effervescence was no longer observed (generally three times). *PC*, *POC* and *PN* were determined by high temperature oxidation using a Carlo Erba NA 1500 series 2 C/H/N/O/S analyser. Samples were run in duplicate. The sulphanylamide standard was used to construct the calibration curve. Carbon and nitrogen contents were expressed as percentage of total solid and as concentration (mg l^{-1}) of filtered water sample. Average blank levels were 2.5 ±0.8 µg C and <0.5 µg N; detection limits (calculated as three times the standard deviation of the blank for carbon, and according to sensitivity of the instrument for nitrogen) were 2 and 0.5 µg for carbon and nitrogen, respectively, corresponding to 0.02% C and 0.005% N for a 10 mg sample. Analytical precision was ±2.3 and ±1.8% of the measured values for total and organic carbon and ±1.6% for nitrogen. Particulate inorganic carbon (*PIC*) was determined by the difference between *PC* and *POC*. Only *POC* data will be discussed in this paper.

Colloidal Organic Carbon. A limited number of sea water samples were processed with a tangential flow ultrafiltration (UF) system (Amicon DC10LA) to investigate the molecular weight distribution of the *DOM* pool. For *DOC* fractionation, about 30 l samples were filtered aboard, immediately after collection, through 0.4 µm polycarbonate filters (Nucleopore, ∅ 142 mm) in a closed pressurized system (N_2), using a Sartorius Teflon-covered apparatus. To avoid contamination, the first 1–2 l of the filtrate were discharged. Filtered samples were then passed in cascade through two polysulphone membranes, which have nominal molecular weight cut-offs of 10 kDa (hollow-fibre cartridge, Amicon, H10P10) and 1 kDa (spiral-wound cartridge, Amicon, S10N1), respectively. Operating pressures were 20–25 psi at the inlet and 10–15 psi at the outlet of the system. UF cartridges were thoroughly cleaned, recirculating sequentially 0.1 N NaOH and 0.01 N HCl solutions for at least 30 min before and between samples and rinsing several times with about 5 l Milli-Q water. Finally, after conditioning the UF cartridges with about 1 l filtered sample, about 20 l of sample were processed and the concentrated colloidal fraction was reduced to about 2 l, thus achieving a 10-fold concentration factor.

Following this procedure, we fractionated the *DOC* pool into a low-molecular-weight or "truly dissolved" fraction (*DOC* < 1 kDa) and two colloidal size classes, operationally defined as low-molecular-weight *COC* (1 kDa < *LCOC* < 10 kDa) and high-molecular weight *COC* (10 kDa < *HCOC* < 0.4 µm). Each sample was stored frozen in duplicate into 25 ml high density polyethylene (HDPE) bottles (as previously described for *DOC*). In the laboratory, *DOC* analyses were performed on 0.4 µm polycarbonate filtered samples and their four different molecular weight fractions (>10 kDa; <10 kDa; 1–10 kDa; <1 kDa), in order to calculate partial mass balances on each cartridge. *DOC*

recovery (R, as a percentage of the initial *DOC*) was calculated according to Dai et al. (1998). For the 1 kDa cartridge, R % ranged from 87 to 120% (with an average of 101 ±8%), while for the 10 kDa cartridge, R % ranged from 83 to 117% (with an average of 100 ±8%). Overall recovery in our ultrafiltration system was close to 100% (±10%) and was within the ranges reported in the literature (Guo et al. 1994; Benner et al. 1997; Dai et al. 1998), indicating that contamination or loss of organic carbon were minimal. While this fractionation procedure is probably the best one available at the moment and the most widely used, we must note that interactions at membrane surface may lead to conformation changes, irreversible adsorption and /or self-coagulation of small molecules resulting in an overestimation of *COC* (Buffle and Leppard 1995; Guo et al. 2000).

Dissolved Free (*DFAA*) and Total Dissolved (*TDAA*) Amino Acids. Samples for total dissolved amino acids (*TDAA*) were analyzed after liquid hydrolysis in 6 N HCl at 110 °C for 22 h (modified from Parson et al. 1984). 2 ml samples were placed in glass ampoules (acid washed and muffled for 3 hours at 500 °C), sealed under a flow of N_2. Each vial was spiked with α-aminoadipic acid, norvaline and hydroxylysine as recovery standards of the acidic, neutral and basic classes, respectively (Cowie and Hedges 1992), and 2 ml of ultrapure 12 N HCl. Hydrolysates were vacuum dried and then redissolved in milli-Q water to achieve a neutral pH. *DFAA* were analyzed without preliminary hydrolysis of the samples.

DFAA and *TDAA* were determined by high performance liquid chromatography (HPLC-Perkin Elmer Series IV) and fluorimetric detection (Perkin Elmer LS4) with a gradient system of methanol/tetrahydrofuran (90:10 v/v) acetate buffer, following derivatization with o-phthaldialdehyde (OPA) and 2-mercaptoethanol (Lindroth and Mopper 1979, as modified in Pettine et al. 1999); 21 individual amino acids were separated according to this procedure (see Fig. 22.1). Daily standards in aged sea water, samples and blanks (aged sea water) were run in triplicate. The average *TDAA* blank amounted to 62 ±40 nM and was mainly due to glycine, aspartic acid, serine and alanine. Recovery for most of the amino acids was within ±10% except for asparagine, glutamine, tryptophane, histidine and methionine. In the analysis of free amino acids, glutamic acid, glutamine, aspartic acid and asparagine are separated into four distinct peaks, but the acid hydrolysis performed for analyzing total dissolved amino acids causes the deamination of asparagine (asn) and glutamine (gln) to form aspartic acid (asp) and glutamic acid (glu) plus ammonium. Therefore, in the *TDAA* analysis, the amino acids pairs (asn + asp and gln + glu) give only two peaks instead of four. Tryptophane is unstable during acid hydrolysis and may not be detected. Histidine is also partially modified by acid hydrolysis and the recovery is only 20–30% (Keil and Kirchman 1991). *DFAA* and *TDAA* are expressed as individual amino acids (nM) and as the sum of the aminoacidic molar carbon (*DFAA*-C or *TDAA*-C) and nitrogen (*DFAA*-N or *TDAA*-N) units.

Total Dissolved Carbohydrates. Total dissolved carbohydrates (*TDCHO*), including mono-, oligo- and polysaccharides, were analyzed by the MBTH method after a preliminary hydrolysis with 0.09 N HCl (20 h at 100 °C) (Burney and Sieburth 1977). This hydrolysis procedure was preferred to the stronger H_2SO_4 attack more recently proposed (Pakulski and Benner 1992; Mopper et al. 1992), mainly because it has been extensively used in estuarine and coastal waters, thus making the comparison with previous find-

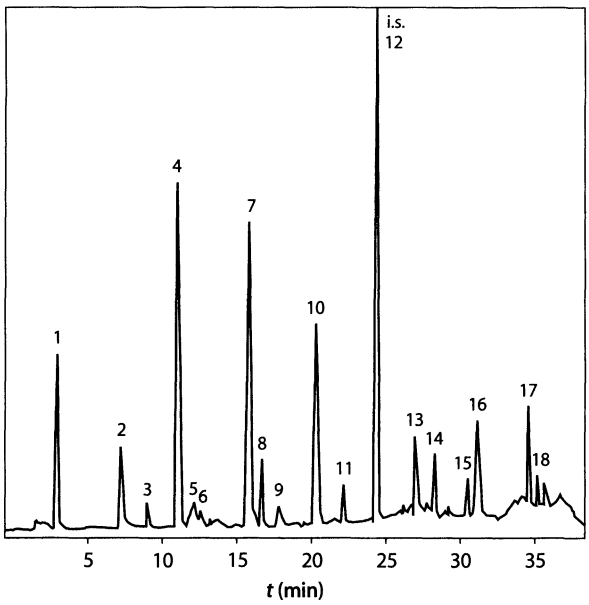

Fig. 22.1. An example of HPLC spectrum of amino acids in a sea water sample; *1*: aspartic acid; *2*: glutamic acid; *3*: asparagine; *4*: serine; *5*: histidine; *6*: glutamine; *7*: glycine; *8*: threonine; *9*: arginine; *10*: alanine; *11*: tyrosine; *12*: γ-aminobutyric acid (internal standard); *13*: valine; *14*: phenylalanine; *15*: isoleucine; *16*: leucine; *17*: ornithine; *18*: lysine; methioninsulphone, methionine, tryptophane and norvaline were not detected in this sample

ings feasible (see Pettine et al. 1999 for more details). Furthermore, polysaccharides determined by this method would more directly reflect changes in the concentration of exuded polymers (Benner 1998), which include transparent exopolymer particles actively involved in the aggregate formation (Passow and Alldredge 1994; Passow 2000). Samples were analyzed in triplicate against glucose standard solutions, and results were expressed in terms of glucose-carbon equivalents (*TDCHO*-C), by assuming 6 moles of carbon per mole of hexose. The relative standard deviation between replicate samples was usually below 5%.

22.3 Role of Organic Matter Dynamics in NA Environmental Problems

The dynamics of the *DOC* pool in the northern Adriatic basin are involved in hypoxic and anoxic crises in bottom waters and massive occurrences of mucilaginous aggregates in the water column.

Anoxic phenomena occur during summer in the western coastal waters, which are influenced by the Po River discharge. Since 1975, when nutrient loads discharged by the Po showed an abrupt increase (Marchetti 1990) as happened in other European rivers (Kempe et al. 1991), large algal blooms have occurred regularly, causing episodes of diffused anoxia at the sea bottom, which resulted in mass mortalities of benthic organisms. The spatial and temporal extensions of areas affected by anoxia have diminished in recent years (Degobbis et al. 1999), probably as a consequence of the reduction and banning of phosphorus in Italian detergents. Toxic algal species on occasion also developed, causing severe damages to mollusc cultures and threatening human health. In addition to these environmental deterioration problems that are typical of eutrophicated systems, the northern Adriatic has experienced a peculiar phe-

nomenon consisting of massive occurrences of mucilaginous aggregates. In 1989, these aggregates covered a large part of the entire surface of the NA basin (Stachowitsch et al. 1990) and drew the attention of public and scientific opinion. Large quantities of sticky mucilaginous masses affected biological, chemical and physical characteristics of the ecosystem (Degobbis et al. 1999). Part of the material floating on the sea surface was deported on beaches by wind and currents, reducing their suitability for bathing and threatening tourism. Suspended and sinking mucilaginous aggregates created serious problems for fisheries and biota. Benthic organisms suffered in many areas from suffocation due to their covering by aggregates.

The impressive mucilage events of 1989–91 stimulated many studies aimed at understanding the possible causes responsible for this phenomenon and its triggering mechanisms; however, in spite of these efforts, this phenomenon remains substantially unknown (Funari et al. 1999). Although it was reported that episodes of massive mucilage formation have been recorded for over a century (Fonda-Umani et al. 1988), the similarities between past and recent phenomena in terms of triggering factors and spatial extensions remain in doubt.

We speculated on the strict temporal parallelism between massive aggregate occurrences and changes in the formulation of detergents (Pettine et al. 1995). In 1988, in fact, phosphorus was banned from domestic detergents and substituted by zeolite A particles and about doubled polycarboxylate concentrations. These changes have further increased the N/P ratio in coastal waters, which was already unbalanced, and probably they were responsible for the shift in the phytoplankton population from dinoflagellate to diatom blooms recently reported (Degobbis et al. 1999).

Therefore, P-substitutes, while contributing to diminish the frequency and extension of anoxia in NA coastal waters, apparently cause an external forcing on biological and chemical processes, which could favour an intensification of macroaggregate occurrences. Possible effects may be on a large scale (changes in algal succession from dinoflagellate to diatoms and on their released chemical compounds; limitation of the bacterial activity due to further increase in N/P ratio and consequently increased residence time for *DOM*) as well as on a micro scale (changes in sorption, partitioning and gelling of polymers, due to the inclusion in colloidal matter of zeolite A particles and polycarboxylates).

22.4 Organic Matter Discharged by the Po River

Concentrations of dissolved and particulate organic carbon (*DOC*, *POC*) were measured in samples taken monthly for a year at two stations in the lower Po River (Figs. 22.2 and 22.3). Samples were collected at each station at two depths (about 0.5 m from surface and 2 m above the bottom) to evaluate possible variations in the water column that may affect the transport. Two major interrelated variables, solid transport and flow conditions, influenced the variability of organic matter concentrations in the water and solid phases, while the water column was reasonably homogeneous (Pettine et al. 1998).

Mass fluxes of *DOC* and *POC* to the northern Adriatic basin were calculated by four different methods. They were based on: (*a*) the mean of products of the instantaneous concentrations and the mean daily discharge of the sampling day; (*b*) the product of

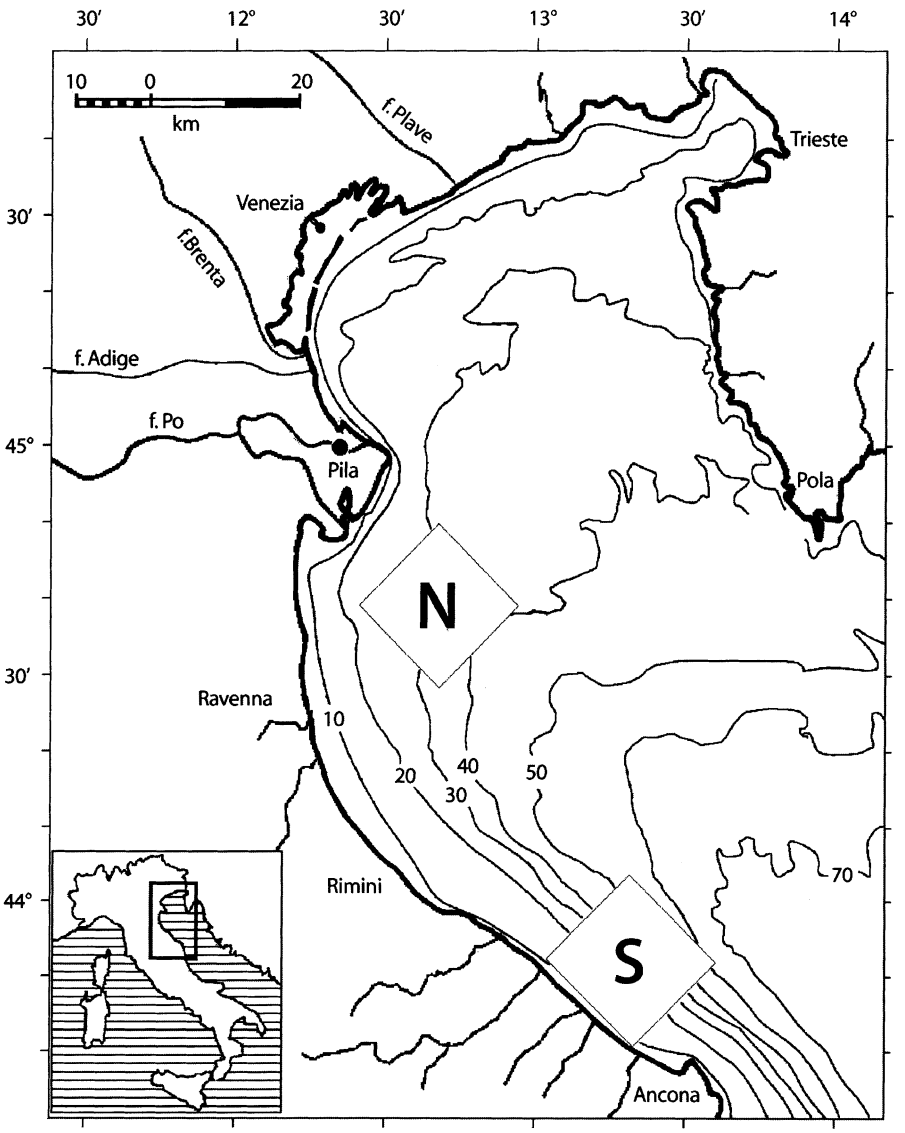

Fig. 22.2. Location of the study area. In the Po River, only the Pila station is shown; the other (Pontelagoscuro) is upstream of the river stretch plotted. In the NA system, the two investigated frontal regions, one in the north (*N*) and the other in the south (*S*), are shown

the arithmetic means of the concentrations and discharges; (*c*) the product of discharge-weighted concentrations and the mean annual discharge; and (*d*) the sum of the products of daily discharge and concentration resulting from the concentration vs. flow equation, extended to a whole year. Methods *a* and *b*, which use the arithmetic mean of instantaneous loads or arithmetic means of concentrations and discharges, give equal weight to each pair of variables. This may introduce a major bias in calcu-

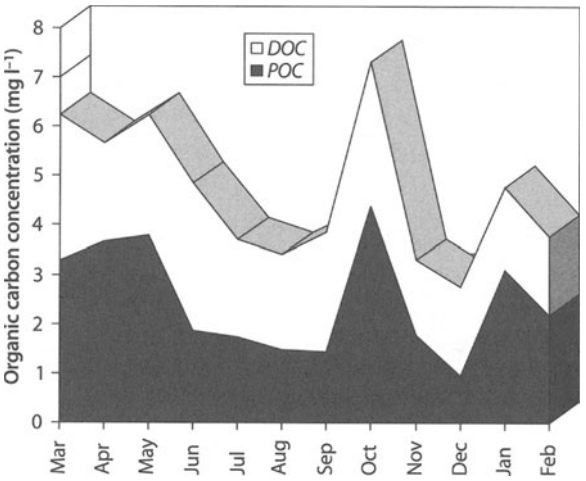

Fig. 22.3. Monthly average organic carbon concentration in the lower stretch of the Po River

lations, since concentrations measured at low discharge have the same importance as those at peak discharge. Method *c* reduces this bias and improves the evaluation of mass transport by use of discharge-weighted means; while Method *d*, based on the total discharge curve, is the more accurate has a better correlation between concentration and discharge. In our case, these different methods provided reasonably close estimations; however, results by Method *c* are more appropriate and gave fluxes of 13.4×10^4 and 12.1×10^4 tonnes year^{-1} for *POC* and *DOC*, respectively.

These loads may be compared with those discharged by the Rhone River, which shows some similarities with the Po River. Both these rivers originate from the Alps, drain large catchment areas (Rhone 96 000 km^2 and Po 70 091 km^2), have reasonably similar solid transport (about 5×10^6tonnes year^{-1}) and water discharge (55 km^3 year^{-1} in the Rhone vs. 47 km^3 year^{-1} in the Po). The *TOC* load for the Rhone was estimated to be 15×10^4 tonnes year^{-1}, one third of which is *POC* (Kempe et al. 1991). Thus, in terms of *TOC*, the Po export rate (25.5×10^4 tonnes year^{-1}) is about 1.7 times higher than that of the Rhone, making the former river the largest contributor of organic matter to the Mediterranean. The Nile River, which is another large river discharging into the Mediterranean, is extensively exploited for irrigation, hence its discharge into the sea is strongly reduced.

Organic carbon appears to be preferentially transported in the solid phase in the Po compared with the Rhone (*DOC* discharges are in fact similar, while *POC* discharges are markedly different), and this different partitioning reflects a high carbon content in the particulate matter transported by the Po, since solid transport in the two rivers is similar. These differences in the particulate and total transport of organic carbon are strongly related to marked differences in population densities in the watersheds of these rivers (232 and 84 inhabitants km^{-2} for the Po and the Rhone, respectively).

However, the *TOC* export rate by the Po (3.57 tonnes km^{-2} year^{-1}), which is given by the ratio between the calculated load and the surface extension of the river catchment, is slightly lower than the average export rate estimated for major temperate rivers

(4 tonnes km^{-2} $year^{-1}$; Meybeck 1982). Therefore, although the Po exhibits a higher *TOC* discharge compared to other Mediterranean rivers, its *TOC* export rate does not suggest a marked alteration by anthropogenic activity, pointing out that the self-purification capacity of the river is able to maintain organic matter concentrations at a low level in the lower stretch.

22.5 Interannual Variability of *DOC* Concentrations in NA Coastal Waters

DOC concentrations have been measured on more than 400 samples from surface and deep waters at different distances from the Po mouth in two frontal regions, (Pettine et al. 1999 and 2001). The location of these frontal regions, which could move depending on the seasonal period, is exemplified in Fig. 22.2 for the June 1996 cruise. The overall ranges of *DOC* concentrations and salinity resulting from all the four cruises were 70 to 280 μM and 30 to 38, respectively. Average *DOC* values in the four cruises carried out in the northern region, under the direct influence of the Po river, are shown in Fig. 22.4. In winter, deep waters assume a typical background value of 76 ±10 μM, averaged from all the available data in both the northern and southern region. This average value is well within the range 50–92 μM characteristic of deep and surface western Mediterranean (Copin-Montegut and Avril 1993), and is also very close to concentrations typical of surface oceanic waters (70–80 μM; Guo et al. 1995). These low winter concentrations suggest that the Adriatic system has a good capacity to react to external forces through degradation processes and water mass exchange between the northern and middle basins.

Surface values in winter show only a slight increase with respect to the background value, while during summer, changes appear much more marked. However, seasonal changes were found to strongly depend on the hydrological regime of the Po River, which is responsible for over 50% of the total riverine discharge into the northern Adriatic system.

In June 1996, average surface values were a factor of 2.6 and 2.1 higher than the background value (76 ±10 μM) in the northern and southern regions, respectively. In June 1997 the corresponding increasing factors were 1.7 and 1.3. This interannual vari-

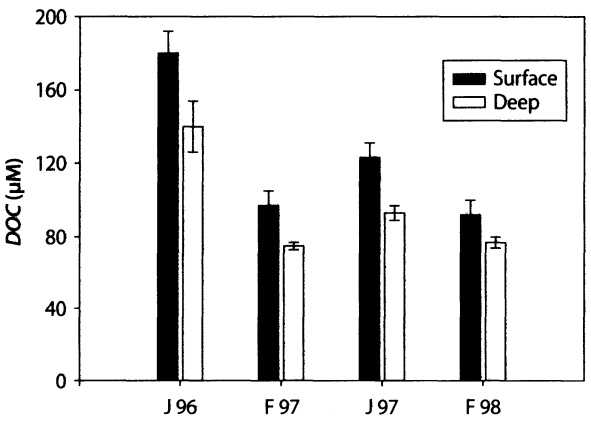

Fig. 22.4. Average *DOC* concentrations in the northern frontal region of the four cruises

ability reflects changes in the Po discharge curve during these two years: in 1996, many peaks preceded the June cruise, while in 1997 a long low flow period prevailed before the June cruise (Fig. 22.5). Accordingly, temporal patterns of chl *a* concentrations in the receiving coastal waters pointed out a much higher productivity in the spring of 1996 than in 1997, which was responsible for the higher increasing factors observed for *DOC* concentrations in the former year compared to the latter (Pettine et al. 2001).

Contrary to the increase in *DOC* concentrations that were stronger in 1996 than in 1997 (Fig. 22.6), mucous aggregates showed a much stronger occurrence in June 1997

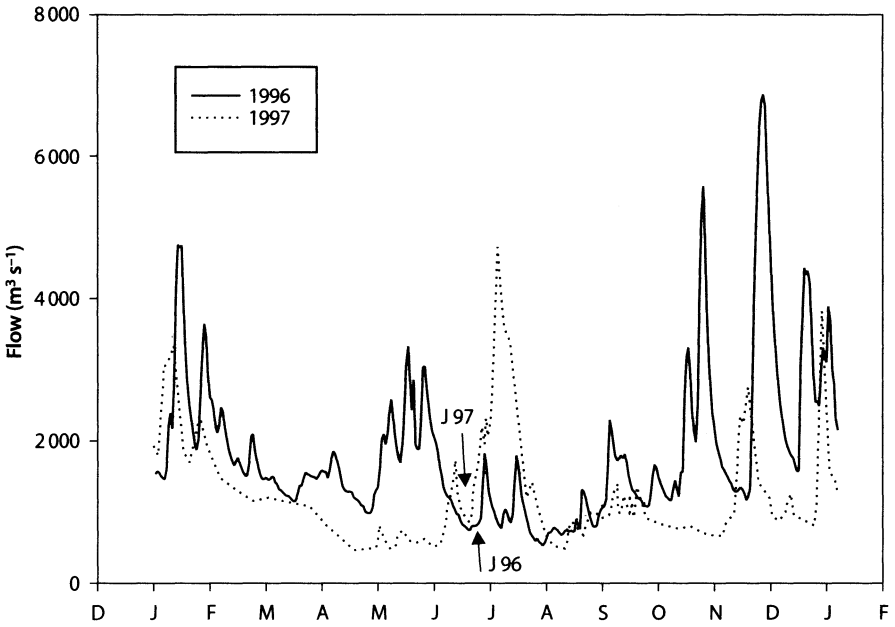

Fig. 22.5. Discharge curves of the Po River in 1996 and 1997. The two *arrows* indicate the two-year cruise period

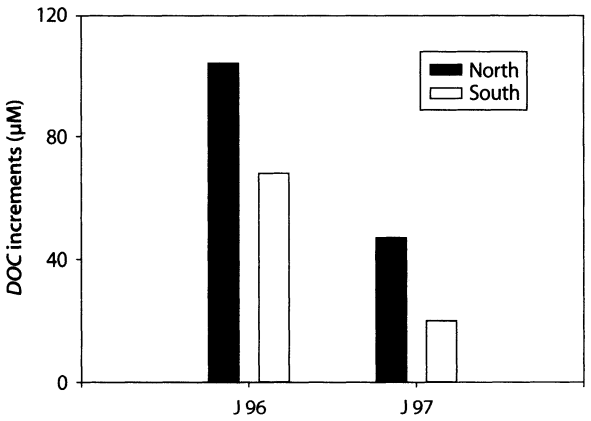

Fig. 22.6. Calculated increments (μM) in *DOC* concentrations over the background winter value of 76 μM in June 1996 and June 1997

compared to June 1996. This was confirmed by the use of the remote observing vehicle (ROV) during the cruises. The scavenging effect exerted in the water column by mucous macroaggregates may partially explain an inverse relationship between macroaggregates and dissolved *DOC* concentrations. However, these findings point out that high *DOC* levels, as in the case of June 1996, do not necessarily produce macroaggregates, strengthening the importance of the qualitative characteristics of the *DOC* pool in the mass transfer between *DOC*, *COC* and the mucous fraction.

The conclusion by Passow (2000) that TEP-precursors, which consist of strongly sulphated polysaccharides actively involved in aggregation processes, appear to be a distinct group of polysaccharides, whose production and standing stocks are uncoupled from bulk carbohydrates, further remarks the importance of the qualitative characteristics of *DOM* in the formation of aggregates. The higher sulphur level found in macroaggregates in our previous investigations (Pettine et al. 1995) is consistent with a large role played by TEP in the formation of macroaggregate.

22.6 Composition of *DOM*

Dissolved organic matter in the northern Adriatic system is characterized by the presence of a high colloidal fraction with a shift in the molecular weight distribution toward the large size fraction and a high contribution of carbohydrates to dissolved organic matter (Pettine et al. 1999 and 2001).

The average values (μM) calculated from all the data were 67 ±14 for the overall colloidal organic fraction (>1 kDa) and 39 ±13 for the truly dissolved organic fraction (*DOC* > 1 kDa). Differences between the June and February cruises were very small (Fig. 22.7). The colloidal organic carbon pool consisted of high (>10 kDa, *HCOC*) and low (1 to 10 kDa, *LCOC*) molecular weight classes. The *HCOC* fraction accounted for

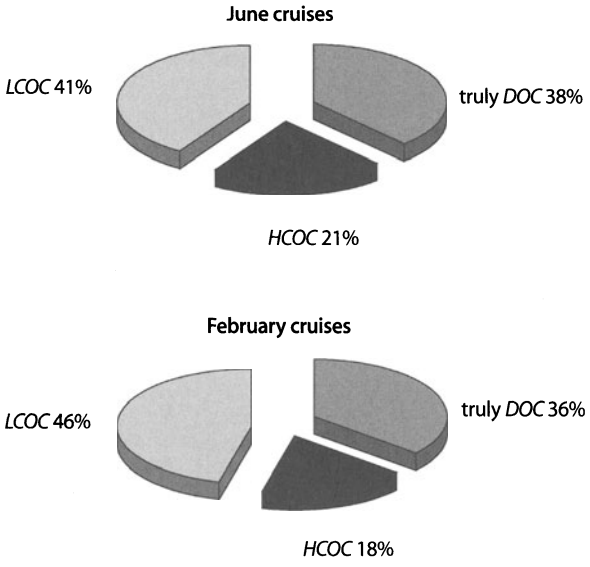

Fig. 22.7. Distribution of dissolved organic matter (<0.7 μm) between the high (*HCOC*) and low (*LCOC*) colloidal classes and truly dissolved components in the June and February cruises

21 ±5 and 18 ±6% of *DOC* in the June and February cruises, respectively. The *LCOC* fraction contributed 41 ±7 and 46 ±6% to the overall *DOC* in the June and February cruises. Both these colloidal classes were tightly correlated to *DOC* (Pettine et al. 2001).

Total dissolved carbohydrate concentrations from the two investigated areas and various cruises ranged from 6.0 to 72.4 μM in terms of carbon (average 18.3 ±12.0) and were tightly correlated to *DOC*. The entire data set (μM) was described by ($p < 0.001$):

$$TDCHO = -10.46\ (\pm 2.22) + 0.28\ (\pm 0.02)\ DOC; \quad n = 155;\ r = 0.74;\ \text{s.d.} = 8.07 \qquad (22.1)$$

The percent contributions of *TDCHO* to *DOC* were 20.3 ±10.7; 15.1 ±4.9; 18.4 ±4.3 and 14.2 ±5.0 in June 1996, February 1997, June 1997 and February 1998, respectively, with average values of 19.1 ±7.3% in the June cruises and 14.5 ±4.9% in the February cruises (Fig. 22.8).

According to the slope of Eq. 22.1, *TDCHO* is responsible for 28% of the *DOC* variations over the study period. This slope is in the high range of values reported for

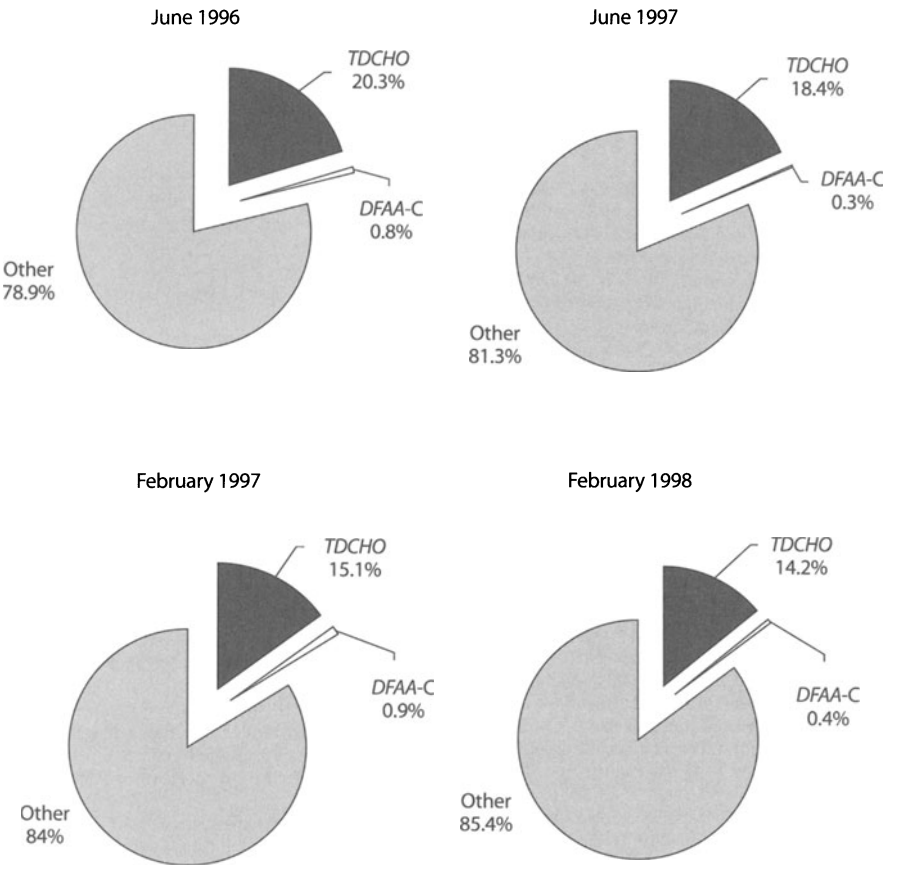

Fig. 22.8. Contributions of total dissolved carbohydrates (*TDCHO*) and free amino acids (*DFAA*-C) to *DOC* in the various cruises

TDCHO vs. *DOC* slopes, which have been found to vary from 0.09 to 0.29 (Burney and Sieburth 1977; Senior and Chevolot 1991; Pakulski and Benner 1994).

Contrary to colloidal and carbohydrate components, *DFAA* varied within the approximate range 100–400 nM reported for marine waters (Thurman 1985) and contributed <1% to *DOC* in the various cruises. However, based on a limited data set available for total dissolved amino acids (*TDAA*), they gave average carbon concentrations (μM) of 3.9 ±0.7, 5.1 ±2.5 and 2.4 ±2.1 in February 1997, June 1997 and February 1998, contributing 4.5, 4.9 and 2.9% to *DOC*, respectively.

Further investigations are needed to improve our knowledge of the qualitative characteristics of *DOM*, with particular emphasis on dominant polymeric compounds that are included in the colloidal fraction and may give rise to coagulation processes leading to the formation of macroaggregates.

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