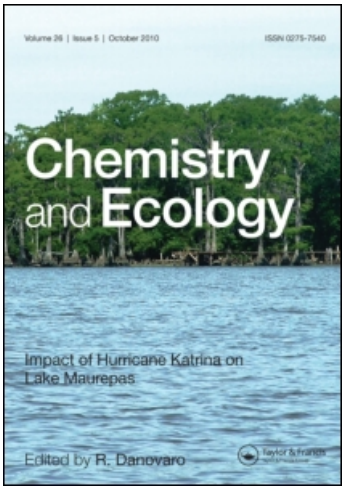

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Effect of environmental forcing on the fate of nutrients, dissolved organic matter and heavy metals released by a coastal wastewater pipeline

S. Cozzi[a]; E. Reisenhofer[b]; L. Di Monte[b]; C. Cantoni[a]; G. Adami[b]
[a] CNR - Marine Science Institute, Trieste [b] Department of Chemical Sciences, University of Trieste, Trieste, Italy

To cite this Article Cozzi, S. , Reisenhofer, E. , Monte, L. Di , Cantoni, C. and Adami, G.(2008) 'Effect of environmental forcing on the fate of nutrients, dissolved organic matter and heavy metals released by a coastal wastewater pipeline', Chemistry and Ecology, 24: 2, 87 — 107
To link to this Article: DOI: 10.1080/02757540801919354
URL: http://dx.doi.org/10.1080/02757540801919354

Chemistry and Ecology
Vol. 24, No. 2, April 2008, 87–107

Taylor & Francis
Taylor & Francis Group

Effect of environmental forcing on the fate of nutrients, dissolved organic matter and heavy metals released by a coastal wastewater pipeline

S. Cozzi[a], E. Reisenhofer[b], L. Di Monte[b], C. Cantoni[a]* and G. Adami[b]

[a] *CNR - Marine Science Institute, Trieste;* [b] *Department of Chemical Sciences, University of Trieste, Trieste, Italy*

(*Received 30 July 2007; final version received 9 January 2008*)

Discharges of nutrients, urea, dissolved organic matter and heavy metals by a sewage underwater pipeline are analysed in comparison to environmental conditions in a shallow coastal zone. Variable thermo-haline stratifications of the water column and currents in upper (2.62–34.97 cm s^{-1}) and deeper (0.83–10.91 cm s^{-1}) layers drive vertical diffusion and lateral transport of wastewaters. Loads of reactive phosphorus (0.13 tons d^{-1}) and ammonium (1.62 tons d^{-1}) by the pipeline are not negligible compared to the major river loads in the gulf. High concentrations of urea ($\leq$11.51 μmol N dm^{-3}) were found in the area of wastewater release. Ammonium uptake (6.14–534 nmol N dm^{-3} h^{-1}) strongly exceeded nitrate uptake (0.19–138 nmol N dm^{-3} h^{-1}), indicating that discharges of ammonium by the pipeline are actively assimilated by plankton community even at low levels of light. Distribution of Zn ($\leq$27.7 ppb), Cu ($\leq$25.6 ppb), Cd ($\leq$0.80 ppb) and Pb ($\leq$13.5 ppb) in the water column and the measurement of their complex-forming capacity in seawater did not indicate a persistent perturbation of the pelagic environment due to heavy metals.

Keywords: sewage disposal plant; dissolved inorganic nutrient; dissolved organic matter; urea; nitrogen uptake; heavy metals.

1. Introduction

The coastal zones are often exposed to a strong anthropogenic pressure, due to the concomitant presence of high human populations, loads of continental waters and pollutants, ship traffics, high concentrations of infrastructures, intense exploitation of the marine resources and possible introduction of non-indigenous species. Loads of nutrients and heavy metals are often among the major risk factors for the maintenance of a good ecological quality of these marine environments. Moreover, it is now recognised that the impact of these anthropogenic compounds is modulated by variable environmental conditions typical of these marine areas, as well as by long-term modification, such as the climate changes [1–6].

*Corresponding author. Email: carolina.cantoni@ts.ismar.cnr.it

ISSN 0275-7540 print/ISSN 1029-0370 online

DOI: 10.1080/02757540801919354
http://www.informaworld.com

The Gulf of Trieste has characteristics typical of the coastal zones in advanced countries. The presence of three main harbours, Trieste and Monfalcone in Italy and Koper in Slovenia, as well as industries, drainage systems and rivers cause the delivery of nutrients, dissolved organic matter and heavy metals into this shallow and semi-closed gulf. This feature constitutes a risk for the quality of coastal waters and sediments, which is in conflict with the concomitant use of this area for fishery, aquaculture and recreational activities.

Isonzo River is the major source of land-born nutrients in the Gulf of Trieste, in particular because of nitrate leaching from agricultural soils of the region [7,8]. Several studies have already pointed out that the spreading of its plume strongly affects the stratification of the water column and the production processes in this area [7,9–13]. Urban and industrial sewages have a potential role on the balance of nutrients in the Gulf of Trieste. However, their importance has been poorly studied with respect to the river inputs [14,15]. As a result of the combination between particular oceanographic conditions and nutrient loads, the Gulf of Trieste was affected in the past by dinoflagellate blooms [16] and by hypoxic and anoxic events [17–20]. Mucilage phenomenon was also observed in concomitance to the largest events in the Northern Adriatic Sea [16,21–24].

The distribution of heavy metals in the Gulf of Trieste has attracted attention, in order to understand the importance of their natural occurrence, both marine and terrigenous, with respect to the anthropogenic inputs [8,25–28]. The sediments of the area were also investigated, being a repository of several contaminants as heavy metals [29–32] and persistent organic compounds (PAHs and PCBs; [33,34]) that may be even more noxious for the benthic organisms than inorganic pollutants. As a consequence of these accumulations, severe alteration of benthic species may occur [30].

The Gulf of Trieste is also a subtropical coastal zone characterised by a pronounced seasonal cycle [7,11–13,35]. Recent studies have analysed the potential relationships between long-term changes of this marine environment and the climate modification. They include the variability of sea-level extremes, river discharges and thermohaline properties [36–38], the northward spreading of the thermophilic ichthyofauna in the Adriatic Sea [39] and long-term trend dynamics of copepods [40]. However, the interactions of these long-term ecosystem changes with the anthropogenic pressure at local scale have not been investigated, to date.

The aim of this work is to analyse the effect of the environmental conditions on the fate of nutrients, dissolved organic matter and heavy metals released by the largest wastewater pipeline of the Gulf of Trieste. The diffusion of these anthropogenic loads are analysed in comparison to meteorological conditions, physical structure of the water column, currents in the upper and deeper layers, nitrogen uptake and physicochemical partition processes. Data were collected from March 2002 to October 2003, during 7 monitoring surveys carried out in the area of wastewater release of the underwater pipeline, and during ancillary experiments carried out in controlled conditions. The high variability of environmental conditions in the Gulf of Trieste permitted the analysis of critical and favourable situations, which are usually met in subtropical coastal zones worldwide. Moreover, an estimate of nutrient and heavy metal discharges by the pipeline is shown, in order to evaluate its current importance for this coastal marine ecosystem compared to Isonzo River.

2. Materials and methods

2.1. *Study site*

The Gulf of Trieste is a semi-closed coastal area (depth <25 m) located at the northernmost end of the Adriatic Sea (Figure 1). Its oceanographic properties are highly variable as influenced

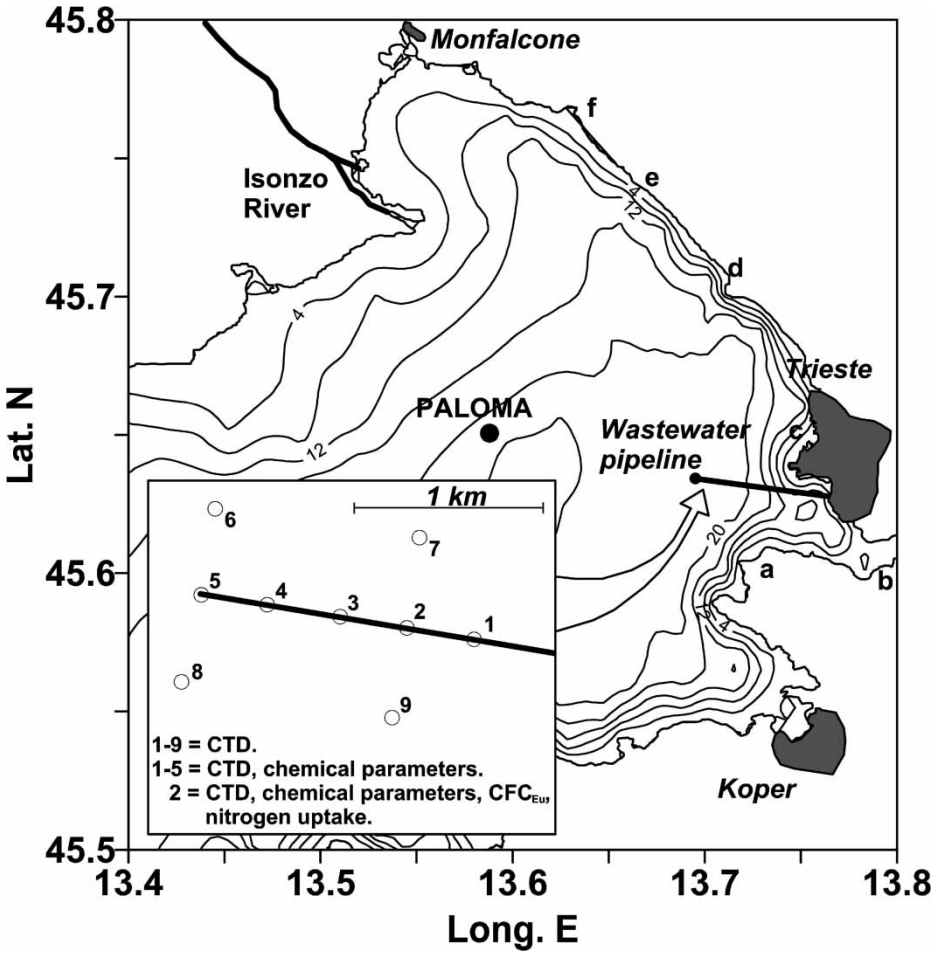

Figure 1. Wastewater pipeline in the Gulf of Trieste and the location of the sampling stations at its terminal (1–9). CNR meteorological station in the centre of the gulf (PALOMA) and location of previous monitoring coastal stations (a–f; see section 3.4) are also shown.

by a pronounced seasonal cycle, local meteorological conditions, river inputs and water masses exchange at the open boundary. The occurrence of relevant heat fluxes in this marine area also causes events of dense water formation [35,41].

The circulation of deeper waters in the gulf is mainly cyclonic, whereas variable and even opposite transports are found in the upper layer. Water exchange in the gulf at the opening is characterised by the intrusion of North Adriatic Deep Waters in the deeper layer at its southern side. The outflow of waters mostly occurs along the shallow northern coast, after mixing with riverine waters [41]. Residual currents in the gulf are in the range 1–3 cm s^{-1}, but total currents as high as 30 cm s^{-1} are found in the upper layer, because of the effects of tides and wind stress [42–44].

The largest sewage disposal plant of Trieste catches urban wastewaters and runoff corresponding to about 220,000 Equivalent Inhabitants. It discharges the wastewaters in the Gulf of Trieste, at the depth of 22 meters, through an underwater pipeline 7.5 km in length. The release of wastewaters in the water column occurs through 600 diffusers placed in the last section of the pipeline (1.5 km in length).

2.2. *Sampling strategy*

Data were collected from March 2002 to July 2003 during seven surveys, using a craft of the Coastguard of Trieste. Each time, monitoring activity was carried out in 9 sampling stations located in a small area of the gulf (about 1.4 km^2) corresponding to the last section of the pipeline (Figure 1).

Mean speed and direction of currents were measured in the upper (1 m of depth) and deeper (16 m of depth) layers using two LaGrange-drifters ('Window Shade Drogue' type). CTD profiles of salinity, temperature and density were acquired in the stations 1–9 using a Seabird 19 plus SEACAT profiler, with a vertical resolution of mean data of 20 cm.

Water samples for chemical analyses were collected at stations 1–5 at three depths (0.5, 10 m and 1 m above the bottom) using 5-litre Niskin bottles. These sampling stations were placed above the underwater pipeline. Dissolved oxygen (DO) was determined immediately after sampling by the Winkler method. Samples for the analyses of inorganic nutrients, urea and dissolved organic matter were filtered on pre-combusted (450°C, 4 h) GF/F filters. For the determination of nutrients and urea, samples were kept refrigerated in the dark and analyzed within one day the sampling. For the determination of total metals and dissolved organic matter, samples were frozen until laboratory analyses.

The complex-forming capacity of Europium(III) in seawater (CFC_{Eu}) was measured at station 2 from July 2002 to July 2003. In the same station, incubations in situ were carried out from August 2002 to July 2003 to measure the uptakes of nitrate (QNO_3) and ammonium (QNH_4) and the concentration of particulate nitrogen (PN). Moreover, two additional experiments of nitrate, ammonium and urea (QUrea) uptakes were performed in controlled conditions in August and October 2003.

2.3. *Analytical techniques*

Dissolved inorganic nutrients (NO_3, NO_2, NH_4, PO_4, SiO_2) were determined by standard colorimetric methods [45], using an ALPKEM (Flow Solution III) autoanalyzer. Dissolved inorganic nitrogen (DIN) was calculated as $NO_3+NO_2+NH_4$. Urea was determined with the same autoanalyzer by diacetyl monoxime method [46].

Dissolved organic nitrogen (DON) and phosphorus (DOP) were analyzed by UV+H_2O_2 photooxidation method [47]. After the step of oxidation, total dissolved nitrogen and phosphorus were determined with the same automated colorimetric methods used for nitrate and reactive phosphorus. The concentrations of DON and DOP were calculated as difference between total dissolved nitrogen and phosphorus and the ambient concentrations of DIN and PO_4, respectively.

Dissolved organic carbon (DOC) was determined by high-temperature catalytic oxidation method, using a SHIMADZU TOC-V analyzer equipped with an ASI-V autosampler [48]. DOC was measured in triplicate (CV $< 2\%$) against standard solutions of potassium hydrogen phthalate. The total DOC blank of the system ($2.6 \pm 1.2\,\mu mol\,C\,dm^{-3}$) and the efficiency of oxidation were checked daily by the analysis of zero-grade (Milli Q) water and standard solutions, respectively.

Total concentrations of Cu, Pb, Cd, Zn were determined by differential pulse anodic stripping voltammetry (DP-ASV) using a Metrohm Polarecord 626 and a rotating glassy carbon disk electrode Metrohm 628 [8]. Samples were pre-treated with HCl (pH ≈ 2.3) and irradiated by UV lamp to destroy organic ligands, added with $Hg(NO_3)_2$ ($0.04\,\mu mol\,dm^{-3}$) and purged with nitrogen. The samples were pre-electrolyzed in a three electrode cell equipped with a rotating working electrode (TFME), a reference (SCE) and a counter (platinum wire). TFME was anodically scanned, starting from the initial potential of -1.250 V *vs.* SCE, for the determination of Zn. Afterward, the working electrode was cleaned and the procedure was repeated with an initial potential of -0.900 V *vs.* SCE, to determine Cd, Pb and Cu, avoiding problems due to the

formation of Zn-Cu intermetallic in the mercury electrode [49]. Quantitative determination of these trace metals was performed by standard addition method.

The determination of CFC_{Eu} was performed by amperometric titration of unfiltered seawater samples with Eu(III) standard solution, using the Differential Pulsed Polarography (DPP) at dropping mercury electrode as working. For this aim, an AMEL Model 433 Polarograph was employed. The titration graph has two regions: the first one does not show amperometric signals of Eu(III), being free metal complexed by dissolved ligands or adsorbed in the particulate contained in the sample. The second one shows increasing signals of free Eu(III) due to its excess in solution. The intersection of these two linear trends is considered as the complex-forming capacity of the seawater sample.

CFC_{Eu} provides important information on the capacity of natural ligands to remove free metal ions from seawater, which is a process that strongly affects bioavailability and toxicity of metals for marine organisms. Despite different metal ions should be used to evaluate each singular complex-forming capacity, we used Europium as a general model ion because it is very effective in forming complexes with natural ligands [50,51]. Moreover, its polarographic features (sharp polarographic peaks at -0.71 V *vs*. S.C.E., corresponding to redox couple Eu^{3+}–Eu^{2+}) allow accurate analytical determinations [52].

Uptakes (nmol N dm^{-3} h^{-1}) of nitrate, ammonium and urea by the living particulate were measured using ^{15}N tracer technique. Seawater samples were placed in 500 ml polycarbonate bottles, spiked with $Na^{15}NO_3$, $^{15}NH_4Cl$ and $^{15}N_2$-Urea labelled standard solutions and incubated for 3 hours.

Incubations for the determination of QNO_3 and QNH_4 were carried out in situ at three depths (0.5, 10 m and 1 m above the bottom) and in duplicate (transparent and dark bottles). After incubations, samples were filtered on precombusted GF/F filters and dried at 60°C. Particulate nitrogen collected on filters and ^{15}N-enrichment were measured using an Europa ANCA elemental analyzer online with an Europa 20/20 isotope ratio mass spectrometer. Nitrogen uptakes were calculated according to Dugdale and Goering [53] and Owens [54].

Two additional experiments of partition N-uptake were carried out in August and October 2003, to estimate the importance of bacteria on the total assimilation of N-nutrients, using bacteria inhibitor technique [55,56]. In these cases, the uptakes of nitrate, ammonium and urea were measured in samples poisoned for 2 h with a broad-spectrum antibiotic (Penicillin-G, Streptomycin and Neomycin: SIGMA P3664; final concentration of 10 mg dm^{-3}) and in untreated (control) samples. Incubations were carried out on deck, at surface seawater temperature and at 45% of surface PAR, to mimic the ambient conditions in the upper layer. Nitrogen uptakes were afterward determined following the same methodology used for the incubations in situ.

Daily integrated precipitation, wind intensity and direction and air temperature were obtained by local meteorological stations of Marine Science Institute (CNR), located in the harbour of Trieste and in the centre of the gulf (PALOMA; Figure 1). Flow rates (daily average), nutrient and metal concentrations (monthly sampling) in the waters of Isonzo River and in the wastewaters were kindly provided by Direzione Regionale dell'Ambiente (Friuli Venezia Giulia Region), ARPA (Agenzia Regionale per la Protezione dell'Ambiente) and AcegasAps.

3. Results and discussion

3.1. *Meteorological and hydrological conditions*

Profiles of salinity, temperature and density were similar in all stations within each survey, indicating the presence of homogeneous hydrological structures of the water column in the area of

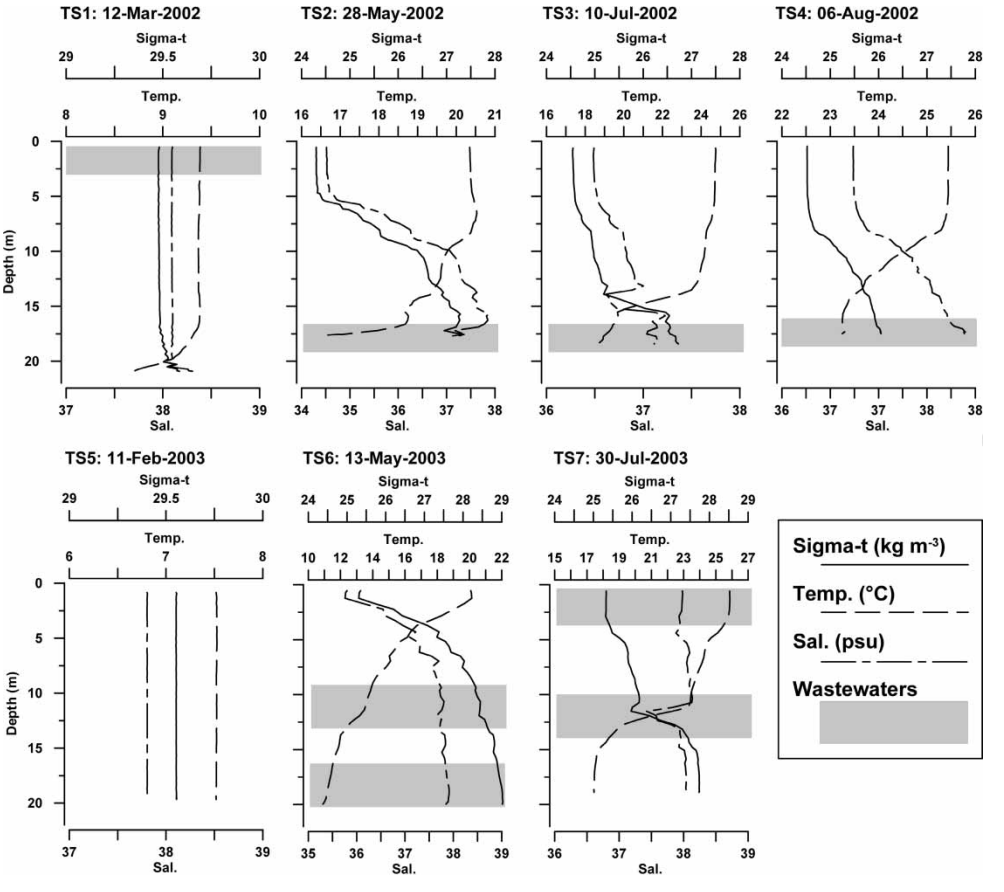

Figure 2. Density (Sigma-t; kg m-3), temperature (°C) and salinity (psu) profiles in the area of the terminal of the pipeline. The layers affected by the presence of diluted wastewaters are also shown (see section 3.2 and 3.4).

sampling. In contrast, the stratification of the water column showed pronounced temporal changes, due to the occurrence of variable thermo- and haloclines (Figure 2).

During the surveys TS1 and TS5, temperature profiles were homogeneous in most of the water column, with the exception of the presence in March 2002 of bottom waters originated by a previous cooling event. In winter, the complete mixing of the water column is favoured by the stress due to Bora wind, as in the case of the survey TS5 (daily average of wind speed $= 4.5\,\mathrm{m\,s^{-1}}$; Table 1). During spring (TS2, TS6) and summer (TS3, TS4, TS7) pronounced thermoclines were observed, being the highest difference of temperature between surface and bottom waters equal to 9°C in July 2003. The warming of waters in the upper layer during the surveys was concomitant to the seasonal increase of the air temperature in the gulf (from 3.3 to 25.9°C; Table 1).

Hydrological data showed that low salinity water bodies can reach the area of the pipeline generating strong haloclines. In case of the survey TS2, a salinity of 34.5 psu was found in the layer from 0 to 5 m of depth, after a period of intense precipitation ($39.8\,\mathrm{dm^3\,m^{-2}}$; Table 1). This value corresponded to the presence in the upper mixed layer of about 8% of freshwater, estimated on the basis of the linear dilution between freshwater and high salinity deeper waters.

Average flow rate of wastewaters discharged by the underwater pipeline is $1.39\,\mathrm{m^3\,s^{-1}}$ (AcegasAps pers. comm.). This value constitutes about 2% of Isonzo River load in the Gulf of Trieste (average $= 114 \pm 174\,\mathrm{m^3 s^{-1}}$, median $= 77\,\mathrm{m^3 s^{-1}}$ in the years 1998–2002). Even if the load of wastewater is scarce, it should be considered that it can vary in dependence of the precipitations.

Table 1. Air temperature (daily average and range; °C), wind speed (daily average, maximum value and main direction; m s^{-1}) and total precipitation in the seven days preceding the surveys (dm^3 m^{-2}).

Survey Name	Date dd-mmm-yy	Air temperature °C	Wind m s^{-1}	Precipitation dm^3 m^{-2}
		avg. (min.–max.)	avg. (max.) dir.	
TS1	12-Mar-02	13.0 (9.7–17.1)	2.3 (13) E	4.0
TS2	28-May-02	15.4 (14.5–16.3)	1.6 (7) SE	39.8
TS3	10-Jul-02	25.9 (22.4–28.9)	1.4 (4.4) WNW	5.0
TS4	06-Aug-02	21.7 (18.6–25.6)	2.8 (16) NNW	13.2
TS5	11-Feb-03	3.3 (1.4–5.7)	4.5 (16) ENE	0.0
TS6	13-May-03	21.1 (17.5–24.2)	1.8 (8) N	0.0
TS7	30-Jul-03	25.8 (22.4–29.0)	2.8 (8) W	4.6

Moreover, precipitations and tides may change the salinity (i.e. density) of the wastewaters, because of their influence on the hydrostatic equilibrium between saltier and fresher waters in the drainage system. High precipitations may cause the decrease of seawater intrusion in the drainage system and the dilution of the wastewaters: both these processes increase the buoyancy of wastewater in the seawater column.

On the whole, the stratification of the water column in the area of interest is the result of the combined effect of seasonal warming of seawater and of the retention of low salinity water bodies. However, strong winds and meteorological conditions may modify the hydrological characteristics of the area on temporal scales of hours.

The comparison between the structure of the water column and the presence of diluted wastewaters, inferred on the basis of chemical parameters (see following sections), permitted the analysis of the mechanisms of vertical diffusion under different hydrological conditions (Figure 2). During the surveys TS2, TS3, TS4 and TS6, highly stratified water columns caused the segregation of the wastewaters in the deeper layer, preventing their undesirable upwelling. In contrast, homogeneous water columns permitted an easier vertical dispersion of the wastewaters, which made their presence undetectable when wind stress induced a strong mixing (survey TS5), or caused their upwelling in calm weather conditions (survey TS1).

The direction and intensity of total currents in the area of interest were highly variable, indicating that the circulation in the upper and deeper layers plays an important role for the lateral transport of wastewaters (Figure 3). Total currents ranged from 2.62–34.97 cm s^{-1} in the upper layer, whereas they were weaker in the deeper layer (from 0.83–10.91 m s^{-1}). The strongest currents were measured during the surveys TS2 and TS4 in the upper layer (N-NE oriented) and during the surveys TS4, TS5 and TS7 in the deeper layer (E-SE oriented). These observations indicated a potential lateral transport of wastewaters toward different zones of the gulf in dependence of their depth of standing.

The statistical analysis was already used to find correlations between the distribution of pollutants in sites of the Gulf of Trieste and wind stress, rainfalls and temperature/salinity gradients [12,27]. Experimental data shown in this study clearly showed that a variable lateral transport also occur in the area of underwater pipeline, both in terms of direction and velocity. It means that the vertical diffusion of wastewaters (i.e. a density driven process) and their lateral transport (i.e. a current driven process) are linked in determining the diffusion of pollutants.

3.2. *Dissolved oxygen, nutrients and DOM*

Dissolved oxygen saturation ranged during the monitoring surveys from 70% to 123%. The strongest oxygen reductions were found in the deeper layer in July 2002 and 2003 (TS3, TS7), as a result of a more prolonged segregation of the bottom waters during the period of summer

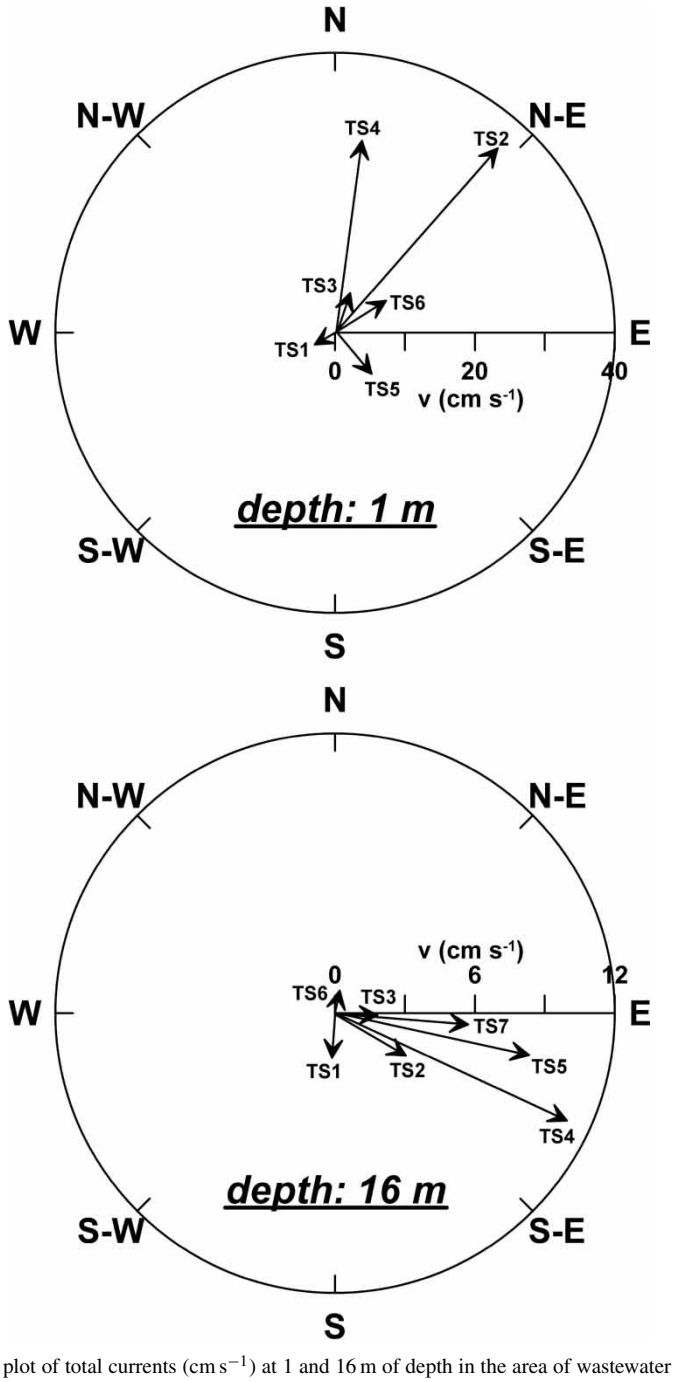

Figure 3. Vectorial plot of total currents (cm s^{-1}) at 1 and 16 m of depth in the area of wastewater pipeline, during all surveys.

stratification. However, these values indicated that oxygen conditions in the area of wastewater release were similar to those often found in the deeper waters of the Gulf of Trieste (50%–70%; [9,12,19]) and not as critical as those found during hypoxic and anoxic events [17–20].

The concentration of dissolved inorganic nutrients strongly varied in the area of interest (Figure 4). In absence of nutrient inputs due to continental waters or wastewater (survey

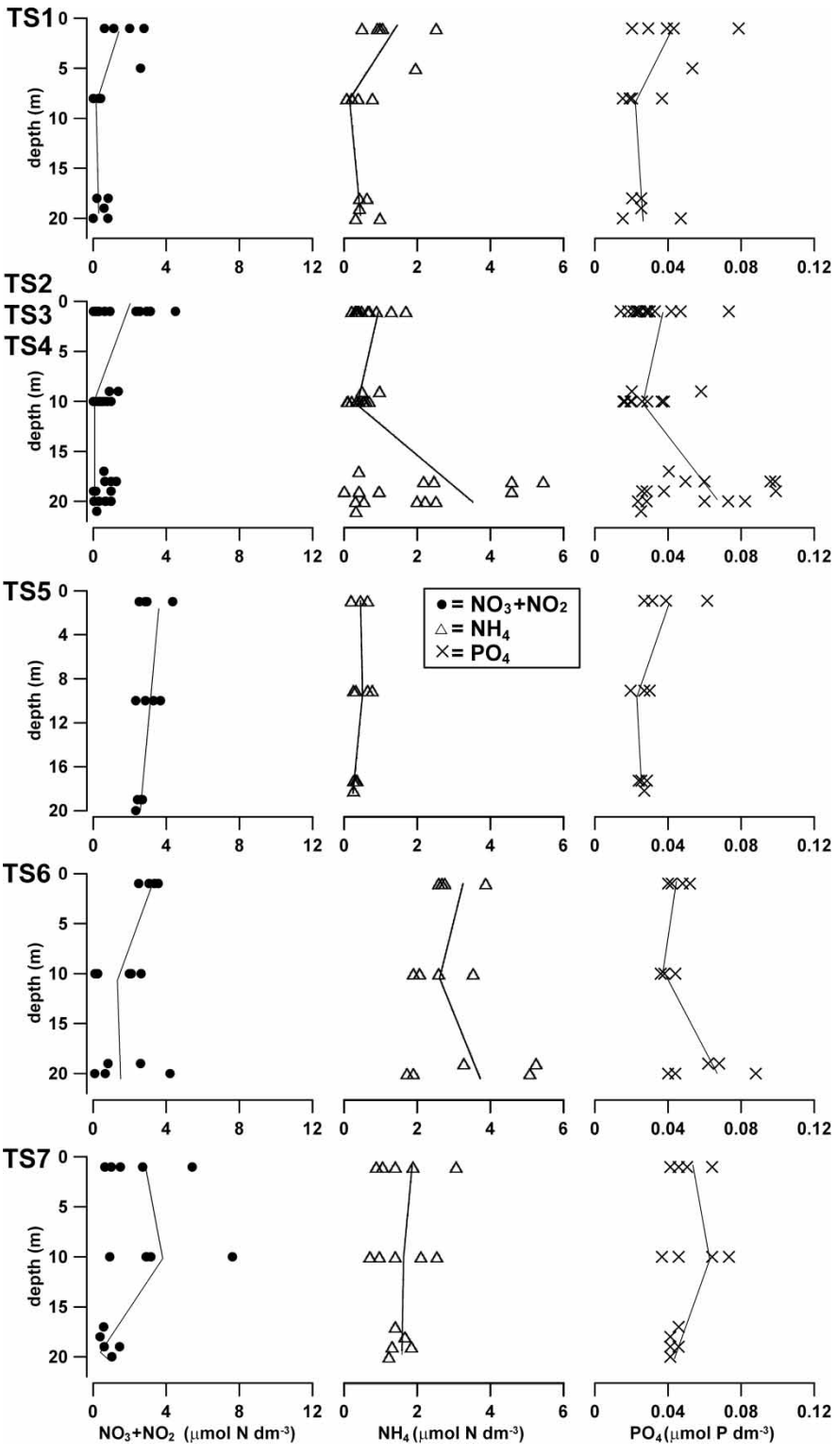

Figure 4. Concentrations ($\hat{\mathrm{I}}\frac{1}{4}$mol dm^{-3}) of nitrate + nitrite, ammonium and reactive phosphorus in the sampling stations 1–5, during surveys TS1–TS7.

TS5), concentrations of NO_3+NO_2 (average = 2.90 ± 0.60, median = $2.77\,\mu mol\,N\,dm^{-3}$), NH_4 (average = 0.41 ± 0.18, median = $0.34\,\mu mol\,N\,dm^{-3}$) and PO_4 (average = 0.03 ± 0.01, median = $0.03\,\mu mol\,P\,dm^{-3}$) were low and in the range of values of offshore waters of Northern Adriatic Sea.

During other surveys, the presence of wastewaters increased the concentrations of NH_4 ($\leq 5.45\,\mu mol\,N\,dm^{-3}$) and PO_4 ($\leq 0.11\,\mu mol\,P\,dm^{-3}$) in the water column below the main pycnocline. In these cases, concentrations of NO_3+NO_2 were not high ($\leq 4.10\,\mu mol\,N\,dm^{-3}$), being the only exception a higher value found at the intermediate depth during the survey TS7 ($7.63\,\mu mol\,N\,dm^{-3}$). High concentrations of NH_4 ($\leq 3.06\,\mu mol\,N\,dm^{-3}$) and PO_4 ($\leq 0.08\,\mu mol\,P\,dm^{-3}$) were also found in the upper layer during the surveys TS1 and TS7, in concomitance to the upwelling of the wastewaters. Peaks of nutrient concentrations in the area of interest were not characteristic of a specific sampling point, as the wastewaters are released along the whole section of the underwater pipeline covered by the sampling stations 1–5.

The concomitance of the survey TS2 with a period of high precipitation (Table 1) permitted the detection of two distinct nutrient inputs in the upper and deeper layers, respectively. In the deeper layer, discharges of NH_4 and PO_4 occurred with a ratio $NH_4/PO_4 = 24.6$ ($r^2 = 0.8897$; $n = 14$), which was similar to the ratio estimated for wastewaters by average nutrient data ($NH_4/PO_4 = 27$; Table 2), and strongly different from that of Isonzo River waters ($NH_4/PO_4 = 7$). In the upper layer, low-salinity water body was characterized by a high ratio NO_3+$NO_2/PO_4 = 39$ ($r^2 = 0.8590$; $n = 5$), typical of the surface continental waters (Isonzo River NO_3+$NO_2/PO_4 = 70$; wastewaters NO_3+$NO_2/PO_4 = 2$). This behaviour indicated that the area of the pipeline is subjected, during events of high precipitation, to a stratification originated by the runoff of the surface continental waters in the upper layer. At the same time, these events cause concomitant peaks of discharge of the wastewaters that are segregated in the deeper layer by pronounced pycnoclines.

The vertical profiles of reactive silicon in the area of the pipeline were affected neither by riverine inputs nor by wastewater discharges. Concentrations of SiO_2 ranged from 0.90 to $3.70\,\mu mol\,Si\,dm^{-3}$ in most of the water column, without significant correlations with the major continental inputs of nutrients observed during the surveys. High concentrations of SiO_2 were found in the bottom waters in July 2002 ($\leq 6.98\,\mu mol\,Si\,dm^{-3}$) and in July 2003 ($\leq 6.21\,\mu mol\,Si\,dm^{-3}$), as a result of the seasonal recycling of biogenic silicon.

Table 2. Average flow rates ($m^3\,s^{-1}$), estimated inorganic nutrient loads (tons d^{-1}) and metal loads (kg d^{-1}) of the Isonzo River and the underwater pipeline. NO_3+NO_2/PO_4 and NH_4/PO_4 molar ratios in the river water and in the wastewater.

Parameter	Isonzo River	Wastewater pipeline
Flow rates ($m^3\,s^{-1}$)	114	1.39
Nutrient loads		
NO_3+NO_2 (tons d^{-1})	13.19	0.14
NH_4 (tons d^{-1})	1.35	1.62
DIN (tons d^{-1})	14.54	1.76
PO_4 (tons d^{-1})	0.42	0.13
Molar ratios of nutrients		
NO_3+NO_2/PO_4	70	2
NH_4/PO_4	7	27
Metal loads		
Cd (kg d^{-1})	1.23	<2.4
Cu (kg d^{-1})	9.10	<12.0
Zn (kg d^{-1})	48.14	<60.0
Pb (kg d^{-1})	2.15	<24.0

On the whole, the behaviour of dissolved inorganic nutrients was affected by wastewater loads, by the presence of continental waters in the upper mixed layer and by their seasonal cycling in the marine environment. The nutrient dispersion in the water column was strongly conditioned by the formation and disruption of pycnoclines, which depends by the combined effects of seasonal warming, freshwater inputs and mixing due to meteorological forcing.

The importance of wastewater load for the balance of nutrients in the Gulf of Trieste was analysed by the comparison of its contribution with respect to that of Isonzo River (Table 2). The riverine load of DIN (14.54 tons d^{-1}) is characterised by a high content of nitrate and nitrite (13.19 tons d^{-1}); mostly as a consequence of the intense farming activity in the southern area of the region. Nitrogen load by the pipeline (1.76 tons d^{-1}) is mainly constituted by ammonium (1.62 tons d^{-1}). Despite water load by the pipeline constitutes only 2% of the river load, its contribution of NH_4 and PO_4 is not negligible, being respectively 120% and 31% of the riverine ones. Moreover, it should be considered that river and wastewater discharges have different effects on the production processes in this coastal ecosystem. The advection of river waters affects the upper mixed layer and it is strongly variable, as river loads during freshets (400–1800 m s^{-1}) are about one order of magnitude higher than during low regimes (<100 m s^{-1}; [7]). Riverine inputs of NO_3, PO_4 and SiO_2 support events of primary production, if the low-salinity water bodies are retained in the gulf and the ambient conditions are favourable [7,11,13]. The nutrient supply due to wastewater loads mainly affects the deeper waters where, in conditions of light limitation, the utilisation of ammonium by bacteria may be relevant [7,57].

The nitrogen inventory of Table 2 does not account of urea loads. Information on this nitrogen form is really scarce for the Gulf of Trieste, being restricted to few past studies in the Southern Slovenian waters [58,59]. Our data have shown, for the first time in the area of the pipeline, the behaviour of urea under different environmental conditions (Figure 5). When the water column was homogeneous and the presence of wastewaters was not detectable (survey TS5), urea was in the typical range of concentrations found in not polluted marine environments (average $= 0.73 \pm 0.28$, median $=0.68$ μmol N dm^{-3}; $n = 11$). This concentration is similar to the background

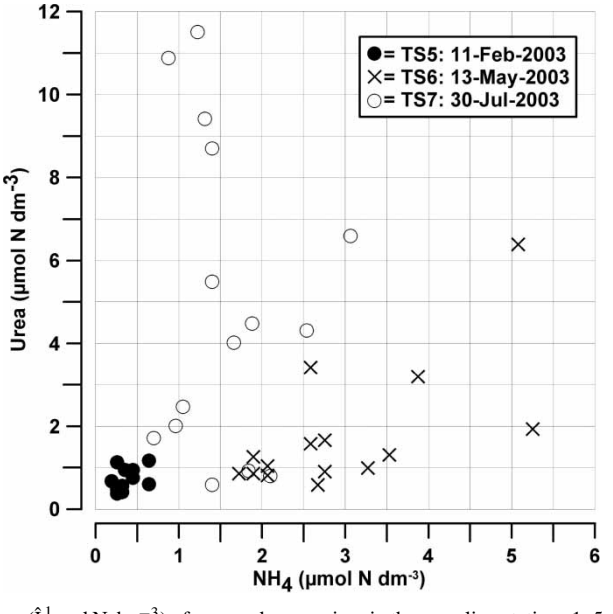

Figure 5. Concentrations (Î $\frac{1}{4}$ mol N dm^{-3}) of urea and ammonium in the sampling stations 1–5, during the surveys TS5, TS6 and TS7.

Table 3. Concentrations (μmol dm^{-3}) of DOC, DON and DOP in the area of the pipeline (Range of values; Avg $\pm$ Std = average and standard deviation; Med. = median).

	DOC (μ mol C dm^{-3})			DOC (μ mol C dm^{-3})			DOP (μ mol P dm^{-3})		
Survey	Range	Avg $\pm$ Std	Med.	Range	Avg $\pm$ Std	Med.	Range	Avg $\pm$ Std	Med.
TS1	52.6–89.8	72.8 $\pm$ 9.1	75.9	3.46–12.65	7.53 $\pm$ 2.42	6.85	0.13–0.19	0.15 $\pm$ 0.02	0.15
TS2	70.6–172.5	116.9 $\pm$ 28.7	107.4	6.61–12.14	8.90 $\pm$ 1.90	8.59	0.11–0.42	0.24 $\pm$ 0.10	0.19
TS3	80.8–154.2	110.4 $\pm$ 25.4	112.3	4.13–10.10	8.20 $\pm$ 1.57	8.69	0.15–0.58	0.25 $\pm$ 0.10	0.23
TS4	73.6–162.0	118.1 $\pm$ 29.2	117.8	6.32–18.48	11.41 $\pm$ 3.20	10.99	0.09–0.35	0.19 $\pm$ 0.08	0.18
TS5	61.7–84.4	74.6 $\pm$ 8.0	76.7	2.47–9.71	6.05 $\pm$ 2.40	5.47	0.02–0.31	0.15 $\pm$ 0.09	0.13
TS6	53.5–127.9	88.2 $\pm$ 20.1	86.6	1.03–15.61	6.71 $\pm$ 4.47	6.17	0.09–0.30	0.17 $\pm$ 0.06	0.14
TS7	86.5–156.7	112.1 $\pm$ 19.5	109.4	2.76–19.04	9.85 $\pm$ 4.87	9.49	0.10–0.29	0.21 $\pm$ 0.05	0.21

average value of 1.20 $\pm$ 1.02 μmol N dm^{-3} reported in other sites of the Gulf of Trieste by Faganeli and Herndl [59]. When the accumulation of NH_4 due to the presence of the wastewaters was observed (surveys TS6; TS7), urea-nitrogen ($\leq$11.51 μmol N dm^{-3}) reached concentrations two times higher than the ammonium-nitrogen, indicating that the inclusion of urea would strongly increase the estimated load of dissolved nitrogen by the pipeline.

The behaviour of DOC, DON and DOP in the area of wastewater release was also investigated, in order to evaluate the contribution of dissolved organic matter by the pipeline (Table 3). In absence of strong riverine and wastewater inputs and in conditions of scarce biological accumulation (survey TS5), the concentrations of DOC (average = 74.6 $\pm$ 8.0, median = 76.7μmol C dm^{-3}), DON (average = 6.05 $\pm$ 2.40, median = 5.47 μmol N dm^{-3}) and DOP (average = 0.15 $\pm$ 0.09, median = 0.13 μmol C dm^{-3}) were comparable to those reported for the oligotrophic waters of the Gulf of Trieste [59–61].

Increases of dissolved organic matter concomitant to the presence of wastewaters were observed in the deeper layer during the survey TS4 (DON = 18.48 μmol N dm^{-3}; DOP = 0.35 μmol P dm^{-3}), in the intermediate layers during the survey TS6 (DON = 14.73 μmol N dm^{-3}) and in the upper layer during the surveys TS7 (DOC = 156.7 μmol C dm^{-3}; DON = 18.14 μmol N dm^{-3}). However, our data did not show high concentrations of DOC, DON and DOP in the diluted wastewaters in the upper layer during the survey TS1 and in the deeper layer during the surveys TS2, TS3 and TS6.

Sewage discharges contribute to the balance of dissolved organic matter in the Gulf of Trieste [57]. However, the major changes of DOC, DON and DOP in the area of the pipeline were ascribable to the seasonal cycle of production processes and regeneration in this marine environment [59–61], which determines an increase of DOM in summer compared to winter (Table 3). The highest concentrations of DOC ($\leq$172.5 μ mol C dm^{-3}) were found from May to August 2002, in a period characterised by high primary production and by the appearance of mucilage in the gulf. The latest phenomenon has recurrently affected large areas of the Northern Adriatic Sea and it is not related to local wastewater loads [16,21–24].

3.3. *Fate of nitrogen loads*

The analysis of nitrogen cycling in this coastal marine environment is of basic importance for the evaluation of the impact of N-nutrients released by wastewater pipeline. For this reason, nitrate and ammonium assimilated by the living particulate were measured in the area of interest during the surveys TS4-TS7 (Figure 6).

QNO_3 ranged from 0.19 to 138 nmol N dm^{-3} h^{-1}, whereas QNH_4 ranged from 6.14 to 534 nmol N dm^{-3} h^{-1}. Vertical profiles of PN were less variable, with concentrations in the range from 1344 to 2566 nmol N dm^{-3}. Ammonium uptake (79–97% of total N-uptake) strongly

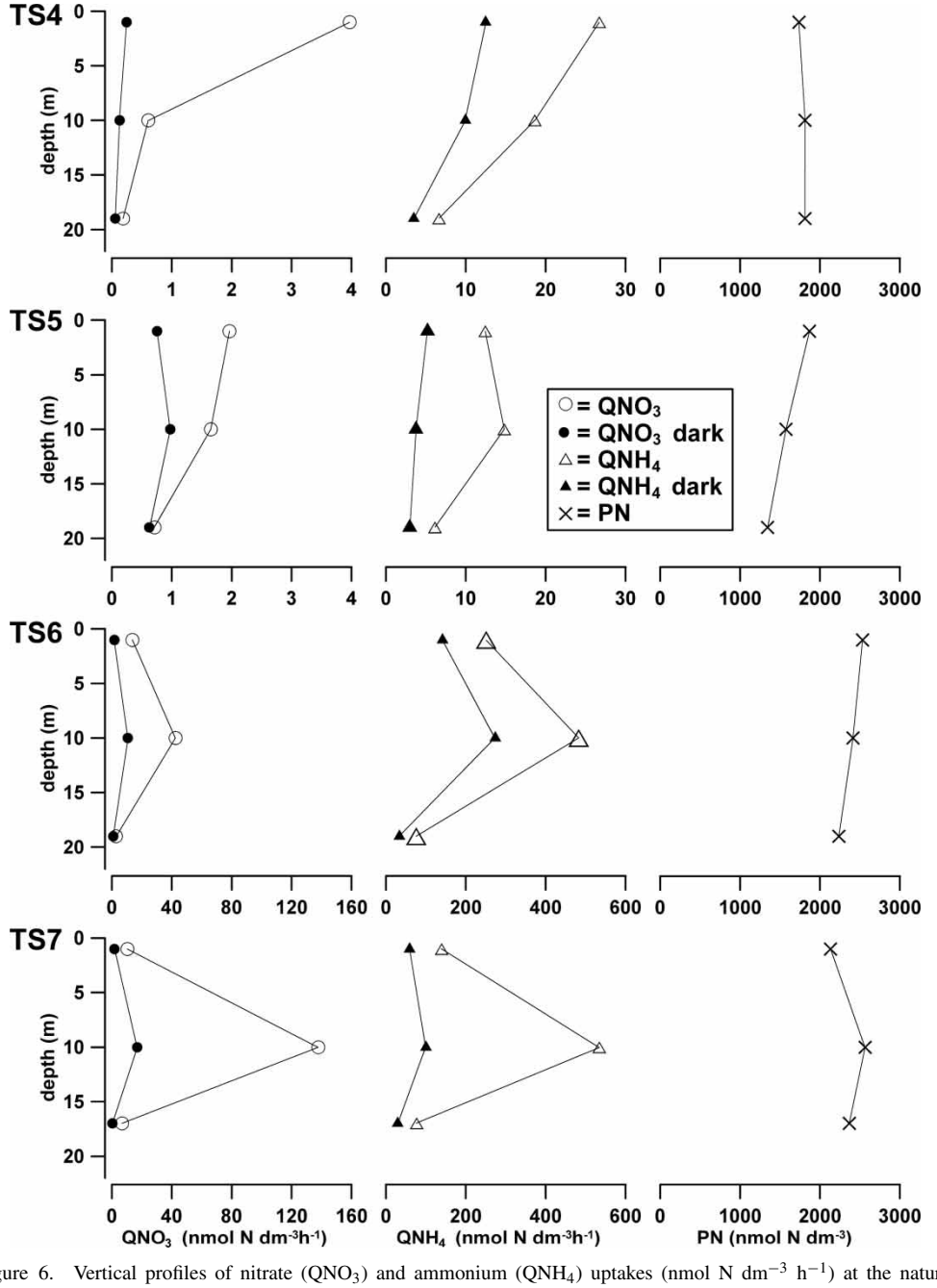

Figure 6. Vertical profiles of nitrate (QNO_3) and ammonium (QNH_4) uptakes (nmol N dm^{-3} h^{-1}) at the natural irradiance level and in the dark in the station 2, during the surveys TS4–TS7. Concentration of particulate nitrogen (PN; nmol N dm^{-3}) in the same station.

exceeded nitrate uptake (3–21% of total N-uptake) during all surveys. The highest values of QNO_3 and QNH_4 were observed in the intermediate layer during the surveys TS6 and TS7, in the presence of diluted wastewaters. This behaviour suggested that anthropogenic loads of the pipeline may enhance the assimilation of N-nutrients.

Turnover times of NO_3 and NH_4 in the area of interest were estimated as ratio between nutrient concentration and N-uptakes. In the presence of wastewaters (surveys TS4, TS6, TS7), turnover time of NO_3 ranged from 1–38 days (median = 2.5 days) and turnover time of NH_4 ranged from 0.03–2.89 days (median = 0.42 days). In absence of wastewater inputs by the pipeline (survey TS5), higher values were calculated for NO_3 (80–127 days), whereas those of NH_4 remained as low as the other cases (1.80–2.17 days).

These results can be compared with those reported by Cantoni et al. [7] for the Northern area of the gulf strongly affected by the Isonzo River plume. Low rates of NO_3 uptake often makes the circulation of water bodies the most important forcing that regulates the dispersion of this nutrient in the gulf. In contrast, the removal of NH_4 occurs on short temporal scales, preventing its wide diffusion in the area. For this reason, ammonium discharged by rivers and wastewaters should be considered as a nitrogen input that fuels the biota within this coastal zone. However, present data also showed that significant decreases of the turnover time of NO_3 may occur in the presence of wastewater loads.

The measurement of N-uptake was carried out in transparent and dark bottles, to evaluate the importance of light penetration in the water column on the assimilation of NO_3 and NH_4 (Figure 6). In the area of interest, irradiance usually varies from 30–60% of the surface PAR in the upper mixed layer, while it decreases down to 1–2% in the bottom waters at 20-25 meters of depth. In absence of light, QNO_3 ($\leq$17.01 nmol N dm^{-3} h^{-1}) and QNH_4 ($\leq$274 nmol N dm^{-3} h^{-1}) were reduced respectively by 71% and 56% compared to the uptakes at natural levels of PAR. In particular, peaks of QNO_3 in the intermediate and upper layers were always reduced almost to zero in absence of light (decreases of 75%–94%).

Light penetration in the water column has a variable effect on N-uptake by plankton communities. However, QNO_3 often decreases more than QNH_4 at low irradiance levels, as the biochemical utilisation of NO_3 for the synthesis of cellular proteins requires an additional expenditure of energy compared to NH_4 for the enzymatic reduction [62–65]. The present data confirm this observation and indicate that the light is an important forcing that regulates the uptakes of N-nutrients in this coastal marine environment.

Wastewaters are usually released by pipelines at the sea floor, to reduce the assimilation of nutrients by keeping them in deeper waters exposed to low irradiance levels. However, as in our case the major emission of nitrogen is NH_4, the efficiency of this mechanism is reduced with respect to an equivalent load of NO_3.

Concentrations of nutrients and N-uptakes were also measured in the surface waters of the area of interest in August and October 2003 (Table 4). The results of these experiments further

Table 4. PAR and seawater temperature during incubations of surface water samples collected in the area of interest. Concentrations of N-nutrients (μ mol N dm^{-3}) and uptakes (QN; nmol N dm^{-3} h^{-1}) of nitrate, ammonium and urea. Last column shows the variation of N-uptakes after poisoning of the samples with a bactericidal agent.

Date Month	PAR %	Temp. °C	Nutrient	Concentration μmol N dm^{-3}	QN nmol dm^{-3} h^{-1}	Variation nmol dm^{-3} h^{-1}
August	45	28	NO_3	0.72	3	+1
			NH_4	0.30	82	−17
			Urea	5.44	37	−28
			NO_2	0.05	–	–
			Total	6.51	122	−44 (−36%)
October	45	13	NO_3	2.93	1	0
			NH_4	3.44	21	0
			Urea	1.26	6	−4
			NO_2	0.23	–	–
			Total	7.86	28	−4 (−14%)

confirmed that high concentrations of urea (1.26 and 5.44 μmol N dm^{-3}) often occur in these coastal waters and that the uptake of urea (21%–30% of total uptake) is not negligible compared to those of NO_3 and NH_4.

After the poisoning of the samples with a bactericidal agent, the total nitrogen uptake decreased by 36% in August 2003 and by 14% in October 2003. The largest decreases of the assimilation regarded ammonium and urea, whereas the assimilation of nitrate did not significantly change in both cases. This behaviour indicates that a relevant fraction of ammonium- and urea-nitrogen was channelled toward the microbial loop, whereas the assimilation of nitrate was mostly ascribable to micro algae. This finding is an experimental confirmation of the different cycling of nitrate and ammonium that has been inferred in early oceanographic studies in the Gulf of Trieste by indirect observations on the relationships between river inputs, ^{14}C primary production and nutrient cycling [7,11].

On the whole, the uptake of N-nutrients in the area of the pipeline depends on the presence of wastewaters, as well as by their exposure to high levels of light due to upwelling. Moreover, the speciation of nitrogen forms discharged by the pipeline influences their assimilation by the plankton community.

3.4. *Heavy metals and complex-forming capacity*

The distribution of Zn (average $= 2.8 \pm 4.4$, median $= 3.0$ ppb), Cu (average $= 1.2 \pm 1.0$, median $= 0.6$ ppb), Pb (average $= 1.4 \pm 1.4$, median $= 1.6$ ppb) and Cd (average $= 0.08 \pm 0.14$, median $= 0.01$ ppb) in the area of wastewater release was the result of their natural occurrence in the coastal waters and of anthropogenic inputs due to river waters and wastewaters (Figure 7).

High concentrations of Zn ($\leq$27.7 ppb), Cu ($\leq$4.3 ppb) and Cd ($\leq$0.50 ppb) were found in the upper layer during the survey TS1, in concomitance to the increase of nutrient concentrations ascribed to the presence of wastewaters. Peaks of Zn were also found in the intermediate layer (5.2 ppb; surveys TS6) and upper layer (5.3 ppb; surveys TS7), affected by the wastewater. In contrast, the concentrations of heavy metals measured in the deeper waters during the surveys TS2, TS3 and TS4 were variable, but not significantly related to NH_4 and PO_4 inputs by the pipeline. Moreover, high concentrations of Zn found in the intermediate and deeper layers during the survey TS5 (9.1 and 7.8 ppb, respectively) were also not matched to nutrient increases.

High concentrations of heavy metals characterise the sediments of the Gulf of Trieste in areas affected by river loads, urban and industrial drainage systems and disposal of inert wastes [27,29,30,32,66]. In the area of the underwater pipeline, concentrations up to 33 and 136 μg g^{-1} were reported in the surface sediments for Cu and Zn, respectively [31]. The resuspension of this sediment can lead to high concentrations of heavy metals in the water column, which are not matched to the pattern of dissolved tracers [29]. The assessment of the environmental impact of wastewater should take in consideration the different behaviours of dissolved pollutants with respect to those associated to the particulate.

The estimate of the heavy metal loads by Isonzo River and by wastewater pipeline indicates that the latter is not negligible for the Gulf of Trieste (Table 2). However, available data for the pipeline refer to the maximal loads and thus they easily overestimate the mean contribution due to the wastewaters.

The toxic effects of metals on living organisms do not depend only by their concentrations in the marine environment, but also by their partition among different physicochemical classes: dissolved free metal, dissolved metal bounded to organic/inorganic ligands, metal adsorbed or included in colloids and particulate. Toxicity studies on Cu, Zn and Pb are usually performed by bioassays on target species in controlled laboratory conditions [67]. It was shown that the formation of complexes reduces the toxicity of Cu, but it enhances those of Hg and Cd [68].

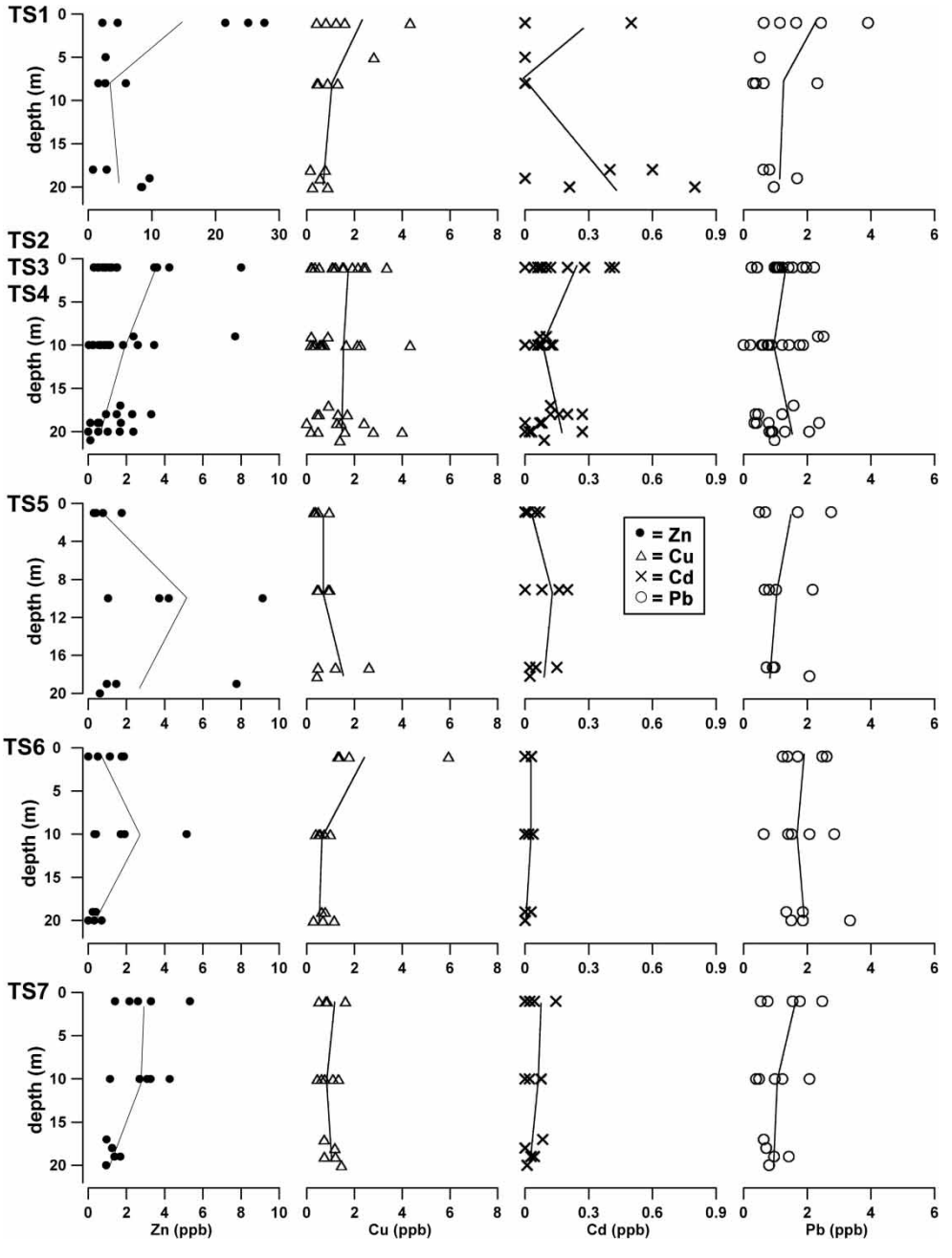

Figure 7. Concentrations (ppb) of Zn, Cu, Cd and Pb in the sampling stations 1–5, during surveys TS1–TS7.

In order to evaluate the potential capacity of natural ligands to remove the inputs of dissolved free metals from the water column, the complex-forming capacity of Eu(III) was measured in unfiltered seawater samples during the surveys TS3–TS7. CFC_{Eu} ranged from 2.2–67.8 μ mol Eu dm^{-3} (average = 29.6 ± 17.6, median = 24.84 μ mol Eu dm^{-3}). These values strongly exceeded the concentration of four heavy metals in seawater (average = 0.05 ± 0.03,

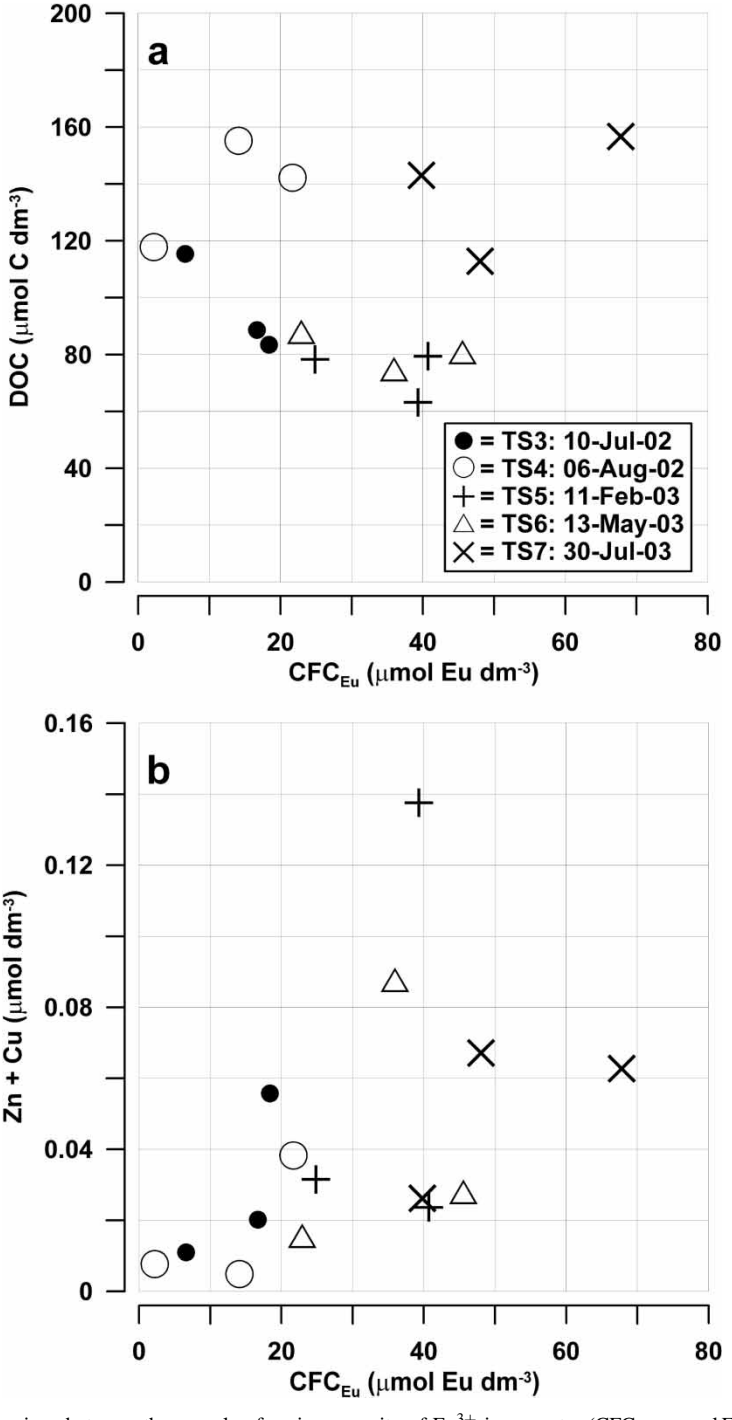

Figure 8. Comparison between the complex-forming capacity of Eu^{3+} in seawater (CFC_{Eu}; μ mol Eu dm^{-3}) and (a) the concentration of DOC ($\hat{I}\frac{1}{4}$mol C dm^{-3}) and (b) the concentration of Zn + Cu ($\hat{I}\frac{1}{4}$mol dm^{-3}) in the station 2, during surveys TS3–TS7.

Table 5. Average and standard deviation (Avg ± Std) and range of values of CFC_{Eu} (μ mol Eu dm^{-3}) in the present study and in 6 monitoring stations located along the coast of the Gulf of Trieste (station a–f; Figure 1).

Sampling site	Wastewater pipeline	Station a	Station b	Station c	Station d	Station e	Station f
Year	2002–2003	1992	1992	1992	1992	1992	1992
Avg ± Std	29.6 ± 17.6	28.0 ± 10.5	34.9 ± 10.8	27.7 ± 9.4	21.4 ± 11.9	29.1 ± 7.2	27.7 ± 7.9
Range	2.2–67.8	8.1–45.4	25.7–63.2	11.1–39.1	6.1–33.3	16.2–45.4	9.2–32.8

median = 0.04 μ mol dm^{-3}). CFC_{Eu} also corresponded to about 29% of DOC concentration, which may be considered the most important natural pool of ligands in the dissolved phase.

However, the comparison between the data of CFC_{Eu} and DOC collected during 5 surveys did not show any significant correlation (Pearson's correlation analysis: $r = 0.035$, $p > 0.05$), as variable values of complex-forming capacity was measured in the presence of high and low DOC concentrations (Figure 8a). This feature suggested that, if dissolved organic matter has a role in determining CFC_{Eu} of seawater, the presence of specific classes of dissolved organic ligands should be analysed, rather then the total concentration of DOC. In contrast, the values of CFC_{Eu} were positively related ($r = 0.507$, $p < 0.05$) to the concentrations of Zn + Cu (Figure 8b). This relationship suggested that the particulate rich of Zn and Cu, which is present in the water column because of anthropogenic inputs and of the resuspension of polluted sediments, might be capable to further adsorb dissolved free metals from the water media. In this hypothesis, the adsorption or inclusion in the particulate matter would be the most important scavenging mechanism of metals from the water column.

The values of CFC_{Eu} measured in the area of the pipeline were also compared to previous data collected in 1992 in 6 sampling stations located along the coast of the Gulf of Trieste (station a–f; Figure 1). These sampling sites include bathing waters, aquaculture areas and the harbour of Trieste. Table 5 shows that the values of CFC_{Eu} measured in the area of wastewater release do not significantly differ from those measured in these sites of the gulf characterised by variable anthropogenic impacts.

On the whole, the behaviour of the heavy metals does not indicate a persistent perturbation in the water column of the site of interest. Concentrations of Zn, Cu, Cd and Pb were not significantly high and they were strongly lower than the complex-forming capacity of the natural ligands in seawater. This capacity was high even in the presence of the highest concentrations of metals and its range of values was comparable to those previously measured in other sites of the Gulf of Trieste.

4. Conclusions

Data presented in this study have shown that the environmental conditions influence the fate of wastewaters discharged by the largest underwater pipeline of the Gulf of Trieste. The vertical diffusion of pollutants in the water column is regulated by the seasonal formation and disruption of thermoclines, as well as by the presence of low salinity water bodies in the upper mixed layer. Physical gradients in the water column, combined to the effects of tides and wind stress, influence the lateral transport of pollutants in the area. Discharges of inorganic nutrients and heavy metals by underwater pipeline are not negligible compared to the major river inputs in the Gulf of Trieste. Moreover, the uptake of nitrogen inputs of the pipeline strongly depends by the speciation of N-nutrients in the wastewaters and by the penetration of light in the water column. The concomitant release of pollutants associated to the dissolved phase and to the particulate matter points out

the need to better distinguish the different fates of these anthropogenic compounds in the marine environment.

Acknowledgements

The authors wish to thank Capitaneria di Porto – Guardia Costiera of Trieste for the craft and facilities provided during the field operations. They also thank Direzione Regionale dell'Ambiente (Friuli Venezia Giulia Region), ARPA (Agenzia Regionale per la Protezione dell'Ambiente) and AcegasAps for the environmental data.

References

[1] M.R. Preston, *Marine pollution*, in *Chemical Oceanography*, Vol. 9, J.P. Riley, ed., Academic Press, London, 1989, pp. 53–196.
[2] UNEP, *Guidelines for Integrated Management of Coastal and Marine Areas with Special Reference to the Mediterranean Basin*, UNEP Re .Seas Re .Stud., no. 161, 1995.
[3] J.C. Post and C.G. Lundin, *Guidelines for Integrated Coastal Zone Management*, Environmentally Sustainable Development Studies Monographs, no 9, The World Bank, 1996.
[4] IPCC, *The Regional Impacts of Climate Change: An assessment of vulnerability. Summary for policymakers*, R.T. Watson, M.C. Zinyowera, R.H. Moss, and D.J. Dokken, eds., A special report of Intergovernmental Panel on Climate Change, Working Group II. OMM, WMO, PNUE, UNEP, 1997.
[5] M. Elliott, *Biological pollutants and biological pollution – an increasing cause of concern*, Marine Poll. Bull. 46 (2003) pp. 275–280.
[6] R. Kay and J. Alder, *Coastal Planning and Management*, 2nd edn, Taylor and Francis, London, New York, 2005.
[7] C. Cantoni et al., *Short-term variability of primary production and inorganic nitrogen uptake related to the environmental conditions in a shallow coastal area (Gulf of Trieste, N Adriatic Sea)*. Oceanol. Acta 26 (2003), pp. 565–575.
[8] E. Reisenhofer, G. Adami, and A. Favretto, *Heavy metals and nutrients in costal, surface seawaters (Gulf of Trieste, North Adriatic Sea): An environmental study by factor analysis,* Fresenius' J. Analyt. Chem. 354 (1996), pp. 729–734.
[9] R. Olivotti, J. Faganelli, and A. Malej, *Eutrophication of coastal waters, Gulf of Trieste,* Water Sci. Technol. 18 (1986), pp. 303–316.
[10] M. Gilmartin, and N. Revelante, *The phytoplankton of the Adriatic Sea: standing crop and primary production*, Thal. Jugoslavica 19 (1983), pp. 173–188.
[11] A. Malej et al. *Phytoplankton responses to freshwater inputs in a small semi-enclosed gulf (Gulf of Trieste, Adriatic Sea)*, Marine Ecol. Progr. Series 120 (1995), pp. 111–121.
[12] P. Barbieri et al., *Survey of environmental complex systems: pattern recognition of physicochemical data describing coastal water quality in the Gulf of Trieste*, J. Environ. Monitor. 1 (1999), pp. 69–74.
[13] P. Mosetič, S. Fonda Umani, and L. Kamburska, *Plankton variability in the Gulf of Trieste (Northern Adriatic)*, Arch. Oceanogr. Limnol. 23 (2002), pp. 7–19.
[14] E. Reisenhofer et al., *Nutrient distribution in locations of the Gulf of Trieste (northern Adriatic Sea) suspected of pollution*, Toxicol. Environ. Chem. 68 (1999), pp. 307–320.
[15] S. Cozzi et al., *Matching monitoring and modelling in the Gulf of Trieste (Italy)*, Marine Poll. Bull. 48 (2004), pp. 587–592.
[16] K.G. Sellner and S. Fonda Umani, *Dinoflagellate blooms and mucilage production*, in *Ecosystem at the Land-Sea Margin – Drainage Basin to Coastal Sea*, T.C. Malone, A. Malej, L.W. Harding, N. Smodlaka, and R.E. Turner, eds., Coastal and Estuarine Studies 55, American Geophysical Union, Washington DC, 1999, pp. 173–206.
[17] J. Faganeli et al., *Bottom layer anoxia in the central part of the Gulf of Trieste in the late summer of 1983*, Marine Poll. Bull. 16 (1985), pp. 75–78.
[18] M. Stachowitsch, *The Gulf of Trieste: A sensitive ecosystem*, Nova Thalassia 8 (1986), pp. 221–235.
[19] F. Aleffi et al., *Oxygen conditions in the Gulf of Trieste (High Adriatic),* in *Marine Coastal Eutrophication*, R.A. Vollenweider, R. Marchetti, and R. Viviani, eds., Elsevier, Amsterdam, 1992, pp. 431–440.
[20] G. Orel, S. Fonda Umani, and F. Aleffi. *Ipossie e anossie di fondali marini L'Alto Adriatico e il Golfo di Trieste*, Regione Autonoma Friuli-Venezia Giulia, Direzione Regionale dell'Ambiente, 1993.
[21] R.A. Vollenweider, R. Marchetti, and R. Viviani. *Marine Coastal Eutrophication*, Elsevier, Amsterdam, 1992.
[22] A. Malej et al., *Changes in particulate and dissolved organic matter in nutrient-enriched enclosures from an area influenced by mucilage: The northern Adriatic Sea*, J. Plankton Res. 25 (2003), pp. 949–966.
[23] S. Cozzi et al., *Dynamics of the oceanographic properties during mucilage appearance in the northern Adriatic Sea: analysis of the 1997 event in comparison to earlier events*, J. Marine Systems 50 (2004), pp. 223–241.
[24] M. Giani, D. Degobbis, and A. Rinaldi, *Mucilages in the Adriatic and Tyrrhenian Seas*, Sci. Total Environ. 353 (2005), pp. 1–380.
[25] E. Reisenhofer, G. Costa, and G. Honsell, *Electroanalytical determination of heavy metals in the Bay of Muggia: correlation with environmental data*, Defence Res. Information Centre Trans., 6548 (1982).
[26] L. Favretto et al., *Terrigenous debris and mussel pollution. A differentiation based on trace element concentration by means of multivariate analysis*, Analyt. Chim. Acta 344 (1997), pp. 251–259.

[27] P. Barbieri et al., *A chemometric survey of three sites in Muggia Bay (Northern Adriatic Sea): meteorological effects on heavy metal patterns in surface costal waters*, Fresenius' J. Analyt. Chem. 361 (1998), pp. 349–352.
[28] G. Adami et al., *Levels of cadmium and zinc in hepatopancreas of reared Mytilus galloprovincialis from the Gulf of Trieste (Italy)*, Chemosphere 48 (2002), pp. 671–677.
[29] E. Colizza, G. Fontolan, and A. Brambati, *Impact of a coastal disposal site for inert wastes on the physical marine environment, Barcola-Bovedo, Trieste, Italy*, Environ. Geol. 27 (1996), pp. 270–285.
[30] G. Adami et al., *Bivalves and heavy metals in polluted sediments: A chemometric approach*, Water Air Soil Pollut. 99 (1997), pp. 615–622.
[31] S. Covelli et al., *Anthropogenic markers in the Holocene stratigraphic sequence of the Gulf of Trieste (northern Adriatic Sea)*, Marine Geol. 230 (2006), pp. 29–51.
[32] S. Covelli, and G. Fontolan, *Application of a normalization procedure in determining regional geochemical baselines*, Environ. Geol. 30, (1997), pp. 34–45.
[33] G. Adami et al., *New data on organic pollutants in surface sediments in the harbour of Trieste*, Annali di Chimica – J. Analyt. Environ. Chem. 88 (1998), pp. 745–754.
[34] G. Adami et al., *Detecting and characterising sources of persistent organic pollutants (PAHs and PCBs) in surface sediments of an industrialized area (harbour of Trieste, northern Adriatic Sea)*, J Environ. Monitor. 2 (2000), pp. 261–265.
[35] HMSO, *Meteorological Office Weather in the Mediterranean, General Meteorology*, London: Her Majesty's Stationery Office, Pub. 391, Vol. 1, 1962.
[36] F. Raicich, *Recent evolution of sea-level extremes at Trieste (Northern Adriatic)*, Continental Shelf Res. 23 (2003), pp. 225–235.
[37] M.V. Struglia, A. Mariotti, and A. Filograsso, *River discharge into the Mediterranean Sea: climatology and aspects of the observed variability*, J Climate 17 (2004), pp. 4740–4751.
[38] V. Malačič et al., *Interannual evolution of seasonal thermohaline properties in the Gulf of Trieste (northern Adriatic) 1991-2003*, J Geophys. Res. 111 (2006), C08009; doi: 10.1029/2005JC003267.
[39] J. Dulcic et al., *The effect of the hemispheric climatic oscillations on the Adriatic ichthyofauna*, Fresenius Environ. Bull. 13 (2004), pp. 293–298.
[40] L. Kamburska, and S. Fonda-Umani, *Long-term copepod dynamics in the Gulf of Trieste (Northern Adriatic Sea): recent changes and trends*, Climate Res. 31 (2006), pp. 195–203.
[41] V. Malačič, and B. Petelin, *Regional Studies, Gulf of Trieste*, in *Physical Oceanography of the Adriatic Sea. Past, Present and Future*, B. Cushman-Roisin, M. Gačič, P.M. Poulain, A. Artegiani, eds., Kluwer Accademic Publishers, Dordrecht, Boston, London, 2001, pp. 167–181.
[42] F. Mosetti and N. Purga, *Courants côtier de différente origine dans un petit golfe (Golfe de Trieste)*, Boll. Oceanol Teor Appl. 8 (1990), pp. 51–62.
[43] F. Mosetti and P. Mosetti, *Measurements on wind driven circulation in the North Adriatic Sea*, Boll. Oceanol. Teor. Appl. 8 (1990), pp. 251–261.
[44] R. Rajar and M. Četina, *Modelling of tidal and wind-induced currents and dispersion in the northern Adriatic*, Acta Adriatica 32 (1991), pp. 785–812.
[45] M. Grasshoff, *Determination of nutrients*, in *Methods of Seawater Analysis*, K.Grasshoff, M. Ehrhardt, K. Kremling, eds., Verlag Chemie, Weinheim, 1983, pp. 125–187.
[46] S. Cozzi, *A new application of the diacetyl monoxime method to the automated determination of dissolved urea in seawater*, Marine Biol. 145 (2004), pp. 843–848.
[47] T.W. Walsh, *Total dissolved nitrogen in seawater: A new-high-temperature combustion method and a comparison with photo-oxidation*, Marine Chem. 26 (1989), pp. 295–311.
[48] M. Pettine, L. Patrolecco, M. Manganelli, S. Capri, and M.G. Farrace, *Seasonal variations of dissolved organic matter in the northern Adriatic Sea*, Marine Chem. 64 (1999), pp. 153–169.
[49] E. Barendrecht, *Stripping Voltammetry*, in *Electroanalytical Chemistry*, A.J. Bard, ed., Vol. 2, Marcel Dekker, New York, 1967, pp.77–78.
[50] L. Carlsen et al., *Interaction between europium ions and selected size fraction of humic acids*, Chemosphere 33 (1996), pp. 659–670.
[51] M. Norden, J.H. Ephraim, and B. Allard, *Europium complexation by an aquatic fulvic acid – effects of competing ions*, Talanta 44 (1997), pp. 781–786.
[52] L. Sudarshan, *Polarography of Europium(III) in various supporting electrolytes*, Fresenius' J. Analyt. Chem. 279 (1976), pp. 203–204.
[53] R.C. Dugdale and J.J. Goering, *Uptake of new and regenerated forms of nitrogen in primary productivity*, Limnology Oceanogr. 12 (1967), pp. 196–206.
[54] N.J.P. Owens, *Rapid and total automation of shipboard ^{15}N analysis: examples from the North Sea*, J. Exp. Marine Biol. Ecol. 122 (1988), pp. 163–171.
[55] J.J. Middelburg and J. Nieuwenhuize, *Uptake of dissolved inorganic nitrogen in turbid, tidal estuaries*, Marine Ecol. Progress Series 192 (2000), pp. 79–88.
[56] J.J. Middelburg and J. Nieuwenhuize, *Nitrogen uptake by heterotrophic bacteria and phytoplankton in the nitrate-rich Thames estuary*, Marine Ecol. Progress Series 203 (2000), pp. 13–21.
[57] J. Faganeli and V. Turk, *Behaviour of dissolved organic matter in a small, polluted estuary*, Scientia Marina 53 (1989), pp. 513–521.
[58] J. Faganeli and Z. Smrkolj, *In situ urea utilization in the sea water in the Gulf of Trieste (North Adriatic)*, Rapp. Comm. int. Mer Médit. 28 (1983), pp. 125–127.

[59] J. Faganeli and G. Herndl, *Dissolved organic matter in the waters of the Gulf of Trieste (Northern Adriatic)*, Thalass. Jugoslavica 23 (1991), pp. 51–63.
[60] S. Terzič, M. Ahel, G. Cauwet, and A. Malej, *Group-specific phytoplankton biomass/dissolved carbohydrate relationships in the Gulf of Trieste (northern Adriatic)*, Hydrobiologia 363 (1998), pp. 191–205.
[61] S. Fonda Umani et al., *First measurements of the main energetic fluxes in the planktonic system of the Gulf of Trieste: Autumn 1998*, Biol. Marina Mediterr. 7 (2000), pp. 180–195.
[62] J.J. Mc Isaac and R.C. Dugdale, *Interactions of light and inorganic nitrogen in controlling nitrogen uptake in the sea*, Deep-Sea Res. Oceanogr. Abstr. 19 (1972), pp. 209–232.
[63] W.P. Cochlan, P.J. Harrison, and K.L. Denman, *Diel periodicity of nitrogen uptake by marine phytoplankton in nitrate-rich environments*, Limnol. Oceanogr. 36 (1991), pp. 1689–1700.
[64] W.P. Cochlan, N.M. Price, and P.J. Harrison, *Effects of irradiance on nitrogen uptake by phytoplankton: comparison of frontal and stratified communities*, Marine Ecol. Progress Series 69 (1991), pp. 103–116.
[65] E. Wada and A. Hattori, *Nitrogen in the sea: forms, abundances and rate processes*, CRC Press, Boca Raton, Florida, 1991.
[66] V. Solis-Weiss, F. Aleffi, N. Bettoso, P. Rossin, G. Orel, and S. Fonda-Umani, *Effects of industrial and urban pollution on the benthic macrofauna in the Bay of Muggia (industrial port of Trieste, Italy)*, Sci. Total Environ. 328 (2004), pp. 247–263.
[67] L. Bat et al., *Toxicity of zinc, copper and lead to Idotea baltica (Crustacea, Isopoda)*, Turkish J. Biol. 23 (1999), pp. 465–472.
[68] J. Sorvari and M. Sillanpää, *Influence of metal complex formation on heavy metal and free EDTA and DTA acute toxicity determined by* Daphnia magna, Chemosphere 33 (1996), pp. 1119–1127.