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Trace metal distributions in shelf waters of the northwestern Black Sea

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Abstract

Measurements of dissolved and leachable particulate trace metals (Mn, Fe, Co, Pb, Cd, Zn, Cu and Ni) and total particulate Mn and Fe were made on seawater samples collected from the northwestern Black Sea during the EROS 2000 expedition conducted in July–August 1995. The investigation concentrated on waters of the shelf and shelf edge, but included one deeper water (1440 m) station. In the oxic layer of the deep station, the suspended particulate fractions of Mn and Fe were a major part of the total metal mass, consistent with the presence of the “Fine Particle Layer” which forms on the shelf and spreads all over the Black Sea with intensities decreasing from the coast. Dissolved and total particulate concentrations were, respectively, Mn, 0.69–9.6, 1.2–29; Fe, 0.79–3.03, 2.3–7.4 nM. Dissolved Cu and Ni concentrations were relatively high (1–8 and 8–12 nM, respectively), and did not show any depletion in surface oxic waters, possibly as a result of strong organic complexation. Dissolved Pb concentrations (100–200 pM) were higher than were generally found on the shelf. This was attributed to atmospheric inputs combined with less efficient scavenging of metals in these low SPM waters. The distribution of dissolved Co closely resembled that of dissolved Mn reflecting coupling through oxidation of Mn. Concentrations of dissolved Cd and Zn were low in surface water (0.07–0.09 and 0.9–2.0 nM, respectively), and increases in concentrations with depth were sharply reversed around the top of the redoxcline. For most metals (Mn, Fe, Co, Pb, Cu, Cd, Zn) dissolved concentrations were low in the anoxic layers as a result of solubility by formation of, or association with, solid sulphide phases. Dissolved Ni was not affected by sulphide precipitation. At most of the shelf stations there were clear enhancements of dissolved Mn and Fe in the deepest waters, consistent with other evidence that significant benthic fluxes of these metals arise through the redox conditions in the region of the sediment-water interface. In the shelf water column, dissolved Mn and Fe concentrations

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ranged between 1.2 and 1350 and between 0.4 and 181 nM, respectively; the highest concentrations were found near the bottom. Particulate concentrations of Mn and Fe were high, implying high oxidation rates of Mn(II) and Fe(II) and/or high supply rates from rivers. Total particulate concentrations of Mn and Fe were 0.7–1050 and 2.3–2650 nM, respectively; the highest concentrations were found in surface and bottom waters. The distributions of particulate Mn and Fe were consistent with the isopycnal transport of Mn and Fe oxyhydroxides from the shelf by the coastal circulation. Distributions of other trace metals (Co, Pb, Cu, Ni, Cd, Zn) were considerably influenced by riverine inputs. Relatively high dissolved and available particulate metal concentrations were generally found in surface waters at stations directly influenced by the Danube River. Some trace metals (Co, Ni, Cd and Zn) were influenced by Mn and Fe cycling and increases in their dissolved concentrations occurred at a number of stations near the sediment–water interface. Dissolved and available particulate metal concentrations (nM) at stations on the shelf were, respectively: 0.171–1.80, 0.003–0.437 (Co); 0.014–0.614, 0.010–1.48 (Pb); 7.6–28.8, 0.048–3.75 (Cu); 11.0–17.5, 0.018–2.10 (Ni); 0.033–0.161, 0.003–0.063 (Cd); 1.01–8.33, 0.135–7.58 (Zn). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Metals; Nutrients; Eutrophication; Anoxia; Danube river; Black Sea

1. Introduction

The Black Sea has become a focus of concern regarding the potential effects on its ecosystem of contaminant substances introduced from the industrialized areas along its coastline. Over the last 20 years, the urban and industrial development of the Danube Catchment area—together with the attendant intensification of agriculture—has raised the level of inorganic nitrogen and phosphorus inputs to the adjoining coastal areas so much as to upset the previous dynamics of nutrient, oxygen, pH and organic carbon regulation in these waters (Sur et al., 1996; Cociasu et al., 1996). Moreover, the recent damming of the Danube river has decreased significantly the riverine load of silica to the northwestern Black Sea and seems to be responsible for dramatic shifts in phytoplankton species composition from diatoms (siliceous) to coccolithophores and flagellates (non-siliceous) (Humborg, 1997). Other manifestations of marine eutrophication include an increase in the overall quantities of phytoplankton (Humborg, 1997; Velikova et al., 1999) as well as in the frequency and intensity of blooms of potentially toxic species (Gomoiu, 1985; Jenkinson, 1989), a reduction in zooplankton species diversity (Bochdansky and Herndl, 1996) and changes in the structure of the benthic communities (Gomoiu, 1985).

Although all the stages of eutrophication have been documented in the western Black Sea environment, less attention has been paid to the impact of physical dynamics on eutrophication effects. The surface circulation in the Black sea is considered to be driven by a seasonal thermohaline circulation (Stanev, 1990; Grégoire et al., 1998) acting in concert with the cyclonic wind field (Moskalenko, 1976; Klimok and Makeshov, 1993). The general circulation in the western basin is cyclonic and the main gyre follows approximately the continental slope. However, mesoscale circulation features, including meanders, eddies and filaments develop along the periphery of the Rim Current (Özsoy and Ünlüata, 1997). One frequently observed feature is an anticyclonic eddy located on the shelf, south of the Danube delta. This recurrent eddy is considered responsible for retaining large amounts of fresh water close to the coast and thus enhancing eutrophication effects (Grégoire et al., 1998). In spring, stratification of the water

column starts to develop and organic-rich aggregates, which accumulate at or around the pycnocline, are rapidly colonized by bacteria (Alldredge and Crocker, 1995; Decho and Herndl, 1995; Leppard, 1995; Rath et al., 1998). With the breakdown of water column stability occurring in the autumn, the organic-rich aggregates sink down the water column, carrying with them high concentrations of microorganisms. Increased production and sedimentation of organic material has led to a greater incidence of marked oxygen depletion and even anoxia in near bottom waters of the northwestern shelf (Friedl et al., 1998). Fluctuations of the redox conditions in the water column and sediment–water interface can have consequences for the distributions of redox sensitive elements (Mn and Fe). Although Fe and Mn are of little direct concern from an environmental quality point of view, they nonetheless can influence the transport and fate of other metals investigated in the present work (Pb, Cd, Zn, Cu, Ni) which can have deleterious effects on organisms at relatively low concentrations. Cd and Pb are regarded as potentially of greatest concern among these metals, in terms of their toxic effects on the ecosystem.

The work reported in this paper was a component of a multidisciplinary study of the northwestern Black Sea undertaken during the pilot phase of the EC-funded EROS 2000 Project. The objective was to understand the biogeochemical functioning of the northwestern shelf region under summer conditions especially with regard to nutrients and trace metals. The station locations were chosen primarily to provide a good coverage of the Danube influence on the northwestern Black Sea shelf. A deep water station was also occupied to allow comparison with adjacent shelf and with deep water profiles reported for other regions of the Black Sea. An account of the behaviour of trace metals during mixing in the Danube Estuary and plume has been given by Guieu et al. (1998).

2. Sampling and analytical methods

The EROS 2000 expedition was conducted in July–August 1995 on board R/V *Professor Vodyanitskiy*. The positions of the stations discussed in this paper are shown in Fig. 1. Samples were taken to obtain detailed coverage of the water column. They were collected using 10-l Teflon-lined Go-Flo bottles, fitted with Teflon taps and deployed on a rosette with a CTD. Water was filtered under nitrogen pressure—to avoid any contamination with oxygen—through Nuclepore filters (0.4 µm pore diameter) using an in-line Teflon filtration unit. Aliquots of the filtrates for dissolved trace metal analyses were acidified with purified nitric acid to a pH of about 2.0 and stored in cleaned low density polyethylene bottles. Filters were rinsed with Milli-Q water and stored in acid-cleaned containers at about –20°C.

Dissolved trace metals were separated and preconcentrated from seawater using dithiocarbamate complexation and subsequent extraction into Freon TF, followed by back extraction into nitric acid. Extracts were analysed for Mn, Fe, Co, Pb, Cd, Cu, Ni and Zn, using graphite furnace atomic absorption spectrophotometry. The method was developed by Danielsson et al. (1978) and modified by Statham (1985).

The gravimetric determination of suspended particulate matter was by reweighing preweighed Milli-Q rinsed filters. The leaching of trace metals associated with suspended particulate matter (SPM) was carried out in two stages, the first removing the more geochemically available fraction. The filter membranes were first leached using acetic acid (25% v/v) then digested with

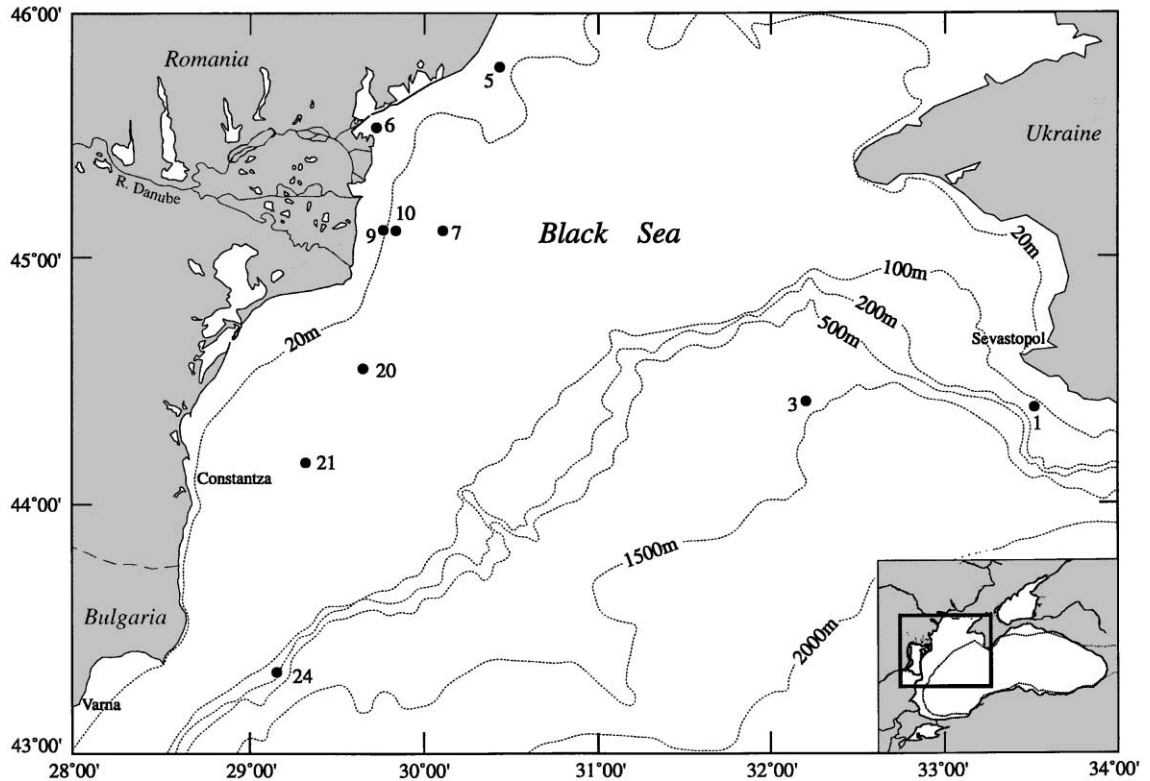


Fig. 1. Sampling locations in the north western Black Sea.

Table 1

Analyses of reference seawater samples (CASS2 and CASS3); concentrations in nM; the limit of detection is calculated as 3 times the standard deviation of the blank

Element	Mn	Fe	Co	Pb	Cu	Ni	Cd	Zn
Typical blank	0.267	0.180	0.008	0.005	0.155	0.026	0.006	0.030
Detection limit	0.119	0.181	0.009	0.003	0.052	0.071	0.001	0.135
CASS-2 Certified value	36.22	21.49	0.424	0.092	10.62	5.08	0.169	30.13
	± 2.70	± 2.15	± 0.100	± 0.029	± 0.61	± 0.61	± 0.035	± 1.83
CASS-2 analyses $n = 4$	36.33	20.06	0.439	0.048	11.13	5.26	0.192	28.45
	± 1.62	± 2.61	± 0.064	± 0.004	± 0.26	± 0.38	± 0.017	± 2.25
CASS-3 Certified value	45.69	22.56	0.696	0.058	8.14	6.58 ± 1.05	0.266	18.97
	± 6.6	± 3.04	± 0.153	± 0.019	± 0.97		± 0.044	± 3.8
CASS-3 analysis $n = 1$	50.2	18.5	0.703	0.032	8.19	5.7	0.284	20.15

concentrated nitric acid using microwave heating. Extracts were analysed as for the dissolved metals. For Co, Pb, Cu, Ni, Cd and Zn, the residual fractions of SPM obtained by digestion with concentrated nitric acid were below detection limit.

Table 2

The determination of total trace metals in reference estuarine sediment material (BCSS-1)

Element	BCSS-1 material certified concentration ($\mu\text{g g}^{-1}$)	Analyses ($n=3$)
Fe	3.05 ± 0.17 (%)	3.32 ± 0.08
Mn	229 ± 15	194 ± 5
Co	11.4 ± 2.1	9.71 ± 0.43
Pb	22.7 ± 3.4	19.7 ± 1.9
Cd	0.25 ± 0.4	0.320 ± 0.080
Zn	119 ± 12	124 ± 11
Cu	18.5 ± 2.7	17.5 ± 1.1
Ni	55.3 ± 3.6	45.6 ± 4.2

In order to provide strict control of contamination, the work was undertaken with stringent precautions inside a clean laboratory. The accuracy of trace metal determinations was indicated by a good agreement between our values and those reported for certified reference materials (CASS-2 and CASS-3 for dissolved trace metals, BCSS-1 for particulate measurements; see Tables 1 and 2), except for dissolved Pb values which were consistently lower than the certified values; for each batch of samples, all dissolved Pb results have been corrected for the low recovery.

Salinities were determined using a calibrated Guildline Autosol salinometer. Nutrient determinations (nitrate + nitrite, ammonium, phosphate and dissolved silicon) were made using the method of Strickland and Parsons (1977). Oxygen was measured using the method of Grasshoff (1983).

3. Hydrographic properties

The water column at Station 3 in the open Black Sea was characterized by strong density stratification between depths of 20 and 120 m as a result of both temperature and salinity gradients (Fig. 2). A maximum in fluorescence possibly due to accumulation of biological debris was associated with the thermocline. Oxygen was completely depleted below 120 m. Nutrients (nitrate + nitrite, ammonium, dissolved silicon and phosphate) were depleted in surface water due to biological uptake (Fig. 3). Nitrate + nitrite and phosphate data showed a maximum at 115 m due to a combination of regenerative processes and factors influencing these constituents in the underlying oxygen depleted waters. Ammonium and dissolved silicon distributions exhibited an increase with depth below the redoxcline (120 m) due to regeneration processes and accumulation in the anoxic waters.

At stations on the shelf, the salinity distribution indicated partially mixed estuarine characteristics with salinity increasing towards the bottom (Fig. 4). The salinity of the surface layer increased seaward, and the depth of the thermocline decreased with weakening influence of the Danube river. At certain stations (7, 10, 20, 21 and 24), salinity increased at some depths by steps apparently reflecting the presence of layers of water, well mixed internally but separated

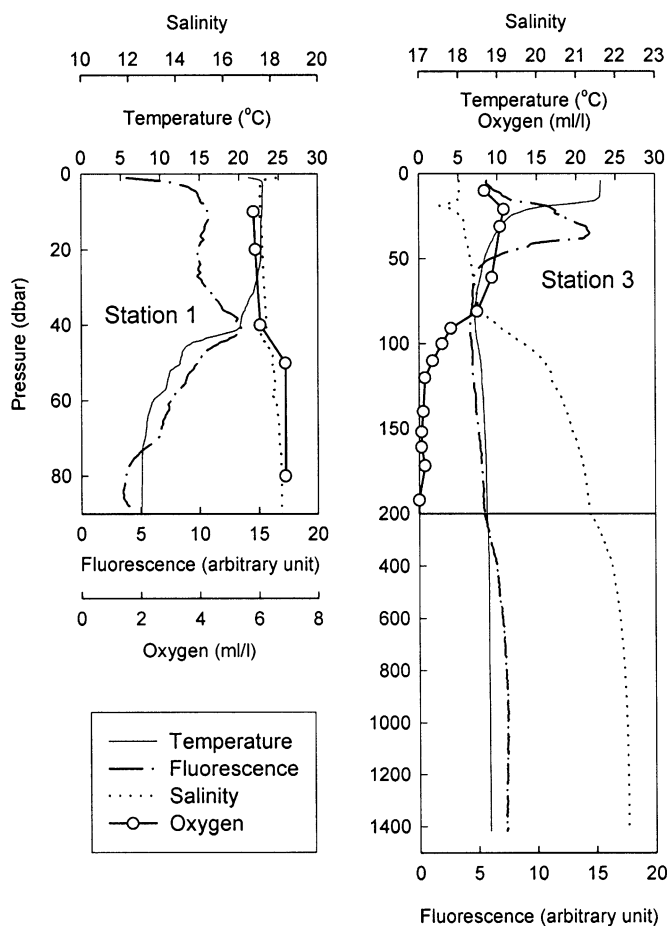


Fig. 2. Hydrographic data (temperature, fluorescence, salinity and oxygen) for Stations 1 and 3.

from the adjoining layers by sharp density gradients. Such lamination could also explain the structure in the fluorescence data.

Oxygen concentrations in the upper water column were generally high at stations on the shelf (4–8 ml/l). Dissolved oxygen concentrations measured in deeper waters were variable (1.8–7 ml/l). There is evidence, however, that concentrations in the benthic interfacial zone can be sufficiently low as to markedly influence redox conditions. Tolmazin (1985) described the occurrence in the mid-1970s of extensive areas of low oxygen concentrations in the bottom waters of the region adjacent to the Dnieper outflow and north of the Danube outflow, with some anoxia within the latter region. Observations (Friedl et al., 1998) at the time of, and in the same area as, the present study, using a benthic lander, showed that water overlying the sediment, enclosed in the benthic flux chambers implanted in the sediment, had oxygen concentrations from undetectable to 0.13 mM. At those stations where oxygen was detectable, complete removal occurred during the period of deployment but sulphate reduction was not observed.

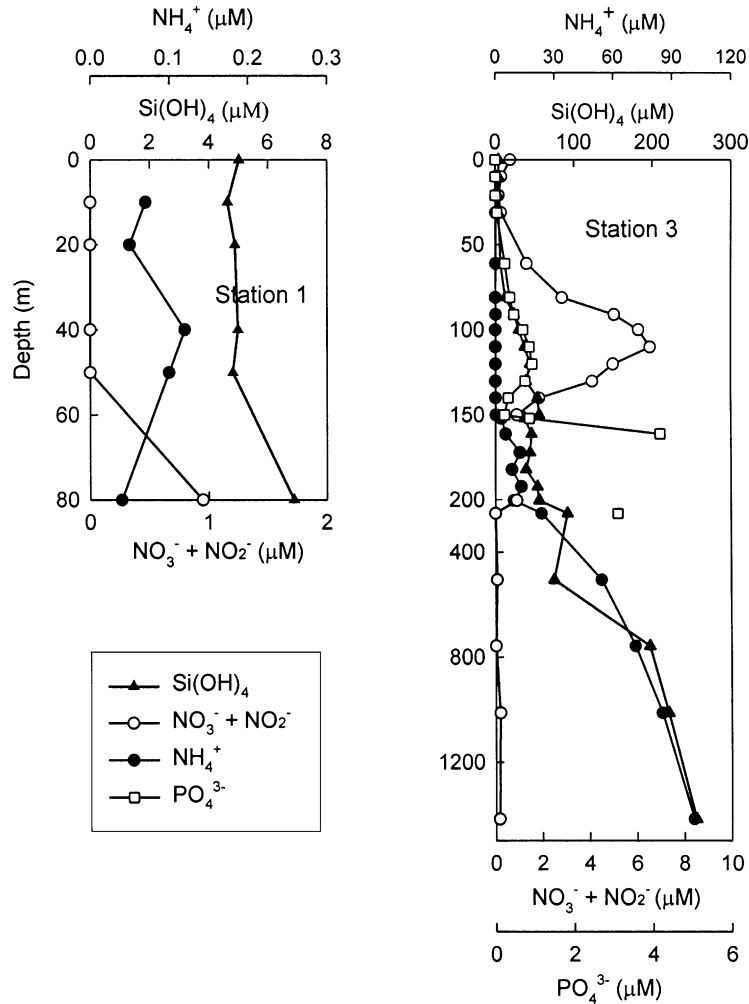


Fig. 3. Distributions of nutrients (ammonia, nitrate + nitrite, phosphate and silicate) at Stations 1 and 3.

In the coastal zone, the stratification of the water column played an important role in the distribution of nutrients (Fig. 5). Above the thermocline, concentrations of dissolved silicon, nitrate and phosphate were generally depleted by biological uptake, while below the thermocline, they increased rapidly with depth due to their regeneration from the sinking biomass. One would expect the well developed pycnocline to delay the sinking of particles thus creating an organic carbon-rich zone characterized by large chemical gradients and high microbial activity. The maxima in Si(OH)_4 , NO_3^- , NH_4^+ and PO_4^{3-} observed in some cases (Stations 5, 20, 21) at the pycnocline may be evidence of this. At stations most directly influenced by the Danube river (Stations 9, 10 situated near the mouth of the river) nitrate, phosphate and dissolved silicon concentrations were highest in surface water and decreased rapidly with distance away from the coast and with depth. At Station 24 an increase in NH_4^+ was observed in the deepest water

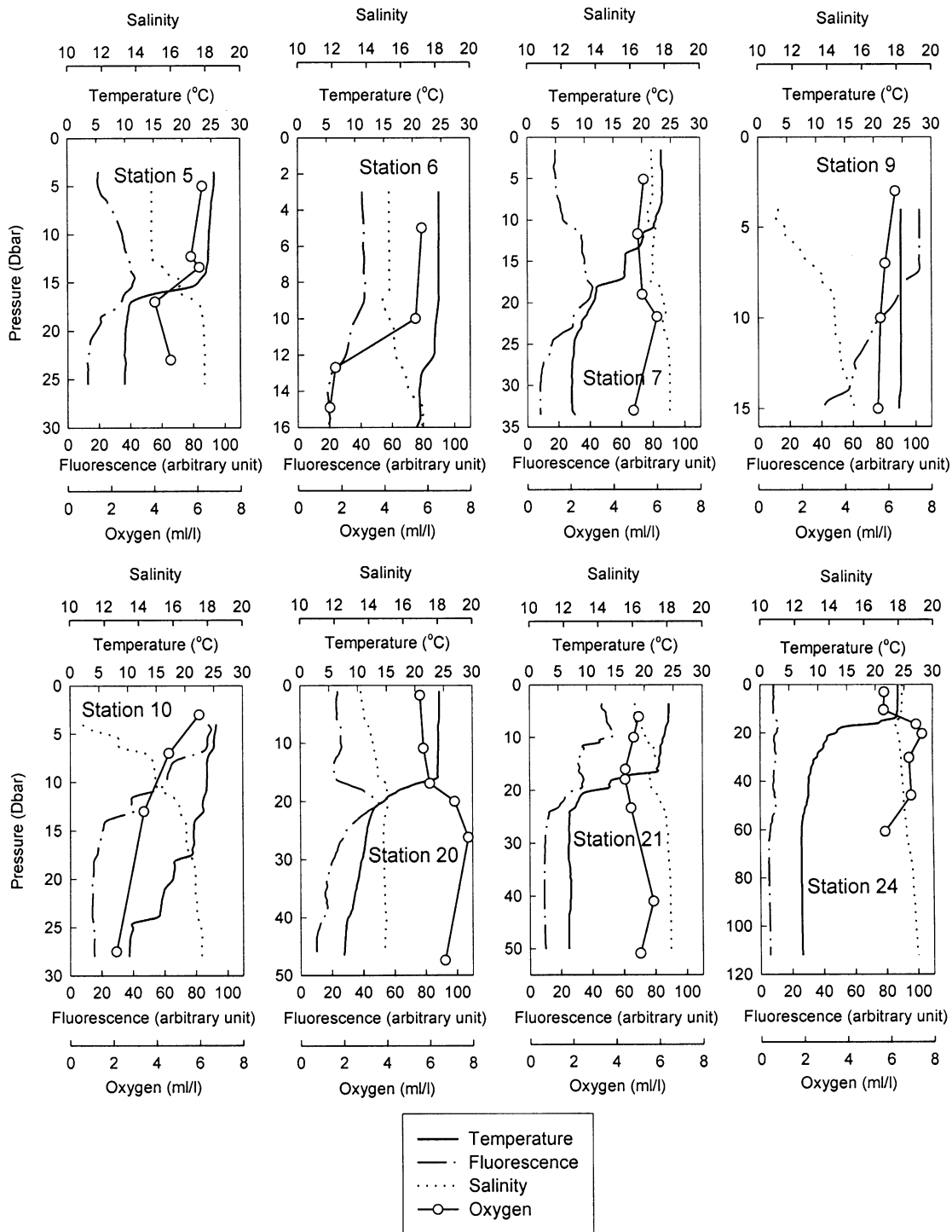


Fig. 4. Hydrographic data (temperature, fluorescence, salinity and oxygen) for Stations 5–7, 9, 10, 20, 21 and 24.

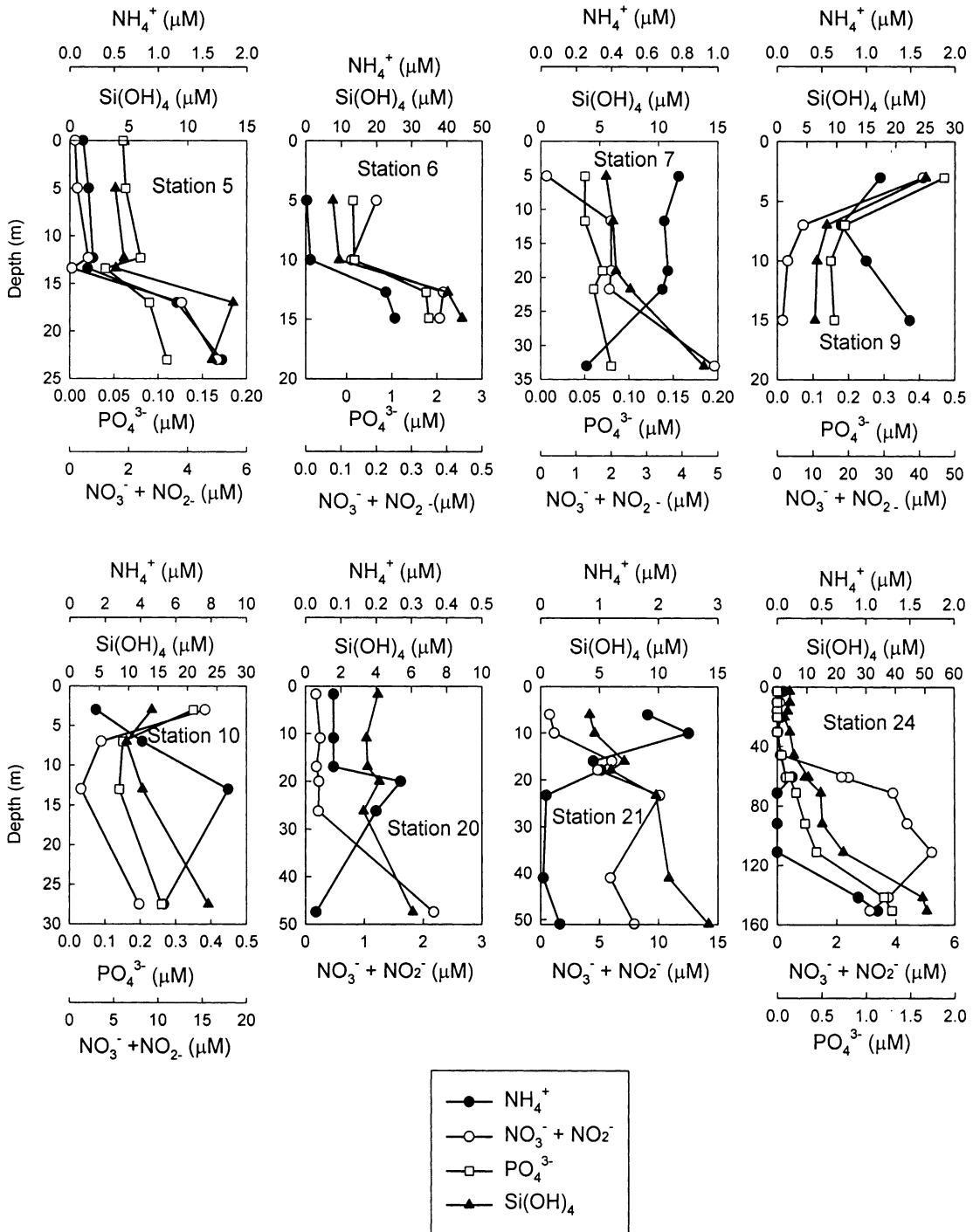


Fig. 5. Distributions of nutrients (ammonia, nitrate + nitrite, phosphate and silicate) at Stations 5–7, 9, 10, 20, 21 and 24.

together with a decrease in $\text{NO}_3^- + \text{NO}_2^-$ which would be consistent with some denitrification; the profiles for Station 21 show somewhat similar features.

4. Trace metals

4.1. Station 3: a deep water reference station

At Station 3, relatively high dissolved Mn concentrations (10 nM) were found in surface water (Fig. 6), possibly due to atmospheric inputs (Chester et al., 1993). The concentrations decreased to reach a minimum of 1 nM between 60 and 110 m. Below 110 m, which was the upper limit of the redoxcline, dissolved Mn concentrations increased rapidly to reach a maximum at 190 m (8750 nM). Below 200 m, dissolved Mn concentrations decreased again with depth. The shape of the Mn maximum is controlled by a dynamic balance between the rates of diffusion and oxidation of Mn(II) (Tebo, 1991) and the rates of sinking and redissolution of solid phase MnO_x . The distribution of Fe was similar to that of Mn (Fig. 7). However, a deeper maximum was observed for dissolved Fe (292 nM at 253 m), as compared to dissolved Mn, as a consequence of the more rapid oxidation of Fe in the upper redoxcline combined with the low solubility of FeS below the redoxcline (Lewis and Landing, 1991; Landing and Lewis, 1991). Available and total particulate metal concentrations were measured in the top 200 m of the water column. Maxima in total particulate Mn and Fe were observed above the dissolved Mn and Fe maxima. Horizontal advective transport of particles enriched in Mn and Fe oxides coupled with oxidation of Mn(II) and Fe(II) diffusing from anoxic waters can explain the vertical distributions of particulate Mn and Fe in this area (Kempe et al., 1991; Tebo et al., 1991).

The distribution of dissolved Co closely resembled that of dissolved Mn throughout the upper water column and redoxcline (Fig. 8), reflecting coupling through oxidation of Mn (Moffett and Ho, 1996). As observed elsewhere concentrations were very low throughout the anoxic zone, consistent with sulphide phase formation (Lewis and Landing, 1991). Available particulate Co had a good correlation with available particulate Mn (Table 3); Moffett and Ho (1996) found that both elements are co-oxidized via the same microbial catalytic pathway, and that this is probably an important mechanism for the incorporation of Co into marine Mn oxides.

Relatively high concentrations of dissolved Pb were observed in open surface water (100–200 pM) and decreased with depth (Fig. 9). The depth distributions of dissolved Cd and Zn showed gradual increases through the oxic layer which were sharply reversed around the top of the redoxcline because of the incorporation of these elements in particulate matter in the anoxic layers (Figs. 10 and 11). In the oxic layers, Zn, Cd and Pb showed features characteristic of open sea profiles observed elsewhere (Boyle and Lea, 1992; Donat and Bruland, 1995). In contrast with Zn and Cd, Cu showed a gradual decrease through the upper water column, suggesting that the rate of Cu adsorption onto ambient particles exceeds the rate of dissolution of the primary Cu-bearing phase (Fig. 12). Dissolved Cu did not show any depletion in surface water possibly as a result of strong organic complexation (Coale and Bruland, 1988, 1990) which would reduce the inorganic free Cu^{2+} pool directly available for biological uptake (Donat and Bruland, 1995). Available particulate Pb, Cu, Cd and Zn correlated better with available particulate Fe than with available particulate Mn (Table 3) suggesting an association with Fe oxides. For Pb, Cu, Cd and

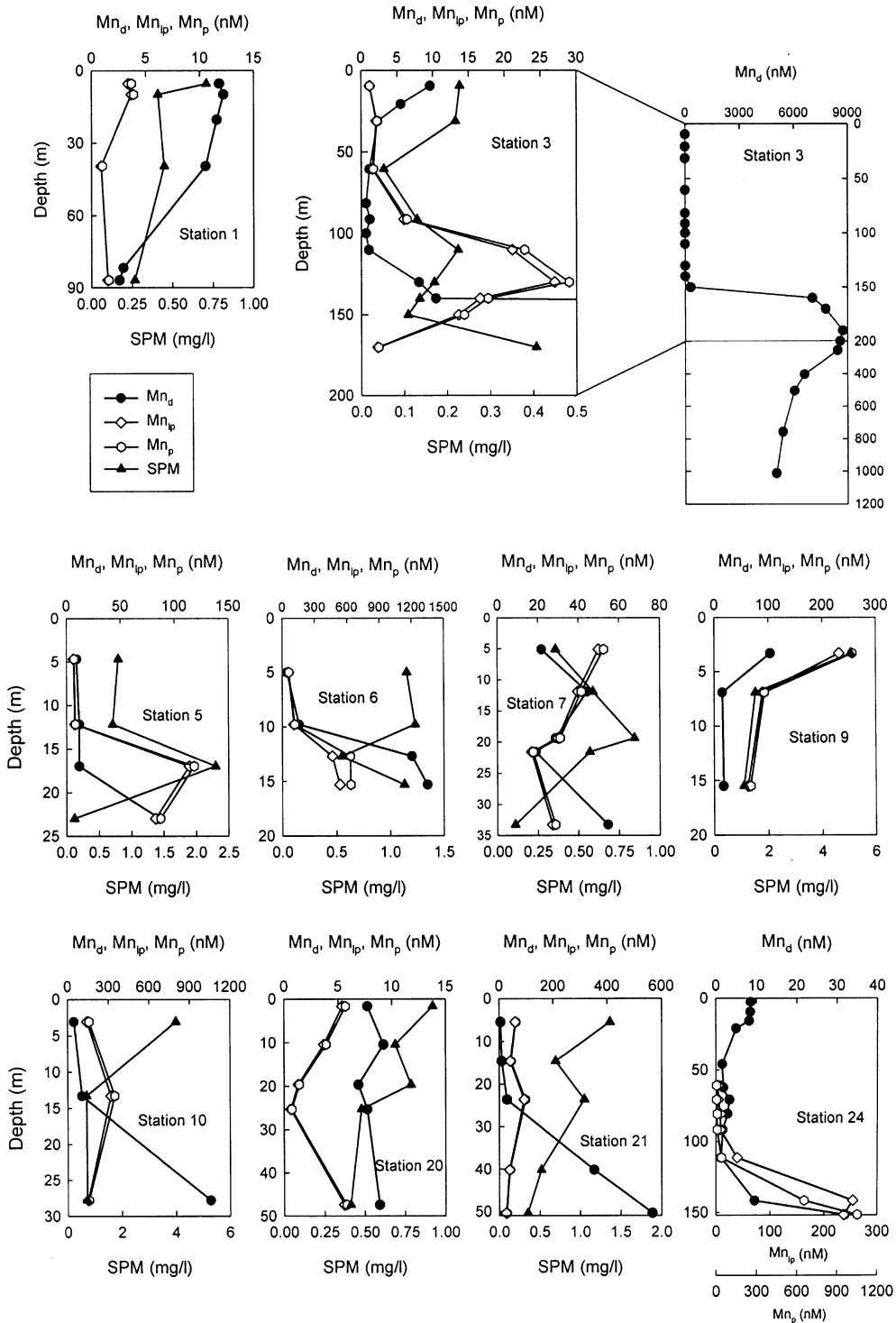


Fig. 6. Distributions of dissolved Mn (Mn_d), leachable particulate Mn (Mn_{ip}) and total particulate Mn (Mn_p) in the northwestern Black Sea.

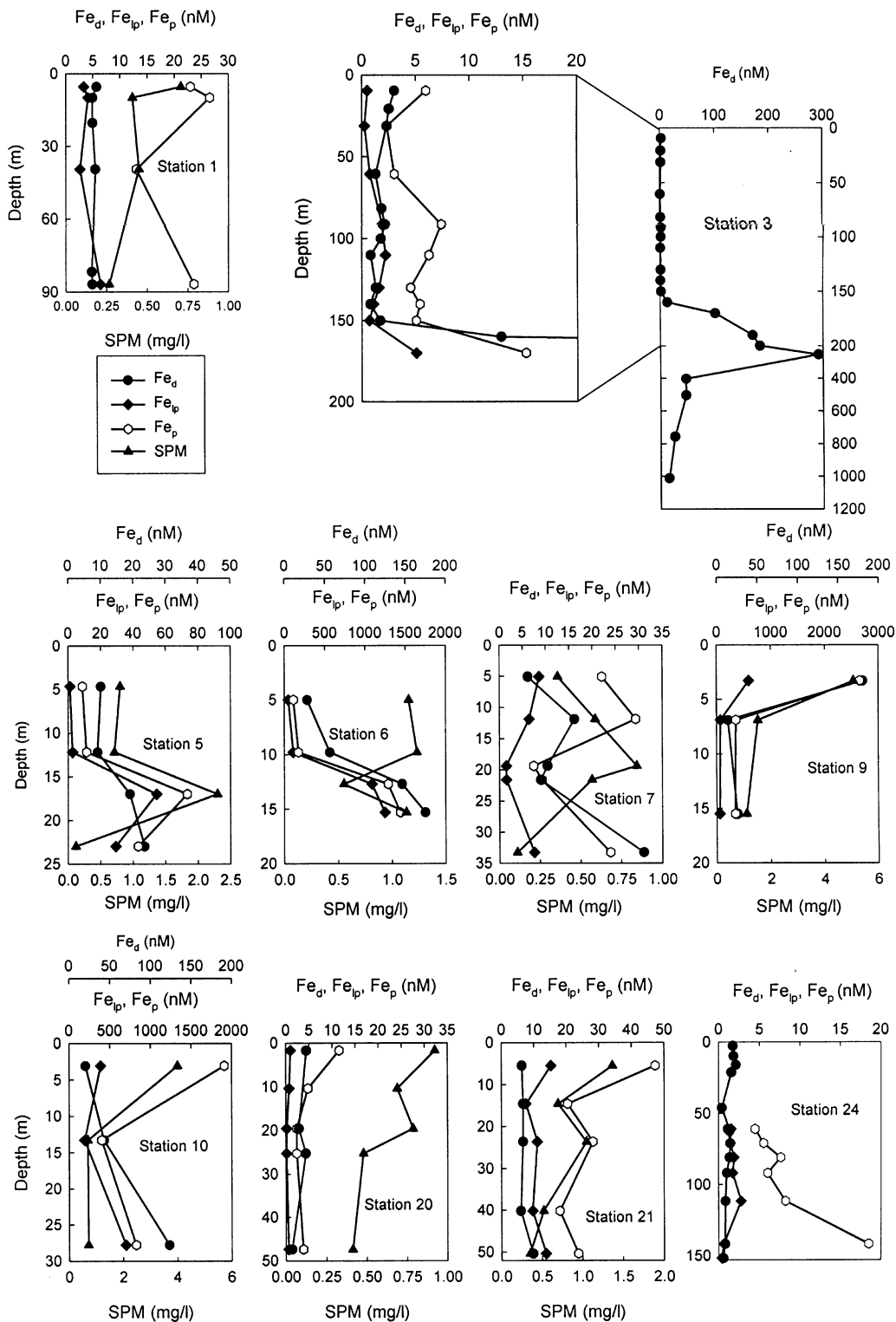


Fig. 7. Distributions of dissolved Fe (Fe_d), leachable particulate Fe (Fe_{ip}) and total particulate Fe (Fe_p) in the northwestern Black Sea.

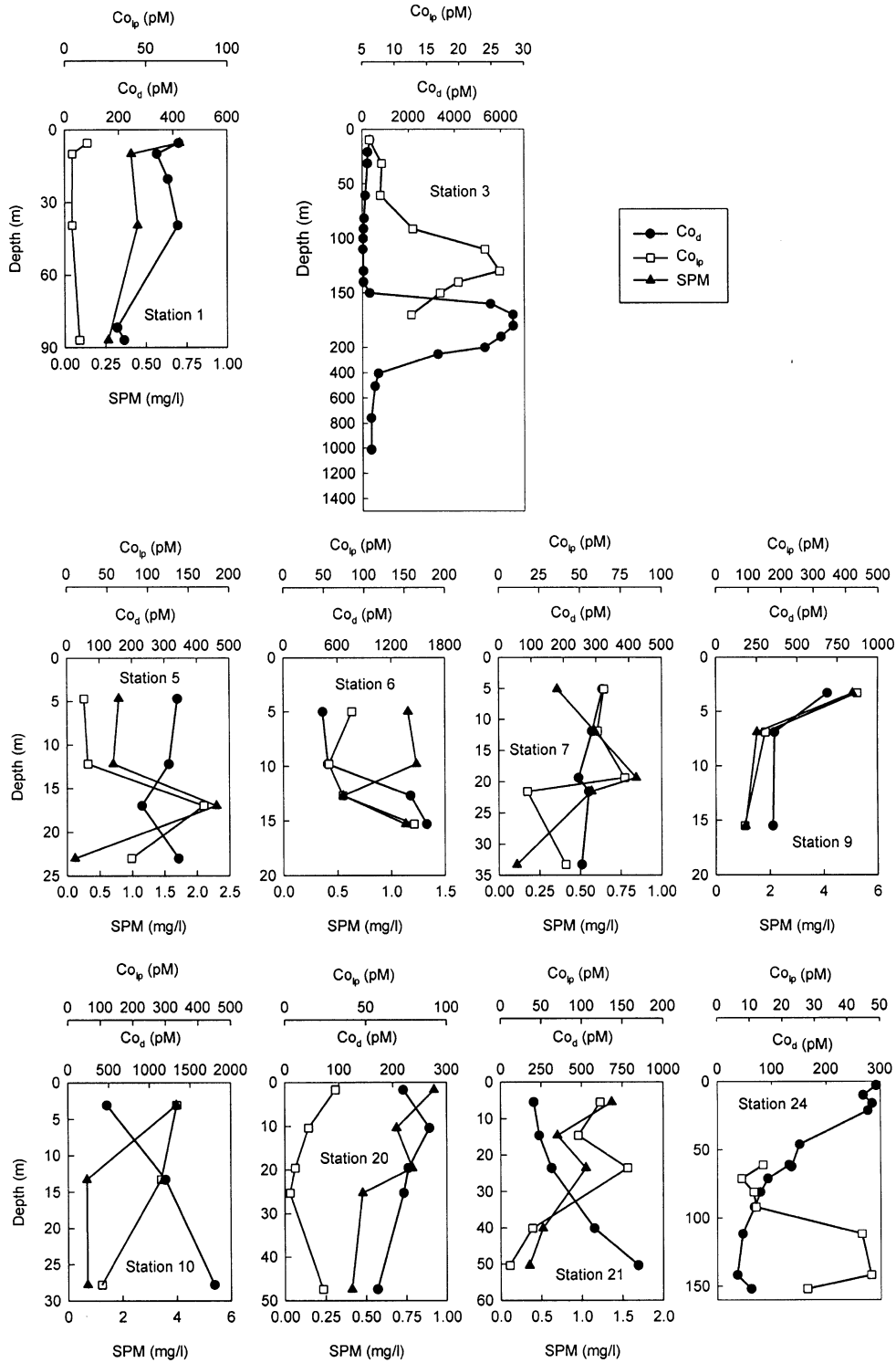


Fig. 8. Distributions of dissolved Co (Co_d) and leachable particulate Co (Co_{lp}) in the northwestern Black Sea.

Table 3
Correlation coefficients between available particulate Pb, Co, Cd, Cu, Ni and Zn and available particulate Mn and Fe in the oxic layer of Station 3

	Pb _{ip}	Co _{ip}	Cd _{ip}	Cu _{ip}	Ni _{ip}	Zn _{ip}
Mn _{ip}	0.33	0.97	−0.37	−0.33	−0.25	−0.35
Fe _{ip}	0.87	0.20	0.94	0.78	−0.17	0.76

Zn, dissolved concentrations were very low in the anoxic layers as a result of control of solubility by formation of, or association with, solid sulphide phases (Morse and Arakaki, 1993; Dyrssen, 1999). Dissolved Ni concentrations varied between 9 and 12 nM above the redoxcline and were constant (*ca* 10 nM) below (Fig. 13). The distribution of Ni was evidently not significantly affected by biological uptake in the oxic layer or by sulphide precipitation in deep anoxic waters probably because of the strong influence of complexation reactions with inorganic and organic ligands (Landing and Lewis, 1991; Donat et al., 1994). There was evidence of removal from the dissolved phase to the particulate phase within the redoxcline. This coincided with maxima in particulate Mn and Fe which could be involved in the removal process.

The distributions of metals at Station 3 were similar to those observed by Brewer and Spencer (1974), Haraldsson and Westerlund (1991) and Lewis and Landing (1991) in the central Black Sea, except that maxima in dissolved and particulate Fe appeared in deeper water nearer the shelf edge due to the dome-shaped isopycnal surfaces.

4.2. Stations in the shelf edge region (Stations 1 and 24)

At Station 24, slightly off the shelf edge, dissolved Mn concentrations varied between 8.2 and 8.6 nM in surface water. Below 16 m, concentrations decreased to a minimum. A maximum occurred at 71 m, which may have been due to horizontal advective–diffusive transport of dissolved Mn from anoxic shelf sediments. Near the bottom, concentrations of dissolved Mn further increased to 32 nM together with NH₄⁺, reflecting reducing conditions in the deeper water or sediment interfacial zone and possibly horizontal advective sources. Dissolved Fe concentrations (0.42–2.1 nM) were relatively low and uniform. Friedl et al. (1998) measured benthic fluxes of O₂, Mn and Fe in the same area and at a similar depth. Oxygen concentration at the sediment water interface was low (0.021 mM) but not completely depleted, which was consistent with the relatively low dissolved Fe and Mn concentrations observed at Station 24. However, remobilization of Mn(II) and Fe(II) increased significantly 10 h after the deployment of the benthic lander suggesting that remobilization of metal might occur in response to changing redox conditions (Friedl et al., 1998). Total particulate Mn and Fe concentrations at Station 24 were relatively low in the upper 90 m (small increases at 80 m were possibly due to advective transport of sediments from the shelf), and increased sharply near the bottom. The magnitude of the Mn increase near the bottom (260 nM for the leachable fraction and 1100 nM for total particulate Mn) was much greater than that observed at Station 3 or at the shelf stations. Tebo (1991) found that Mn(II) oxidation rates were 1–2 orders of magnitude higher at a nearshore station than at a station in the central Black Sea. Differences in rates were attributed to differences in the biological

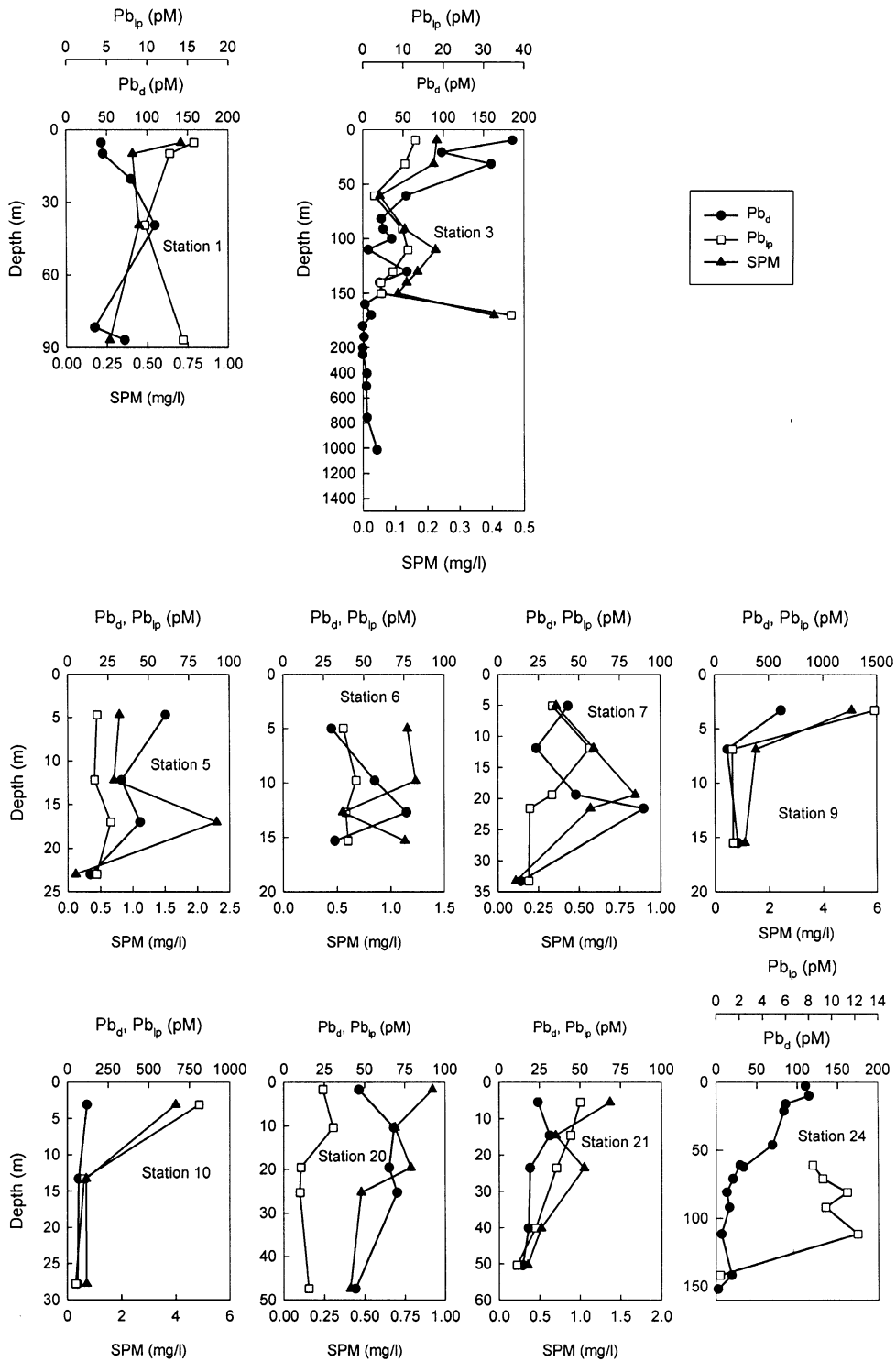


Fig. 9. Distributions of dissolved Pb (Pb_d) and leachable particulate Pb (Pb_{lp}) in the northwestern Black Sea.

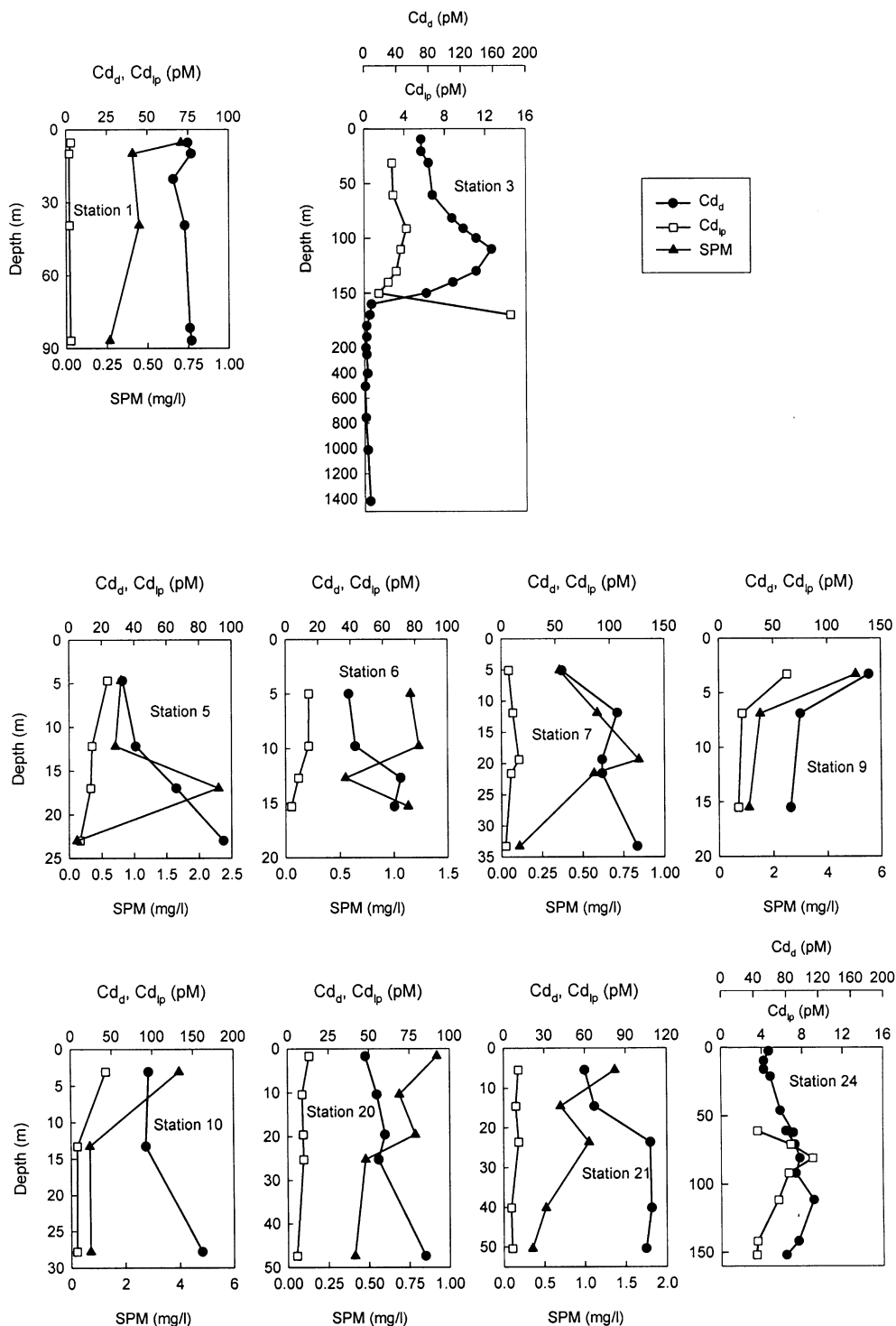


Fig. 10. Distributions of dissolved Cd (Cd_d) and leachable particulate Cd (Cd_{ip}) in the northwestern Black Sea.

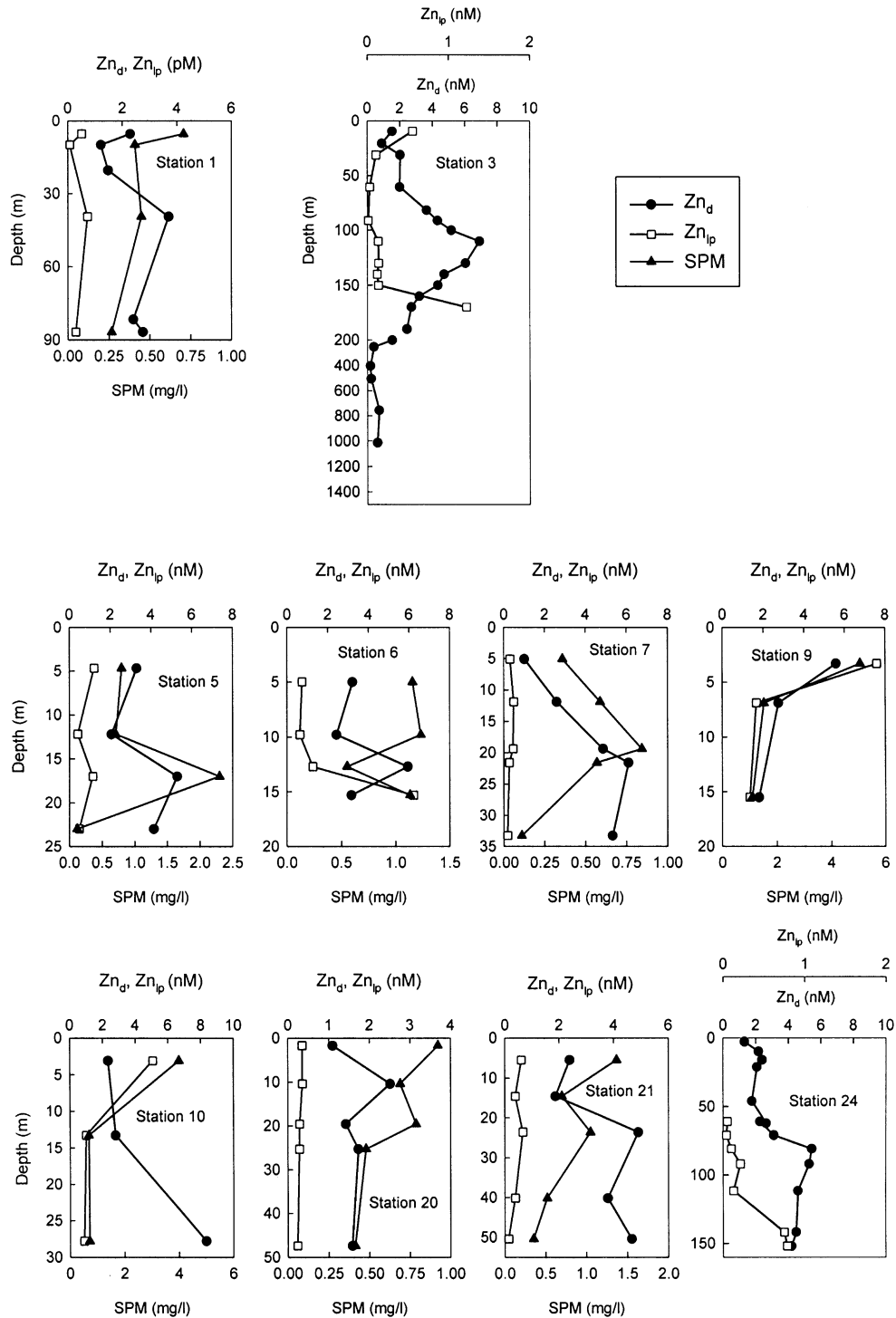


Fig. 11. Distributions of dissolved Zn (Zn_d) and leachable particulate Zn (Zn_{ip}) in the northwestern Black Sea.

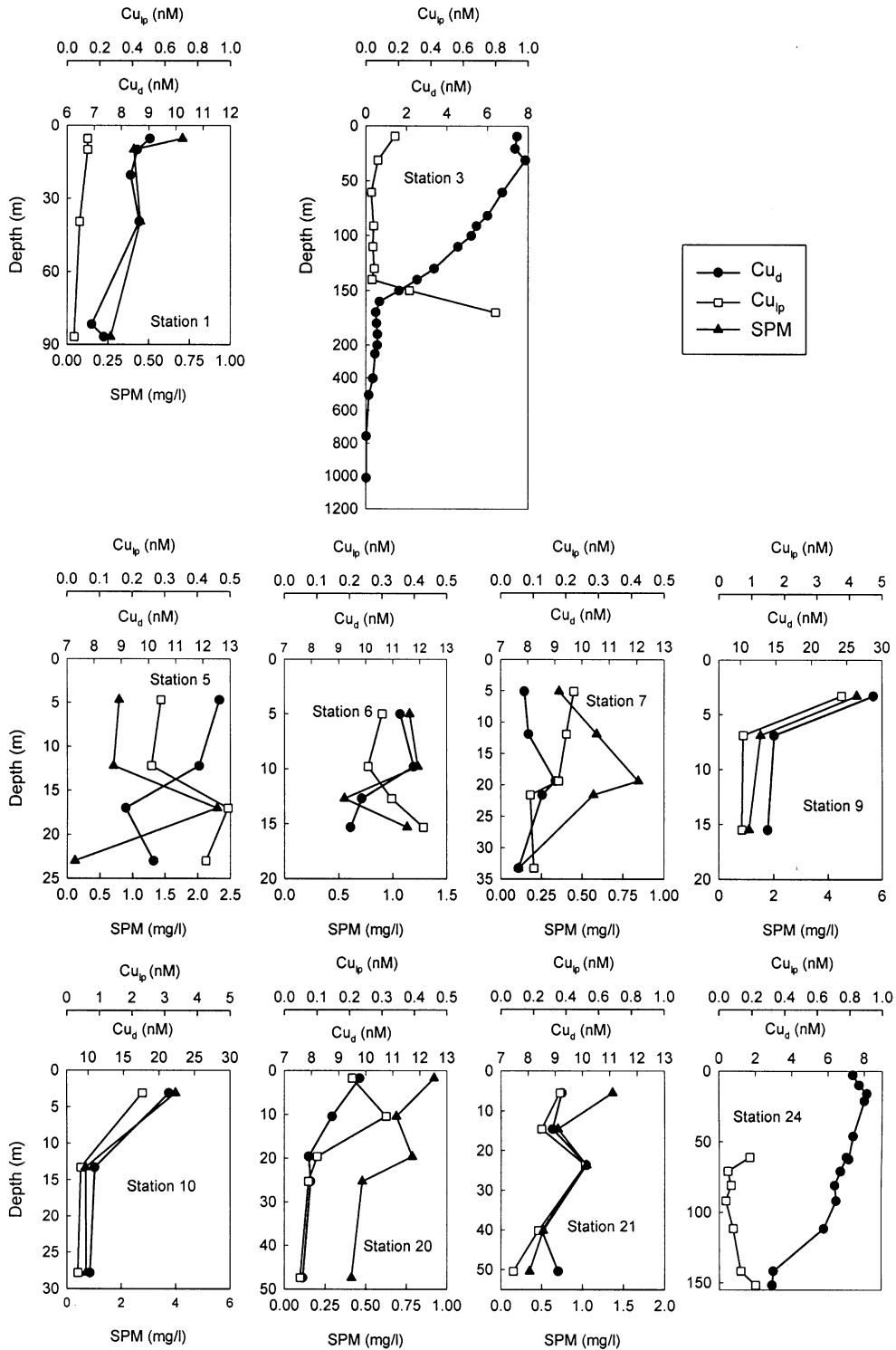


Fig. 12. Distributions of dissolved Cu (Cu_d) and leachable particulate Cu (Cu_{ip}) in the northwestern Black Sea.

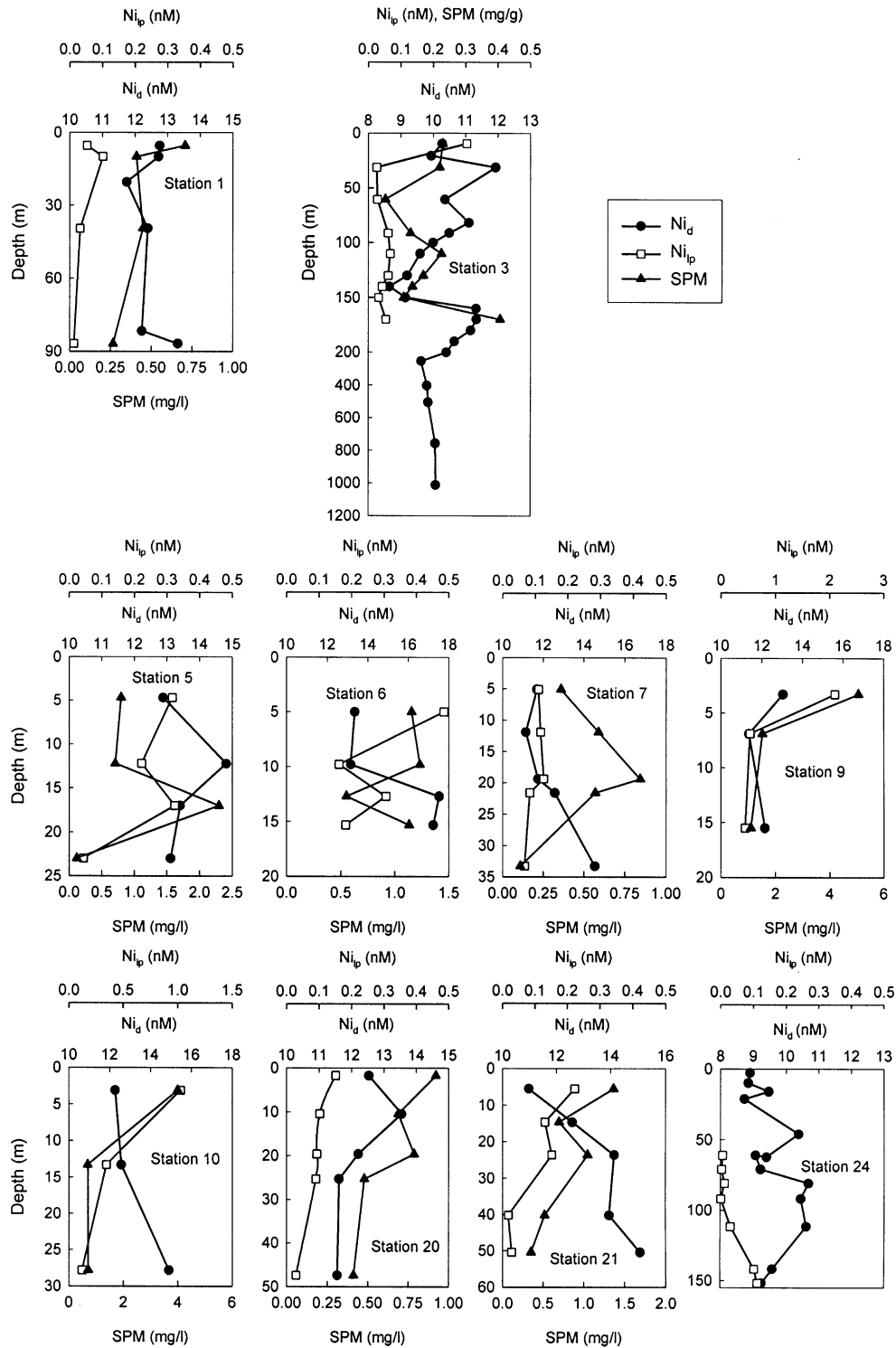


Fig. 13. Distributions of dissolved Ni (Ni_d) and leachable particulate Ni (Ni_{ip}) in the northwestern Black Sea.

(e.g. numbers and types of bacteria) and chemical (e.g. presence or absence of inorganic surfaces or reductants) components present in the water.

The observations above were in general agreement with Lewis and Landing (1991) and Kempe et al. (1991), who suggested that a “manganese pump” was operating in Black Sea coastal waters to produce vertically highly structured Mn-rich particle layers with intensities decreasing from the coast. The argument runs as follows. Seasonal variability of the depth of the pycnocline and the associated chemocline causes the surface sediments found at the same depth to be exposed to fluctuating redox conditions. One of the consequence of these fluctuations is that they periodically expose sediments to more reducing and higher saline water. This water replaces the more oxidizing pore waters of surface sediments, mobilizing whatever oxidized Mn is present or has recently been deposited by settling macroflocs. In the second part of this seasonal cycle, which is typical of the winter regime, the pycnocline dips down and the surficial sediments of the sea bed are once again exposed to oxic conditions. Upon mixing with the more oxic ambient water, particles of MnO_x are formed which are subject to lateral transport by the coastal current. Since these fine-grained particles settle very slowly they can disperse over considerable distances and form the fine particle layer (FPL) all over the Black Sea.

At Station 24, dissolved Co, Pb, Cd, Cu, Zn and Ni showed similar distributions to those in the oxic layer of Station 3. Significant differences occurred in the particulate fraction, however. For Co, Cu, Ni and Zn, available particulate concentrations increased below 110 m to reach maxima near the bottom or just above the bottom in the case of Co. These maxima could be due to resuspension and/or adsorption onto Mn- and Fe-oxides since there were good correlations with total particulate Mn and Fe and available particulate Co, Cu, Ni and Zn (with total particulate Mn: $r=0.49, 0.69, 0.96, 0.96$, respectively; with total particulate Fe: $r=0.55, 0.62, 0.98, 0.96$, respectively). Available particulate Pb and Cd profiles showed maxima between 60 and 110 m, with depletions near the bottom. No significant correlation with Mn- or Fe-oxides was found suggesting that Pb and Cd were less influenced by the redox-sensitive behaviour of Fe and Mn.

Station 1 was at the Ukrainian shelf edge, but shallower than station 24. All metal profiles were very similar to the upper 100 m of Station 24 and no significant benthic influence was observed in bottom waters.

4.3. *Shallow shelf stations*

4.3.1. *Manganese*

In the shallow shelf waters, Mn distributions (Figs. 4–6) were affected by changes in redox conditions which occurred in the water column and at the sediment–water interface and by riverine inputs in surface water. At most stations dissolved Mn concentrations increased below the thermocline and reached maxima near the sediment–water interface. This was attributable to the degradation of settling organic carbon (Nealson et al., 1991; Nealson and Myers, 1992; Nealson and Saffarini, 1994; Joye et al., 1996). Manganese oxides were reduced to dissolved Mn which diffused from the sediment into the water column creating high concentrations of dissolved Mn in bottom waters at Stations 5–7, 10 and 21. This was consistent with benthic fluxes calculated for a station on the Danube delta (Friedl et al., 1998). At that station, the oxygen concentration in the water captured in their benthic chambers was low but not completely depleted (0.13 mM). However, the oxygen consumption was relatively high ($26 \text{ mmol m}^{-2} \text{ d}^{-1}$) and reduction of Mn

oxides was significant ($0.43 \text{ mmol m}^{-2} \text{ d}^{-1}$). The high total particulate Mn concentrations in bottom waters of Stations 5–7 and 20 are consistent with reoxidation of dissolved Mn in more oxygenated waters, a process which is strongly influenced by microbial catalysis (Vandenabeele et al., 1992; Tebo et al., 1998).

At Station 7, a maximum in dissolved Mn was found at the thermocline suggesting that reductive dissolution of Mn oxides occurred in the water column. The dissolution of Mn from particles may have involved the use of the MnO_x phase in the oxidation of organic matter but may also have been a more general consequence of the influence of low O_2 concentrations on redox states of other constituents. Oxygen concentrations were not markedly low (4–6 ml/l), so the bulk water conditions would not have favoured the release of Mn by either process. It could be that some reduction was occurring in microenvironments (for example decomposing organics within the aggregates) in the dominantly oxic medium (Decho and Herndl, 1995).

Station 9 was located at the mouth of the Danube. Concentrations of both dissolved and particulate Mn were highest in surface water because of the high fluvial inputs from the Danube. The SPM concentrations were relatively high in surface water (5 mg/l) reflecting the high particulate load of the Danube river (35–38 mg/l). This had the effect of reducing light penetration into the water column, which in turn limited primary productivity, which may, through a reduced supply rate of organic carbon to the sediment, have led to less intensive Mn cycling in the benthic interfacial zone.

4.3.2. Iron

Elevated concentrations of both dissolved and total particulate Fe were found near the sediment–water interface at stations on the shelf. The highest concentrations occurred near the bottom at Station 6 (175 nM for the dissolved phase and 1440 nM for the total particulate phase) and at Station 10 (123 nM for the dissolved phase and 824 nM for the total particulate phase), i.e. where oxygen concentrations were the lowest actually measured in the water column (1.8–2 ml/l). High dissolved Fe concentrations indicates reduction of Fe oxides by bacteria during mineralization of organic carbon in the sediment and diffusion into bottom waters (Nealson, 1982; Arnold et al., 1986; Lovley and Phillips, 1988; Nealson and Myers, 1990). This explanation is consistent with the high benthic fluxes of Fe ($0.38\text{--}0.53 \text{ mmol m}^{-2} \text{ d}^{-1}$) measured independently in the same area (Friedl et al., 1998). High total particulate Fe concentrations reflects Fe(II) oxidation. In the presence of oxygen at neutral pH, Fe(II) oxidation is very rapid and biological catalysis is assumed to be unnecessary (Nealson, 1997). However, the likely presence of organic complexing agents in the water column will tend to keep a non-negligible fraction of this Fe in solution, even as it oxidizes to Fe(III) (Wu and Luther, 1995; van den Berg, 1995; Lewis et al., 1995; Rue and Bruland, 1995). As for Mn, maxima in dissolved and total particulate Fe were also found at Station 7 at the thermocline where there was accumulation of particulate material. The maximum in dissolved Fe could be due to reduction of Fe oxides occurring within aggregates in the dominantly oxic medium (Decho and Herndl, 1995).

The region of direct influence of the Danube river (Stations 9) was characterized by high concentrations in both dissolved and total particulate Fe in surface waters (respectively, 190 and 2800 nM). Concentrations in surface waters decreased during mixing with more saline water (Stations 10 and 7). In the surface plume, high Fe concentrations in the dissolved phase were due to riverine inputs and may have been further enhanced by the photoreductive dissolution of

Fe(III)-oxides (Waite and Morel, 1984; Rich and Morel, 1990). Total particulate Fe concentrations were high in surface waters of Stations 9 and 10 (2653 and 1910 nM, respectively), while the available fraction was low (20–22%), reflecting the dominantly terrestrial origin of the particles.

4.3.3. Cobalt

At stations on the northwestern Black Sea shelf, dissolved Co concentrations were generally in the range 200–1700 pM (Fig. 8). Higher concentrations were found near the bottom at Stations 5, 6, 10 and 21 where data already discussed are consistent with reduction of Mn- and Fe-oxides. Dissolved Co concentrations exhibited a closer relationship with Mn ($r=0.90$) than with Fe ($r=0.77$) which is consistent with a closer coupling of the redox cycling of the element with that of Mn (Moffet and Ho, 1996). At high levels of dissolved Mn and Fe (Station 6), however, no further increases in dissolved Co were observed, supporting the idea that Co^{2+} concentrations were possibly limited by adsorption onto Mn- and Fe-oxides; the available Co content in SPM was significantly correlated to the total Mn ($r=0.81$) and total Fe contents ($r=0.84$) in SPM.

Relatively high dissolved and particulate Co concentrations were also observed in surface waters of Stations 9 and 10 where the influence of the Danube inflow was strong.

4.3.4. Lead

Lower concentrations of dissolved Pb were observed in the surface waters at stations in the coastal zone (20–130 pM) with the exception of Station 9 than in open Black Sea surface water (100–200 pM at Station 3). This probably reflects the effects of atmospheric inputs combined with less efficient scavenging in offshore waters with lower SPM concentrations, allowing the diffuse atmospheric inputs to sustain higher dissolved Pb concentrations (Fig. 14). Similar observations have been made in the North Sea (Althaus, 1992; Tappin et al., 1995).

High concentrations were found in the Danube plume. At Station 9 dissolved and available particulate Pb concentrations were highest and reached 610 and 1500 pM, respectively, reflecting strong riverine inputs. Decreases of dissolved Pb concentrations near the bottom at most stations of the shelf can be attributed to scavenging of Pb from solution onto particles (Mart et al., 1982; Balls, 1985, 1988); however, no significant increases in the particulate phase was observed. Station 20 showed higher concentrations in dissolved Pb (44–70 pM) than Station 21 (15–48 pM) possibly reflecting the episodic nature of inputs of atmospheric material.

4.3.5. Copper

On the northwestern Black Sea shelf, Cu was mainly in the dissolved phase (typically in the range 7–15 nM) and concentrations were higher than at shelf edge stations due to riverine inputs. The behaviour of dissolved Cu was essentially conservative over the range of salinities between 13 and 19 (Fig. 15). The intercept from the linear regression (38.7 nM) was similar to the value measured at zero salinity in the Danube river (36 nM, Guieu et al., 1998) suggesting conservative mixing between Danube river water and coastal Black Sea water. However, two points deviated from the regression line by more than $\pm 2\sigma$, and corresponded to surface samples taken within the region of freshwater influence of the Danube river (Stations 9 and 10). Inputs of dissolved Cu to the surface waters were the likely explanation for the two high values observed. Two types of enrichment processes for Cu are possible. One relates to the increasing Cu solubility with

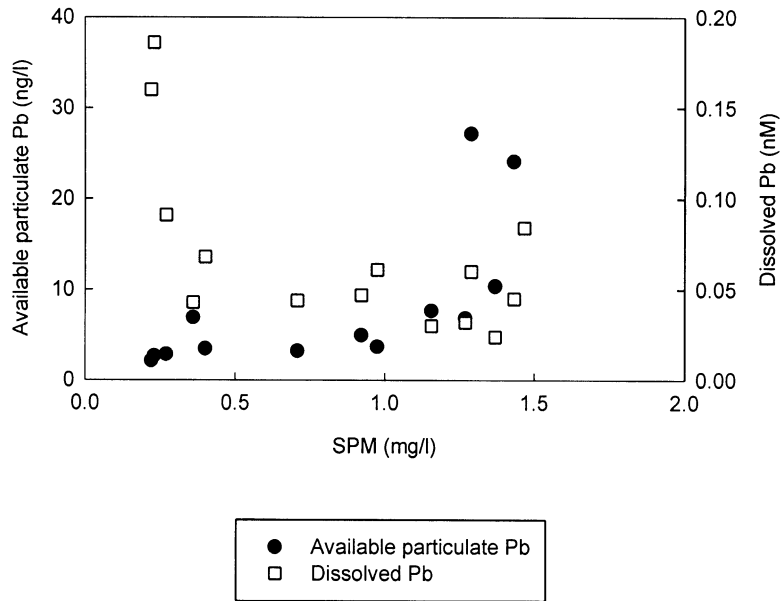


Fig. 14. Dissolved and available particulate Pb plotted versus SPM in surface waters of the Northwestern Black Sea.

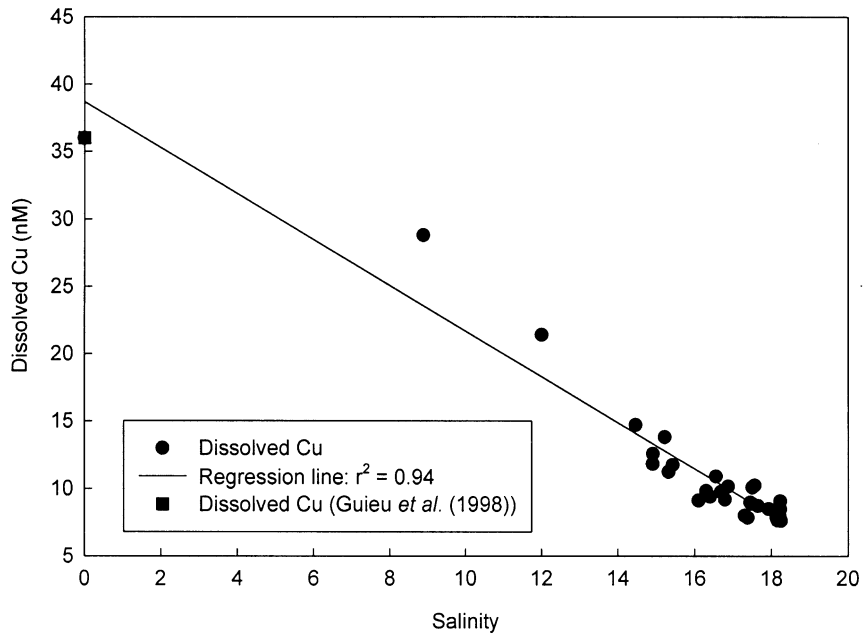


Fig. 15. Dissolved Cu plotted versus salinity at stations on the Northwestern Black Sea shelf.

increasing pH; the second one relies on the desorption of the exchangeable fraction of Cu associated with high river discharge as a result of dilution, ionic strength, and cation competition (Windom et al., 1983). The second mechanism is likely to be dominant in the lower salinity region,

dissolved Ni concentrations in bottom waters at most stations on the Shelf (Stations 6, 7, 9, 10 and 21) consistent with the latter process.

4.3.7. Cadmium

Dissolved Cd concentrations (Fig. 10) were relatively uniform throughout the northwestern Black Sea but available particulate Cd concentrations were higher in shelf waters (20–50 pM) than in the open sea (2–16 pM) as a result of riverine inputs (Fig. 17). At most stations on the shelf (except Station 9 which was affected by strong riverine inputs) dissolved Cd concentrations increased gradually with depth suggesting that coupling with the cycle of production and decomposition of organic material was important, i.e. that dissolved Cd was depleted in surface waters through uptake by phytoplankton (Schneider and Pohl, 1996; Loscher et al., 1998; Cullen et al., 1999) and/or adsorption onto biogenic particles. These processes were consistent with the good correlation observed between dissolved Cd and nutrients ($\text{NO}_3^- + \text{NO}_2^-$, PO_4^{3-} and $\text{Si}(\text{OH})_4$) at most stations (Table 4). At Stations 5–7 and 10, higher dissolved Cd concentrations were observed in bottom waters suggesting benthic inputs. Moreover, high correlation coefficients were found at these stations between dissolved Cd and dissolved Mn and Fe (Table 4) consistent with

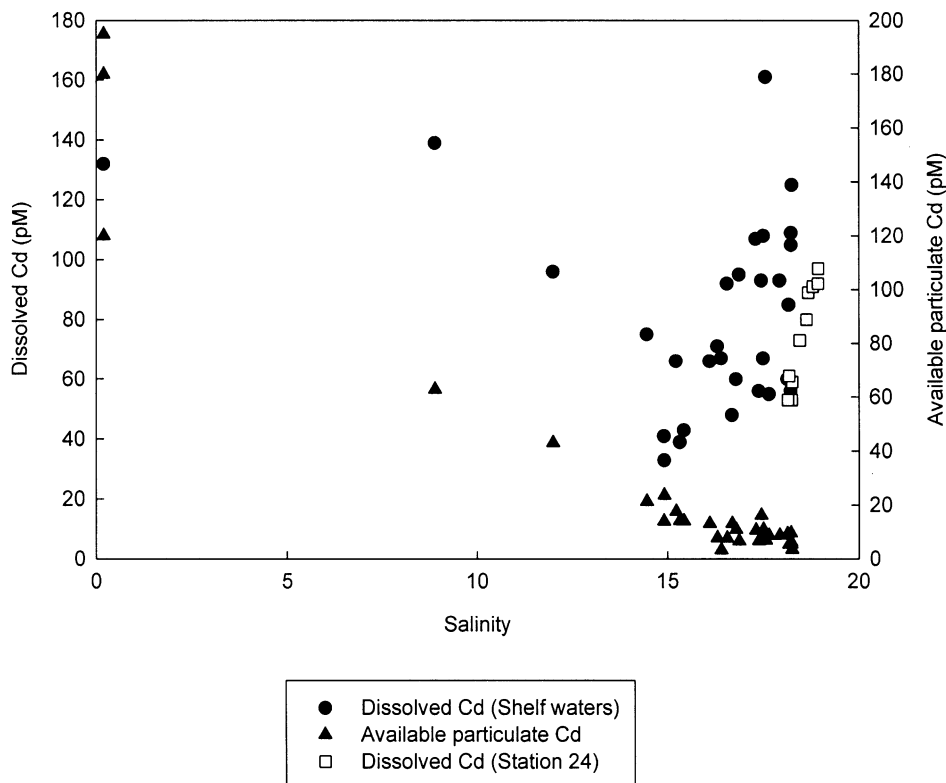


Fig. 17. Dissolved and available particulate Cd plotted versus salinity at stations on the Northwestern Black Sea shelf.

Table 4

Correlation coefficients between dissolved Cd and $\text{NO}_3^- + \text{NO}_2^-$, Si(OH)_4 , PO_4^{3-} , dissolved Mn and dissolved Fe

Station	$\text{NO}_3^- + \text{NO}_2^-$	Si(OH)_4	PO_4^{3-}	Dissolved Mn	Dissolved Fe
1	—	—	—	−0.43	−0.01
3 (oxic layer)	0.98	0.87	0.93	−0.28	−0.66
5	0.97	0.83	0.97	0.87	0.97
6	0.95	0.98	0.99	0.99	0.97
7	0.92	0.73	0.64	0.81	0.86
9	0.99	0.99	0.99	0.99	0.99
10	0.015	0.99	0.13	0.99	0.97
20	0.96	0.87	—	0.34	−0.33
21	0.77	0.86	—	0.63	0.30
24	0.93	0.57	0.48	−0.21	−0.59

release of Cd adsorbed onto Mn- and Fe-oxides following reductive dissolution of the host phases.

4.3.8. Zinc

Dissolved and available particulate Zn concentrations were relatively uniform throughout the NW Black Sea (1–6 and 0–1 nM, respectively) (Fig. 11). Exceptions were Stations 9 and 10 which were influenced by large riverine inputs and thus exhibited higher available particulate Zn concentrations (8 and 5 nM, respectively), in surface waters. At Station 6, available particulate Zn concentrations were also high near the bottom possibly due to adsorption of dissolved Zn onto Mn- and Fe-oxides although such an increase was not observed at Station 24 where total Mn and Fe concentrations were higher. The vertical distribution of dissolved Zn was generally similar to that of dissolved Cd. Common trends included lower dissolved concentrations in surface water than in deeper water consistent with coupling with the cycle of production and decomposition of organic matter; at most stations on the shelf (except Stations 10 and 20), dissolved Zn concentrations correlated better with (nitrate + nitrite) or Si(OH)_4 concentrations than with phosphate or dissolved Mn and Fe concentrations (Table 5). At Stations 10 and 20, relatively high dissolved Zn concentrations were observed in bottom waters suggesting benthic inputs. As with Cd, Zn adsorbed onto Mn- and Fe-oxides might be released alongside Mn and Fe, following the reductive dissolution of Mn- and Fe-oxides. Increases in dissolved Zn in surface waters were observed at some stations (1, 5, 6, 9 and 21), as a result of riverine and/or atmospheric inputs.

4.4. Comparison between the Black Sea and the Adriatic Sea

Like in the northwestern Black Sea, high concentrations of nutrients and advanced eutrophication have been also reported in the northern Adriatic Sea (Justic, 1991; Justic et al., 1987, 1993, 1994). Dissolved Mn and Fe concentrations were much higher in the northwestern Black Sea than in the northern Adriatic Sea (Table 6), suggesting that the effects of the degradation of organic carbon on the redox cycling of Mn and Fe were more intense in the

Table 5

Correlation coefficients between dissolved Zn and $\text{NO}_3^- + \text{NO}_2^-$, Si(OH)_4 , PO_4^{3-} , dissolved Mn and dissolved Fe

Station	$\text{NO}_3^- + \text{NO}_2^-$	Si(OH)_4	PO_4^{3-}	Dissolved Mn	Dissolved Fe
1	0.12	0.22		-0.34	0.43
3 (oxic layer)	0.98	0.87	0.93	-0.28	-0.66
5	0.74	0.87	0.44	0.22	0.76
6	0.69	0.57	0.62	0.56	0.47
7	0.64	0.54	0.72	0.09	0.34
9	0.99	0.99	0.99	0.96	0.95
10	-0.10	0.97	0.01	0.99	0.99
20	-0.07	-0.34		0.68	0.88
21	0.73	0.78		0.55	0.44
24	0.88	0.70	0.68	0.09	-0.40

Table 6

Concentrations (nM) of dissolved Mn, Fe, Co, Pb, Cu, Ni, Cd and Zn in the northern Adriatic Sea and the northwestern Black Sea shelf

Metal	Northern Adriatic Sea ^a	Northwestern Black Sea (This study)
Mn	6.7–192	1.2–1350
Fe	0.05–25	0.4–181
Co	0.235–1.07	0.04–1.89
Pb	0.039–0.750	0.03–0.61
Cu	3.14–24.4	2.9–28.8
Ni	6.1–21	8.6–17.5
Cd	0.071–0.220	0.033–0.161
Zn	2.3–22	1–45

^aTankéré (1998).

northwestern Black Sea than in the Adriatic Sea. This was consistent with larger organic carbon inputs to the seafloor of the northwestern Black Sea shelf (Primary productivity in the Danube estuary = $0.3\text{--}4.4 \text{ gC m}^{-2} \text{ d}^{-1}$; Humborg, 1997) than in the Northern Adriatic Sea (Primary productivity in the Po estuary = $0.2\text{--}2.0 \text{ gC m}^{-2} \text{ d}^{-1}$; Poniz et al., 1996). Dissolved concentrations of Co, Pb, Cd, Cu, Ni and Zn were generally similar in the northern Adriatic Sea and the northwestern Black Sea. Concentrations of Mn and Fe in particles were generally higher in the Black Sea than in the northern Adriatic Sea (Table 7). This is expected as a result of oxidation of higher dissolved Mn and Fe concentrations in the Black Sea than in the Adriatic. By contrast, concentrations of Pb, Cu, Ni, Cd and Zn in particles were higher in the northern Adriatic Sea than in the Black Sea. The relative enrichment of these metals in shelf waters of the Adriatic may be associated to the higher loading of metals through wastewater discharges or to the more restricted exchange with the open sea.

Table 7
Concentrations of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb in particles ($\mu\text{g g}^{-1}$) in the northern Adriatic Sea and the northwestern Black Sea shelf

Metal	Northern Adriatic Sea ^a	Northwestern Black Sea (This study)
Mn	56–5460	80–62,700
Fe	800–78,700	166–130,000
Co	—	0.38–39
Ni	12–92	2–36
Cu	21–1560	5–225
Zn	166–2020	12–359
Cd	0.66–20	0.34–6.3
Pb	9.7–496	2.4–121

^aPrice et al. (1996).

5. Conclusions

Measurements of dissolved and reactive particulate metals (Mn, Fe, Co, Pb, Cd, Cu, Ni and Zn) and total particulate metals (Mn and Fe) have provided a systematic picture of the operation of biogeochemical processes in the northwestern Black Sea. They have demonstrated the importance of the magnitude of metal and nutrient inputs from the Danube and from other localized sources, together with the importance of the Mn and Fe cycles in determining trace metal distributions.

Dissolved and particulate Mn and Fe were highest where there is strong evidence from other work that low oxygen conditions occurred, i.e. at inshore stations and near the sediment–water interface. Unexpectedly high concentrations were also observed at the thermocline at one site (Station 7), probably as a result of the reductive remobilization of particulate Mn and Fe trapped within a biofilm matrix. Dissolved and particulate Mn and Fe distributions were also strongly influenced by riverine inputs and by water column stability. Trace metal distributions, especially those of Co, Ni, Zn and Cd, were influenced by the redox (and phase) transformations of Mn and Fe. Elevated concentrations of dissolved Pb were observed in surface waters at the outermost stations. This may be attributed to atmospheric inputs combined with less efficient scavenging of metals in these low SPM waters. The similarities of Cd and Zn profiles suggest some interdependence in their cycles, in particular a common benthic source. Dissolved Cu and Ni were found in relatively higher concentrations (relative to other metals) in the northwestern Black Sea shelf than in the oxic layer of the deep basin reflecting the proportionally greater impact of riverine and anthropogenic inputs on this land-locked system.

This study considers the result of biogeochemical processes on the bulk properties of the water column. Understanding of these processes for the purpose of understanding and forecasting environmental changes in the Black Sea will only be made possible by further process studies of the chemical transformations and fluxes occurring at some of the key interfaces identified here (pycnocline, sediment–water interface). Because many of the processes involved are ultimately driven by the microbial decomposition of organic matter, greater attention will need to be given to metal–microbiological interactions. Only then will it become possible to predict the consequences

on metal cycling of the currently proposed reductions in both nutrient and metal loads carried by inflowing rivers.

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