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Distribution and transfer of trace metals in the Aegean Seawater (Eastern Mediterranean Basin)

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Abstract

Recent measurements of dissolved Cd, Cu, Ni and Mn in 324 water samples of the Aegean Sea fill the gap of missing knowledge in this part of the Eastern Mediterranean and try to identify their main input sources and spreading pathways. The analyses indicate that trace metal concentrations in the North and South Aegean Sea are generally in good agreement with those reported for the Western Mediterranean Sea. In the North Aegean Sea the trace metal distribution patterns differentiate mainly according to the existing water masses. Hence, a strong influence of the Black Sea Water, enriched in trace metals, is clearly recorded for Mn. Concentrations of this metal are one order of magnitude higher in the surface layer than those of the deeper waters. This feature is followed to a lesser degree also by Cd, Cu and Ni. Trace metal concentrations in the South Aegean Sea reveal almost constant values throughout the watercolumn similar to those observed in the North Aegean Sea below the depth of 100 m. Manganese values in the South Aegean Sea are considerably lower comparing with the North Aegean ones, showing relatively enhanced surface values which decrease with depth.

Keywords: Trace metals (Cd, Cu, Ni, Mn), Seawater, Aegean Sea, Black Sea Water.

Introduction

During the last decades, much of the research effort on the oceanographic studies concerning the Mediterranean Sea was focused in the trace metal analysis. The "PHYCEMED" Project (1981-1983) gave the first systematic knowledge about the biogeochemical cycles of the trace metals in the Western Mediterranean Sea: concentrations, distribution, behaviour and chemical speciation of dissolved and particulate matter were among the priorities of this Project. A more thorough and in depth investigation had been gained through the CEC "EROS" Project. Trace metal concentrations concerning the W. Mediterranean Sea from the Straits of Gibraltar, the adjacent Atlantic Ocean, the Alboran Sea and the Straits of Sicily have been reported (MORLEY *et al.*, 1990; ZHANG & WOLLAST, 1993; ACHTERBERG *et al.*, 1997; CHOU & WOLLAST, 1993; MARTIN *et al.*, 1993; MORLEY & BURTON, 1992, etc). MORLEY &

BURTON (1993) estimated fluxes of Cd, Co, Cu, Mn, Ni, Pb and Zn expressed as inputs to the W. Mediterranean.

Much less attention has been given to the eastern part of the Mediterranean Sea. Until the CEC/MAST supported Project "PELAGOS", which started on 1994, the information about trace metal concentration in Eastern Mediterranean Seawater remains sparse. This Project afforded an opportunity to investigate systematically a group of trace metals in the watercolumn of the South Aegean Sea, a region where limited data were available, and also to evaluate the importance of processes determining the distributions and transfers of metals. Reviewing the existing literature we can find few data concerning the Aegean Sea: ROZHANSKAYA (1973) reported Mn, Cu and Zn concentrations for eight surface seawater samples collected from the Aegean Sea; RYABININ and LAZAREVA (1980) in a very dense grid of stations covering both North and South Aegean Sea depicted Cd, Ag and Cu concentrations in seawater samples from the whole watercolumn. Also, distributions of Cd, Cu, Zn, As, Hg, Ni, Cr, Fe, Pb in Aegean Seawater samples have been reported by FUKAI & HUYNH-NGOC, 1976; ROMANOV *et al.*, 1977; HUYNH-NGOC & FUKAI, 1978; AUBERT *et al.*, 1980; SCOULLOS & DASSENAKIS, 1981 and 1983; FERRARA *et al.*, 1990. Several results concerning coastal situations characterized by the presence of pollution of anthropogenic origin (FYTIANOS & VASSILIKIOTIS, 1983; SCOULLOS, 1981, 1983) are also available.

More recently (1996-1998) and within the framework of the European MATER Project (Mediterranean Targeted Project MTP-II/MAST), a systematical study of dissolved trace metal distributions in both North and South Aegean Sea has been carried out. In the present work the first results obtained on dissolved Cd, Cu, Ni and Mn, during two oceanographical cruises, March and September 1997, are reported.

The metals investigated are chosen to represent a variety of biogeochemical characteristics. Manganese, is scavenged, strongly hydrolised and highly particle-reactive metal, with relatively short residence time <103 years (BURTON & STATHAM, 1990). The aquatic chemistry of manganese is strongly influenced by reduction-oxidation reactions, with highly dynamic cycling associated with the mobilization into solution of the metal as Mn(+II), where reduction occurs, and its conversion to Mn(+III) and Mn(+IV), which are of much more limited solubility, in environments which are oxidizing for manganese (BURTON *et al.*, 1993). Nickel, copper, and cadmium, which show some degree of positive correlation with the micronutrients, are less particle-reactive. Nevertheless, in the stratified open ocean their concentrations are influenced by down-column transport in association with biogenous particulate material, a behaviour which is particularly marked for cadmium. Of the metals studied, Cd and Cu are considered of significant ecotoxicological importance.

Generally, in the Mediterranean Sea the nutrient-like metals exhibit surface concentrations relatively high as compared to surface concentrations of the Atlantic or Pacific Oceans and at depths >300m the concentrations appear quite homogenous (BETHOUX *et al.*, 1990). The vertical profiles of trace metals are more or less homogenous and such distribution differs from the one observed in the open ocean, the latter being similar to nutrient profiles with a depleted surface layer and increasing concentrations with depth. In order to explain such a peculiarity in the Mediterranean Sea, limited recycling of nutrients (BOYLE *et al.*, 1985), surface enrichment from sources outside the Mediterranean (SHERRELL & BOYLE, 1988), trace-metal-enriched source waters West of the Strait of Gibraltar (VAN GEEN *et al.*, 1988), inputs probably derived from increase in industrial, agricultural and

urban activities of the surrounding countries (BETHOUX *et al.*, 1990), have been sustained.

The main objectives of this work are to obtain the first systematic baseline information regarding the spatial and vertical distribution of the trace metal concentrations in this part of the Mediterranean Sea. Also, to identify the main input sources and spreading pathways of the trace metals and to understand the mechanisms which are responsible for the trophic differentiation between North and South Aegean Sea ecosystems.

Materials and Methods

Seawater samples were collected from 7 stations in the North and 6 stations in the South Aegean Sea (Fig. 1) during two cruises (March and September '97) with the *R/V Aegeo*. The stations locations were:

North Aegean	*Locations*	
MNB1	40.16,00 N	25.12,00 E
MNB2	40.04,65 N	24.63,20 E
MNB3	39.13,45 N	25.00,00 E
MNB4	39.46,70 N	25.30,66 E
MNB5	40.12,65 N	25.28,50 E
MNB6	40.34,70 N	25.08,00 E
MNB7	40.16,60 N	24.50,50 E
South Aegean		
MSB1	36.04,50 N	25.17,00 E
MSB2	35.44,70 N	25.06,00 E
MSB3	36.00,00 N	25.42,30 E
MSB4	36.15,00 N	24.06,30 E
MSB6	36.00,00 N	25.42,30 E
MSB7	35.40,00 N	26.13,00 E

The total number of the samples analysed was three hundred twenty-four. The samples were collected with the use of 10-lt modified Teflon-coated Go-Flo bottles, deployed by a rosette in conjunction with CTD probe. The samples were pres-

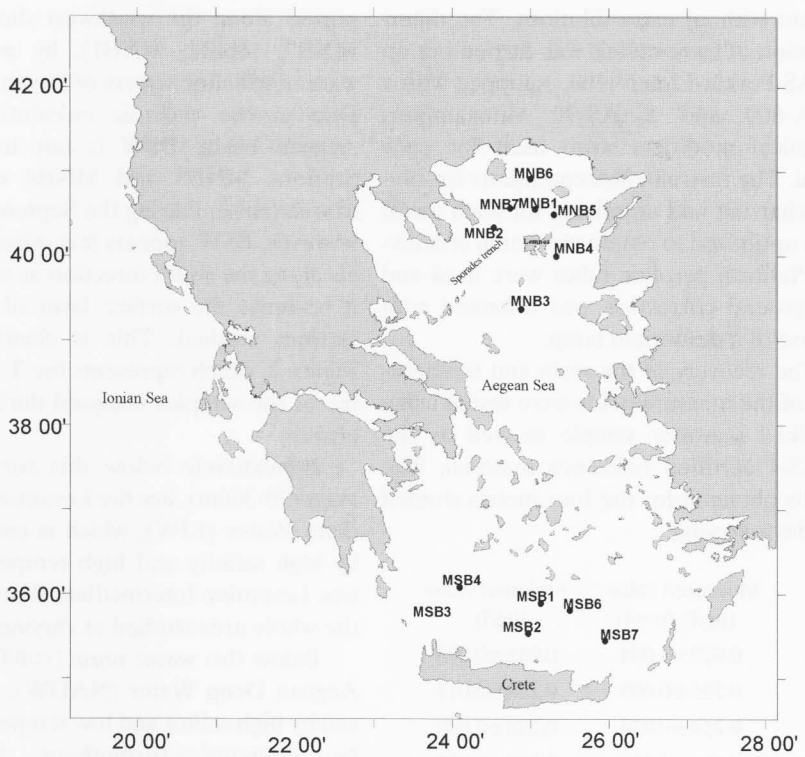

Fig.1: The stations sampled in the North and South Aegean Sea.

sure filtered directly from the Go-Flo bottles through acid-clean Millipore membrane filters, held on Teflon holders. The changing of filters, the acidification and the storage on board, were performed in the "clean container" of the *R/V Aegeo*. Ashore, a preconcentration step using Chelex-100 resin was followed within a clean laminar hood (class 100 U.S. Stds). The procedure is a slight modification of that proposed by Riley and Taylor (1968) and Kingston, et al., (1978). Volumes of 500ml of samples were neutralized to pH 7.5 with suprapure NH_3 and then passed through polyethylene columns filled with the resin. The flow rate was kept at ~0.5ml/min using a peristaltic pump. The system allowed the simultaneous preconcentration of eight samples. Trace metals were then eluted from the resin using suprapure HNO_3 2N and HCl 1N in a 2:1 ratio. The preconcentration factor achieved (100) was suitable for trace metal determinations without extra dilutions. The determination of trace metals was carried out on a AAS Perkin-Elmer 4100, equipped with a HGA-600 and a AS-70 autosampler. Chemical modifiers were used for each metal. The instrumental conditions for drying, charring and atomizing for each metal were optimized to obtain maximum sensitivity. Platform pyrolitic tubes were used and background correction was obtained with the use of a deuterium lamp.

The recovery of the resin and the accuracy of the measurements were tested using a spiked seawater sample as well as the NASS-4 certified reference material. The results obtained for the four metals studied are the following:

	Measured value (μg/l) (n=4)	Assigned value (μg/l)
Cd	0.022±0.004	0.016±0.003
Cu	0.235±0.009	0.228±0.011
Ni	0.254±0.034	0.228±0.009
Mn	0.353±0.019	0.380±0.023

All plastic-ware used during the analytical procedure was precleaned with suprapure HCl 10%, and the deionized water was provided by a Milli-Q system. Precautions were taken in all stages in order to avoid contamination.

Results and Discussion

Hydrographic features

North Aegean Sea

Three major water bodies can be identified in the area under investigation (ZERVAKIS, *et al.*, 1998). Black Sea Water (BSW) originating from the Dardanelles Straits, with low temperature and low salinity values, is detectable as a surface water body (0-75m) at Stations MNB5 and MNB6 situated NW of the Straits. This distinct surface water mass is modified as it is transported along the southwest direction (Sts MNB7, MNB2, MNB1), by mixing with warm and saline waters of Levantine origin. Due to the cyclonic circulation in the Aegean basin, BSW is not traceable at Stations MNB3 and MNB4 during the March cruise. During the September cruise, however, BSW appears less mixed and travels along the south direction as well, so that it occupies the surface layer of almost all stations studied. This is clearly seen in Figure 2, which represents the T-S diagramme of the samples analysed during the two cruises.

Immediately below this surface water mass (70-300m), lies the Levantine Intermediate Water (LIW), which is characterized by high salinity and high temperature values. Levantine Intermediate Water occupies the whole area studied at varying depths.

Below this water mass (<400m), North Aegean Deep Water (NADW), characterized by high salinit and low temperature, can be detected throughout the area. Furthermore, as it can be seen from the

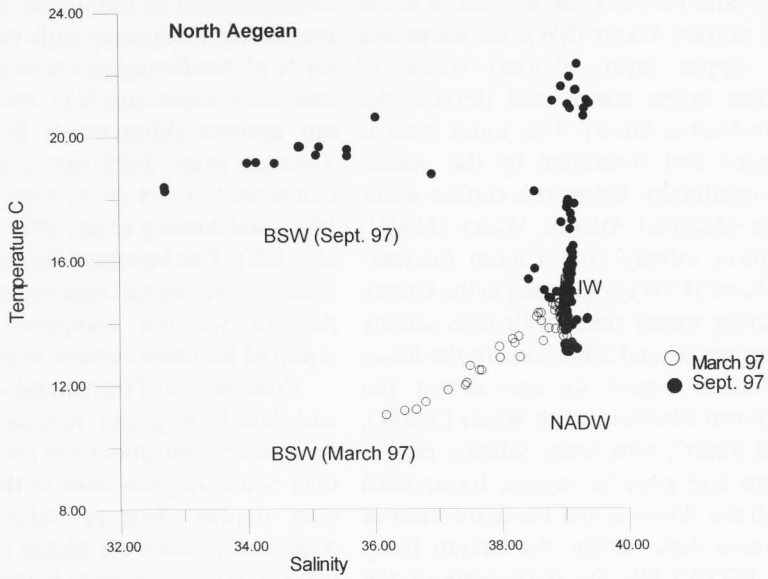

Fig. 2: Temperature - Salinity diagramme in the North Aegean Sea.

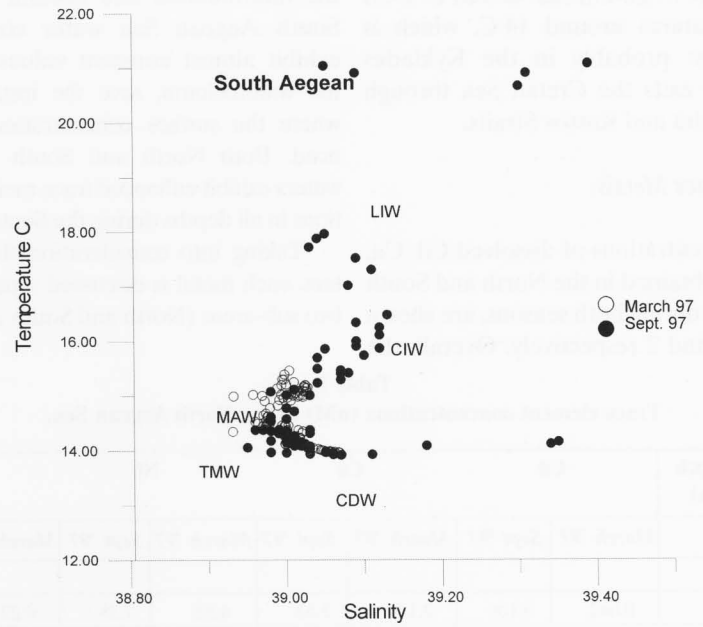

Fig. 3: Temperature - Salinity diagramme in the South Aegean Sea.

detailed T-S diagramme of March, NADW formed in the Skyros Basin (St. MNB3) is of different origin than the one formed in the Sporades Trench (Sts MNB2, MNB7, MNB1).

South Aegean Sea

From the T-S diagramme of the stations sampled (Fig. 3), we can distinguish the fol-

lowing water masses (THEOCHARIS, *et al.*, in press): Surface Water (SW), the warm and saline upper layer (0-70m) water of Levantine origin transported through the Eastern Cretan Straits. This water mass is influenced and controlled by the atmospheric conditions. Below this surface water lies the Modified Atlantic Water (MAW) with lower salinity. The Cretan Intermediate Water (CIW) originating in the Cretan Sea during winter times with high salinity lies between 50 and 200-300m. In the lower intermediate layers we can detect the Transitional Mediterranean Water (TMW), an "old water", with lower salinity, rich in nutrients and poor in oxygen, transported through the Western and Eastern Straits of the Cretan Arc. Finally, the Cretan Deep Water (CDW) fills the deep parts of the area. This water mass is characterized by high salinity (>39 p.s.u.), high density (>29.2) and temperatures around 14°C, which is formed most probably in the Kyklades Plateau and exits the Cretan Sea through the Antikythira and Kassos Straits.

Dissolved Trace Metals

The concentrations of dissolved Cd, Cu, Ni and Mn obtained in the North and South Aegean Sea, during both seasons, are shown in Tables 1 and 2 respectively. Overall, the concentrations of the metals studied are in reasonable agreement with those reported for N.W. Mediterranean Seawater, Gibraltar and Sicily Straits and N.E. Atlantic, by various authors (MORLEY & BURTON, 1992; TANKERE *et al.*, 1995; SPIVACK *et al.*, 1983; COPIN-MONTEGUT *et al.*, 1986; YOON *et al.*, 1995, and Morley *et al.*, 1997, van Geen *et al.*, 1988). This becomes obvious in Table 3, where trace metal concentrations in the Aegean Sea are compared with those reported for other oceanic regimes.

Comparison of the two sub-areas (North and South Aegean) reveals that North Aegean concentrations are generally higher than South Aegean ones in the corresponding depths. Surface values in North Aegean Sea water are higher in the case of Cd, Cu, Ni or extremely higher (one order of magnitude) in the instance of Mn than the intermediate and bottom layers ones. South Aegean Sea water concentrations exhibit almost constant values throughout the watercolumn, save the instance of Mn, where the surface concentrations are enhanced. Both North and South Aegean Sea waters exhibit enhanced trace metal concentrations in all depths during the September cruise.

Taking into consideration these parameters, each metal is discussed separately in the two sub-areas (North and South Aegean Sea).

Table 1
Trace element concentrations (nM) in the North Aegean Sea.

Stations	Depth (m)	Cd		Cu		Ni		Mn	
		March '97	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*
MNB1									
	3	0.042	0.106	2.14	2.52	4.52	7.38	4.27	12.60
	25	0.038	0.125	1.92	2.91	4.78	6.62	4.80	0.90
	75	0.043	0.198	1.78	1.78	4.24	5.24	3.81	4.40
	125	0.045	0.098	1.91	1.45	4.45	4.85	1.93	1.87
	200	0.048	0.170	2.15	1.94	4.53	5.34	3.16	1.83
	275	0.045	0.243	1.46	1.94	4.78	5.76	2.65	2.49
	400	0.038	0.150	1.35	1.38	4.56	5.23	1.25	1.39

Table 1 (continued)

Stations	Depth (m)	Cd		Cu		Ni		Mn	
		March '97	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*
	570	0.038	0.114	1.48	1.35	4.71	4.12	2.11	1.35
	740	0.042	0.105	1.65	1.74	4.49	4.81	0.95	1.28
	910	0.039	0.122	1.88	1.57	4.64	5.04	1.31	0.98
	1080	0.040	0.108	1.35	1.58	4.05	4.77	1.44	1.05
	1280	0.036	0.111	1.68	1.67	4.25	4.95	4.84	1.24
min.		***0.036***	***0.098***	***1.35***	***1.35***	***4.05***	***4.12***	***0.95***	***0.90***
max.		***0.048***	***0.243***	***2.15***	***2.91***	***4.78***	***7.38***	***4.84***	***12.60***
mean		***0.041***	***0.138***	***1.73***	***1.82***	***4.50***	***5.34***	***2.71***	***2.62***
MNB2									
	3	0.036	0.203	2.22	3.23	4.76	8.43	4.89	13.74
	25	0.044	0.212	2.31	1.91	5.77	5.45	3.76	8.40
	50	0.039	0.111	2.09	1.65	5.16	4.83	2.91	6.16
	75	0.035	0.130	3.41	1.60	7.81	4.96	2.59	4.38
	125	0.032	_	2.00	_	3.89	_	1.11	_
	170	0.044	0.114	2.03	1.53	5.21	4.76	0.95	0.99
	200	0.052	0.096	1.75	1.05	4.07	4.33	0.78	0.91
	300	0.053	0.110	2.08	1.44	4.58	4.37	0.74	1.34
	450	0.050	0.108	2.40	1.32	6.07	4.40	0.88	0.79
	600	0.060	0.117	2.41	1.32	5.65	4.63	0.84	1.03
	750	0.058	0.110	2.05	1.31	3.71	4.31	0.46	0.52
	990	0.059	0.108	2.59	1.35	3.08	4.35	1.44	1.46
min.		***0.032***	***0.096***	***1.75***	***1.05***	***3.08***	***4.31***	***0.46***	***0.52***
max.		***0.060***	***0.212***	***3.41***	***3.23***	***7.81***	***8.43***	***4.89***	***13.74***
mean		***0.047***	***0.129***	***2.28***	***1.61***	***4.98***	***4.98***	***1.78***	***3.61***
MNB3									
	3	0.363	0.118	2.82	2.92	3.79	7.13	4.31	35.49
	50	0.217	0.114	1.61	2.27	2.26	7.40	3.85	5.38
	125	0.101	0.111	1.64	2.12	4.67	4.23	3.62	3.47
	175	0.105	0.073	1.50	1.98	4.69	4.72	3.12	1.76
	240	0.119	0.086	3.31	2.35	4.91	4.29	3.05	1.35
	320	0.106	0.084	1.73	2.06	4.73	5.15	1.51	1.17
	440	0.085	0.104	1.51	1.90	4.72	4.17	0.92	1.30
	550	0.087	0.091	1.64	2.09	4.80	5.32	0.62	0.97
	650	0.082	0.084	2.10	1.07	4.66	4.50	1.03	0.76
	695	0.085	0.092	1.78	1.86	4.06	4.41	1.28	0.63
	715	0.080	0.073	2.25	2.03	4.74	4.62	1.65	0.65
	810	0.041	0.073	2.09	2.07	4.25	4.50	2.41	0.69
min.		***0.041***	***0.073***	***.50***	***1.07***	***2.26***	***4.17***	***0.62***	***0.63***
max.		***0.363***	***0.118***	***3.31***	***2.92***	***4.91***	***7.40***	***4.31***	***35.49***
mean		***0.123***	***0.092***	***2.00***	***2.06***	***4.36***	***5.04***	***2.28***	***4.47***

Table 1 (continued)

Stations	Depth (m)	Cd		Cu		Ni		Mn	
		March '97	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*
MNB4									
	3	0.420	0.154	3.13	4.87	2.40	3.87	4.62	44.98
	35	0.083	0.106	1.63	3.01	2.22	4.72	4.31	11.34
	65	0.105	0.137	1.57	2.64	2.33	5.30	4.64	4.80
	90	0.118	0.148	1.36	3.10	2.31	5.38	4.46	4.81
min.		***0.083***	***0.106***	***1.36***	***2.64***	***2.22***	***3.87***	***4.31***	***4.80***
max.		***0.420***	***0.154***	***3.13***	***4.87***	***2.40***	***5.38***	***4.64***	***44.98***
mean		***0.181***	***0.136***	***1.92***	***3.41***	***2.31***	***4.82***	***4.51***	***16.48***
MNB5									
	3	0.064	0.107	3.53	3.55	3.25	7.31	7.40	15.48
	25	0.035	0.131	2.12	3.00	5.60	6.64	6.19	14.35
	70	0.028	0.110	1.61	2.05	4.77	4.85	2.03	4.70
	100	0.033	0.125	1.65	2.65	5.04	4.65	0.27	4.17
	150	_	0.088	_	2.17	_	4.85	_	2.31
	200	0.022	0.088	1.50	1.98	4.92	4.50	0.07	1.61
	310	0.032	0.091	1.32	2.48	4.21	4.58	0.36	1.41
	420	0.035	0.109	1.65	2.11	4.64	4.70	2.77	2.53
	540	0.043	_	1.58	_	4.89	_	3.38	_
min.		***0.022***	***0.088***	***1.32***	***1.98***	***3.25***	***4.50***	***0.07***	***1.41***
max.		***0.036***	***0.131***	***3.53***	***3.55***	***5.60***	***7.31***	***7.40***	***15.48***
mean		***0.064***	***0.106***	***1.87***	***2.50***	***4.66***	***5.26***	***2.81***	***5.82***
MNB6									
	3	0.026	0.109	2.28	4.95	5.92	6.74	3.43	16.60
	10	0.037	0.121	2.29	3.81	5.85	7.71	3.25	16.30
	21	0.038	0.088	2.22	3.13	5.59	6.45	5.46	15.03
	36	0.028	0.096	2.16	4.14	5.47	7.01	4.83	19.34
	43	0.033	0.125	2.40	3.54	5.29	6.42	3.60	11.38
	85	0.036	0.175	1.95	2.71	5.42	4.41	1.90	3.60
	130	0.031	0.102	1.33	2.77	4.80	5.12	2.63	4.53
	147	0.019	0.082	1.60	2.97	4.26	3.95	2.30	3.69
min.		***0.019***	***0.082***	***1.33***	***2.71***	***4.26***	***3.95***	***1.90***	***3.60***
max.		***0.038***	***0.175***	***2.40***	***4.95***	***5.92***	***7.71***	***5.46***	***19.34***
mean		***0.031***	***0.112***	***2.03***	***3.50***	***5.32***	***5.98***	***3.42***	***11.31***
MNB7									
	3	0.037	0.210	3.12	5.02	3.93	8.46	3.54	18.01
	25	0.037	0.135	2.68	4.35	3.76	7.89	2.85	15.55
	60	0.062	0.137	1.67	5.93	3.53	6.61	1.91	5.92
	100	0.034	0.135	1.93	2.73	3.80	4.90	2.23	2.82
	120	_	0.097	_	3.34	_	6.82	_	1.90
	150	0.040	0.062	1.89	4.06	4.19	5.85	0.66	1.43
	180	0.042	0.162	1.73	2.61	3.33	6.15	0.30	2.42

Table 1 (continued)

Stations	Depth (m)	Cd		Cu		Ni		Mn	
		March '97	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*
	300	0.033	0.056	0.74	3.51	4.44	5.10	0.37	1.21
	450	0.034	0.077	1.22	2.68	4.93	5.22	3.18	0.94
	490	0.038	0.136	1.59	3.23	4.41	6.14	0.47	2.05
	560	0.041	0.120	1.81	5.01	4.27	6.15	1.04	1.08
	300	0.033	0.056	0.74	3.51	4.44	5.10	0.37	1.21
	450	0.034	0.077	1.22	2.68	4.93	5.22	3.18	0.94
	490	0.038	0.136	1.59	3.23	4.41	6.14	0.47	2.05
	560	0.041	0.120	1.81	5.01	4.27	6.15	1.04	1.08
	640	0.040	0.135	2.00	4.46	3.80	6.43	0.48	1.15
	710	0.039	0.097	2.20	3.52	4.41	5.40	0.82	2.47
min.		***0.033***	***0.056***	***0.74***	***2.61***	***3.33***	***4.90***	***0.30***	***0.94***
max.		***0.062***	***0.210***	***3.12***	***5.93***	***4.93***	***8.46***	***3.54***	***18.01***
mean		***0.040***	***0.120***	***1.88***	***3.88***	***4.07***	***6.24***	***1.49***	***4.38***

Table 2
Trace element concentrations (nM) in the South Aegean Sea.

Stations	Depth (m)	Cd		Cu		Ni		Mn	
		March '97	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*
MSB1									
	2	0.061	0.095	1.67	1.81	3.71	5.16	1.85	6.47
	25	0.050	0.056	2.11	1.70	3.72	4.89	1.89	6.30
	50	0.078	0.048	1.76	1.81	3.93	5.03	2.03	3.31
	75	0.086	0.096	1.64	3.21	3.47	5.76	1.78	4.45
	100	0.081	0.170	1.76	2.62	3.36	6.33	1.95	4.16
	150	0.093	0.074	2.04	2.78	3.48	5.72	2.09	1.66
	200	0.090	0.047	3.50	2.70	3.20	5.29	0.66	1.17
	250	0.096	0.067	3.79	1.08	4.46	4.99	0.46	0.56
	400	0.060	0.054	3.22	1.92	4.26	5.47	1.23	0.68
	500	0.050	_	1.87	_	3.75	_	1.00	_
	700	0.050	0.065	4.08	3.30	3.34	4.25	0.71	0.65
	800		0.074	_	1.37	_	4.50	_	0.67
	950	0.067	0.042	4.34	3.32	3.77	4.95	0.37	0.80
	1100	0.073	_	1.99	_	3.87	_	0.64	_
	1250	0.059	0.067	3.65	1.42	2.91	4.92	0.68	0.35
	1500	0.083	0.076	1.55	1.33	3.15	6.12	0.78	2.08
	1750	0.055	0.030	2.44	3.08	2.96	5.34	0.76	1.98
min.		***0.050***	***0.030***	***1.55***	***1.08***	***2.91***	***4.25***	***0.37***	***0.35***
max.		***0.096***	***0.170***	***4.34***	***3.32***	***4.46***	***6.33***	***2.09***	***6.47***
mean		***0.071***	***0.071***	***2.59***	***2.23***	***3.58***	***5.25***	***1.18***	***2.35***

Table 2 (continued)

Stations	Depth (m)	Cd		Cu		Ni		Mn	
		March '97	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*
MSB2									
	2	0.051	0.054	2.28	1.89	6.10	4.82	2.49	6.76
	25	0.050	0.067	2.05	1.29	6.82	4.38	2.42	7.17
	50	0.016	0.059	2.01	1.10	6.16	4.62	0.51	4.55
	75	0.146	0.050	5.19	1.58	_	5.00	3.74	3.50
	100	0.048	0.061	1.94	1.16	6.33	4.29	2.37	1.98
	150	0.084	0.068	2.07	1.00	5.62	4.52	2.47	1.09
	200	0.048	0.068	1.81	1.24	5.83	4.36	0.81	0.85
	250	0.032	0.068	2.38	1.15	5.91	4.63	0.18	0.64
	450	0.063	0.045	3.50	1.85	7.46	5.07	2.42	0.55
	600	0.079	0.044	2.98	1.40	8.17	4.78	0.62	0.60
	750	0.061	0.040	1.59	2.03	6.41	5.11	0.70	1.04
	900	0.080	_	2.36	_	6.72	_	1.30	_
	1000	0.084	_	1.72	_	6.00	_	1.46	_
	1100	0.086	0.076	1.45	1.29	6.42	4.73	1.67	0.42
	1200	0.118	0.056	1.98	1.39	6.72	4.80	1.34	0.52
	1270	0.176	0.072	4.65	1.14	6.89	4.54	1.23	0.50
	1400	_	0.050	_	1.26	_	4.33	_	0.78
min.		***0.016***	***0.040***	***1.45***	***1.00***	***5.62***	***4.29***	***0.18***	***0.42***
max.		***0.176***	***0.076***	***5.19***	***2.03***	***8.17***	***5.11***	***3.74***	***7.17***
mean		***0.076***	***0.059***	***2.50***	***1.38***	***7.64***	***4.67***	***1.61***	***2.06***
MSB3									
	2	0.099	0.081	3.40	4.61	4.74	5.63	2.32	4.44
	25	0.141	0.056	2.48	3.64	8.31	5.84	2.27	4.22
	50	0.054	0.076	1.69	2.72	4.83	5.13	2.00	2.03
	75	0.068	0.081	2.11	2.64	4.26	5.25	1.66	1.75
	100	0.092	0.161	1.94	4.53	4.58	4.84	0.86	1.21
	150	0.104	0.041	1.75	2.79	4.71	5.50	2.35	0.86
	200	0.068	0.096	1.51	3.86	4.99	6.09	0.80	0.74
	250	0.046	0.134	2.74	4.37	5.66	6.24	0.44	0.78
	300	0.045	0.059	2.40	2.59	5.60	5.49	0.70	0.50
	400	0.039	0.086	1.66	3.72	4.89	5.32	0.40	0.51
	550	0.039	0.080	1.76	3.30	5.06	5.27	0.76	0.25
	700	0.088	0.071	1.71	2.92	4.85	5.34	0.53	0.22
	900	0.120	0.156	2.07	2.17	5.12	6.44	0.26	0.35
	1100	0.089	0.101	1.76	3.05	4.94	5.88	0.38	0.25
	1125	0.066	0.060	1.98	3.45	5.34	5.69	0.38	0.22
	1183	0.035	0.145	1.52	4.81	4.37	5.68	0.20	0.35
min.		***0.035***	***0.041***	***1.51***	***2.17***	***4.26***	***4.84***	***0.20***	***0.22***
max.		***0.141***	***0.161***	***3.40***	***4.817***	***8.31***	***6.44***	***2.35***	***4.44***
mean		***0.075***	***0.093***	***2.03***	***3.454***	***5.14***	***5.60***	***1.02***	***1.17***

Table 2 (continued)

Stations	Depth (m)	Cd		Cu		Ni		Mn	
		March '97	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*
MSB4									
	3	0.032	0.078	3.95	1.59	2.69	6.14	1.61	5.35
	10	0.093	_	1.62	_	4.13	_	1.50	_
	25	0.093	0.097	1.83	2.38	5.05	5.58	1.69	6.90
	50	0.055	0.080	1.46	1.73	4.54	5.09	2.14	3.58
	75	0.073	0.050	1.41	1.85	4.18	6.43	2.48	2.59
	100	0.083	0.095	3.15	2.49	4.74	3.85	1.80	2.52
	150	0.070	0.040	3.68	1.98	4.90	5.11	1.55	1.51
	200	0.062	_	1.35	_	4.29	_	0.24	_
	250	0.123	0.109	1.77	1.47	4.82	6.97	0.28	1.01
	300	0.004	_	0.48	_	0.61	_	0.12	_
	400	0.071	0.076	2.79	1.94	4.93	3.61	0.18	0.87
	500	0.003	_	1.14	_	1.12	_	0.17	_
	600	0.007	0.095	1.93	3.27	5.17	4.25	<0.002	1.25
	700	0.062	_	2.00	_	1.41	_	0.37	_
	800	n.d.	0.098	2.09	1.40	5.71	4.88	<0.002	0.41
	850	0.034	0.100	1.58	1.61	4.89	4.85	<0.002	0.35
	915	0.146	0.095	_	1.91	7.05	5.26	<0.002	0.45
min.		***n.d.***	***0.040***	***0.48***	***1.40***	***0.61***	***3.61***	***0.00***	***0.35***
max.		***0.146***	***0.109***	***3.95***	***3.27***	***7.05***	***6.97***	***2.48***	***6.90***
mean		***0.059***	***0.084***	***2.01***	***1.97***	***4.13***	***5.17***	***1.09***	***2.23***
MSB6									
	2	0.058	0.125	1.67	3.92	4.92	5.54	2.50	8.98
	25	0.037	0.107	2.00	3.38	4.89	2.16	2.20	9.31
	50	0.073	0.102	1.28	2.29	0.08	3.93	2.08	4.21
	75	0.065	0.114	1.57	2.21	5.03	3.84	1.85	4.24
	100	0.070	0.172	1.23	2.70	4.90	4.53	1.42	2.71
	150	0.041	0.152	1.24	2.93	4.83	4.79	1.32	2.10
	200	0.043	0.137	1.43	3.20	4.89	4.15	1.09	1.69
	250	0.069	0.163	1.60	3.72	9.59	5.07	1.13	1.83
	300	0.054	0.137	1.35	3.28	9.83	4.06	0.72	1.43
	400	0.046	0.102	1.13	3.18	5.42	4.20	0.99	1.76
	550	0.075	0.135	1.20	3.66	5.40	4.08	0.57	1.12
	700	0.042	0.061	1.16	3.08	4.58	5.90	0.63	3.90
	850	0.067	0.104	2.11	2.50	5.48	3.53	0.54	0.50
	1000	0.049	0.122	1.35	2.59	5.14	4.01	0.68	0.60
	1150	0.053	0.096	1.32	2.54	5.07	3.13	0.56	1.23
	1300	0.037	0.116	1.23	2.50	5.60	3.57	0.51	_
min.		***0.037***	***0.061***	***1.13***	***2.21***	***0.08***	***2.16***	***0.51***	***0.50***
max.		***0.075***	***0.172***	***2.11***	***3.92***	***9.83***	***5.90***	***2.50***	***9.31***
mean		***0.055***	***0.122***	***1.43***	***2.98***	***5.35***	***4.16***	***1.13***	***3.04***

Table 2 (continued)

Stations	Depth (m)	Cd		Cu		Ni		Mn	
		March '97	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*	*March '97*	*Sept '97*
MSB7									
	2	0.083	0.092	1.51	3.39	4.84	2.98	2.44	8.35
	25	0.034	0.076	2.97	2.90	4.44	2.93	2.59	6.71
	50	0.033	0.079	1.32	2.90	4.51	2.93	2.21	3.80
	75		0.078	_	2.95	_	2.74	_	3.42
	90	0.041	0.077	1.66	2.91	3.96	3.36	2.29	1.80
	140	0.045	0.085	1.32	2.97	4.98	3.00	1.69	1.15
	180	0.059	0.086	1.19	2.66	5.59	2.88	1.27	0.88
	250	0.031	_	0.98	_	4.74	_	0.44	_
	290	0.031	0.086	1.03	3.84	5.28	3.74	0.42	1.11
	400	0.054	0.085	1.32	3.26	5.16	3.53	0.73	0.89
	650	0.045	0.086	1.36	3.43	5.86	3.72	0.54	0.80
	800	0.032	0.094	1.55	3.57	4.47	3.43	0.53	0.69
	1000	0.036	0.100	1.24	4.47	4.74	4.03	0.82	0.86
	1250	0.028	0.093	1.66	3.11	4.72	3.61	0.78	0.51
	1400	0.031	_	1.38	_	4.77	_	0.32	_
	1600	0.031	0.104	1.16	3.78	5.17	3.88	0.45	0.37
	1740	0.030	0.094		3.11	4.69	2.92	0.48	0.48
	2320	_	0.091	1.74	2.71	_	2.93	_	1.34
min.		***0.028***	***0.076***	***0.98***	***2.66***	***3.96***	***2.74***	***0.32***	***0.37***
max.		***0.083***	***0.104***	***2.97***	***4.47***	***5.86***	***4.03***	***2.59***	***8.35***
mean		***0.040***	***0.088***	***1.46***	***3.25***	***4.87***	***3.29***	***1.12***	***2.07***

Table 3
Comparison with other areas.

Area	Depth range	Cd (nM)	Cu (nM)	Ni (nM)	Source
Western Mediterranean	Surface (1-100m) Deep (150-2700m)	0.044 0.064	1.4 1.6	2.3 3.6	Morley *et al.*, 1997
Gulf of Lions (shelf region)		0.070	2.8	4.2	Morley *et al.*, 1990
Northern Adriatic		0.100	7.14	9.06	Tankere & Statham, 1996
Southern Adriatic	Surface (1-50m) Deep (200-600m)	0.076 0.067	2.95 1.51	5.27 4.72	Tankere & Statham, 1996
North Atlantic	Surface (1-500m) Deep (500-4300m)	0.100-0.125 0.200-0.350	0.7-1.7 1.7-3.5	1.7-3.0 3.0-5.0	Saagher *et al.*, 1997
North Aegean	Surface (1-100m) Deep (100-300m)	0.108 0.080	2.68 2.01	5.34 4.74	This study
South Aegean	Surface (1-100m) Deep (100-2300m)	0.076 0.073	2.45 2.20	4.82 4.72	This study

North Aegean Sea

Cadmium distribution

Cadmium concentrations in the North Aegean fluctuate between 0.019 nM and 0.420 nM. The elevated Cd levels (>0.100 nM) are only comparable with N.E. Atlantic deep waters (SAAGHER *et al.*, 1997) as well as with waters influenced by coastal inputs, such as the Spanish coastal shelf waters (VAN GEEN *et al.*, 1988) and surface waters of the northern Adriatic Sea (TANKERE & STATHAM, 1996).

From the vertical profiles of the North Aegean stations (Fig. 4) it appears that overall, there is no definite recycling behaviour (surface depletion and increase with depth) for Cd, on the contrary, in some cases, enhanced values of Cd are found at the surface waters. Taking into account Cdanalytical reproducibility, Cd distributions are quite uniform below 100m depth. In this part of the water column, consisting of LIW and NADW, mean Cd concentration for the two seasons studied fluctuates around 0.080 nM. So, it becomes apparent that Cd enhancement is limited in the surface layer. This is true, in particular, for Stations MNB3 and MNB4 during the March cruise (Fig. 5) and for Stations MNB2 and MNB7 during September, where extremely high Cd concentrations are found. River inputs from the northern Greek coasts, aeolian transport and the influence of BSW, are the most probable reasons of this distribution.

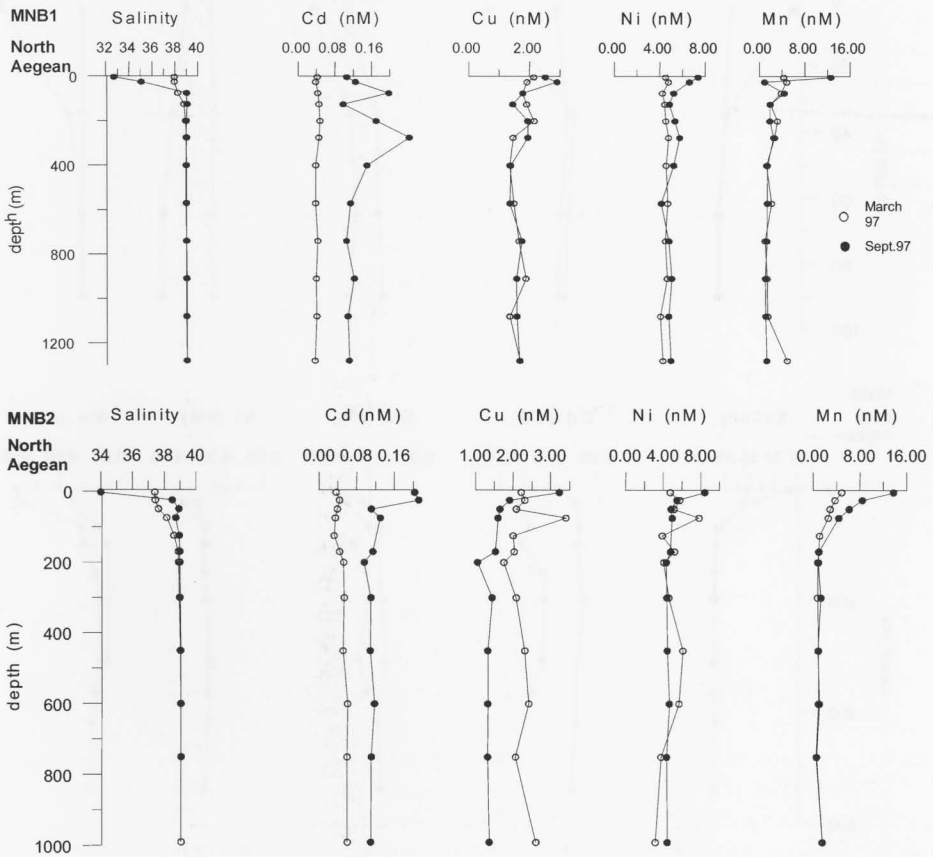

Fig. 4: Vertical profiles of salinity and trace elements in the North Aegean Sea.

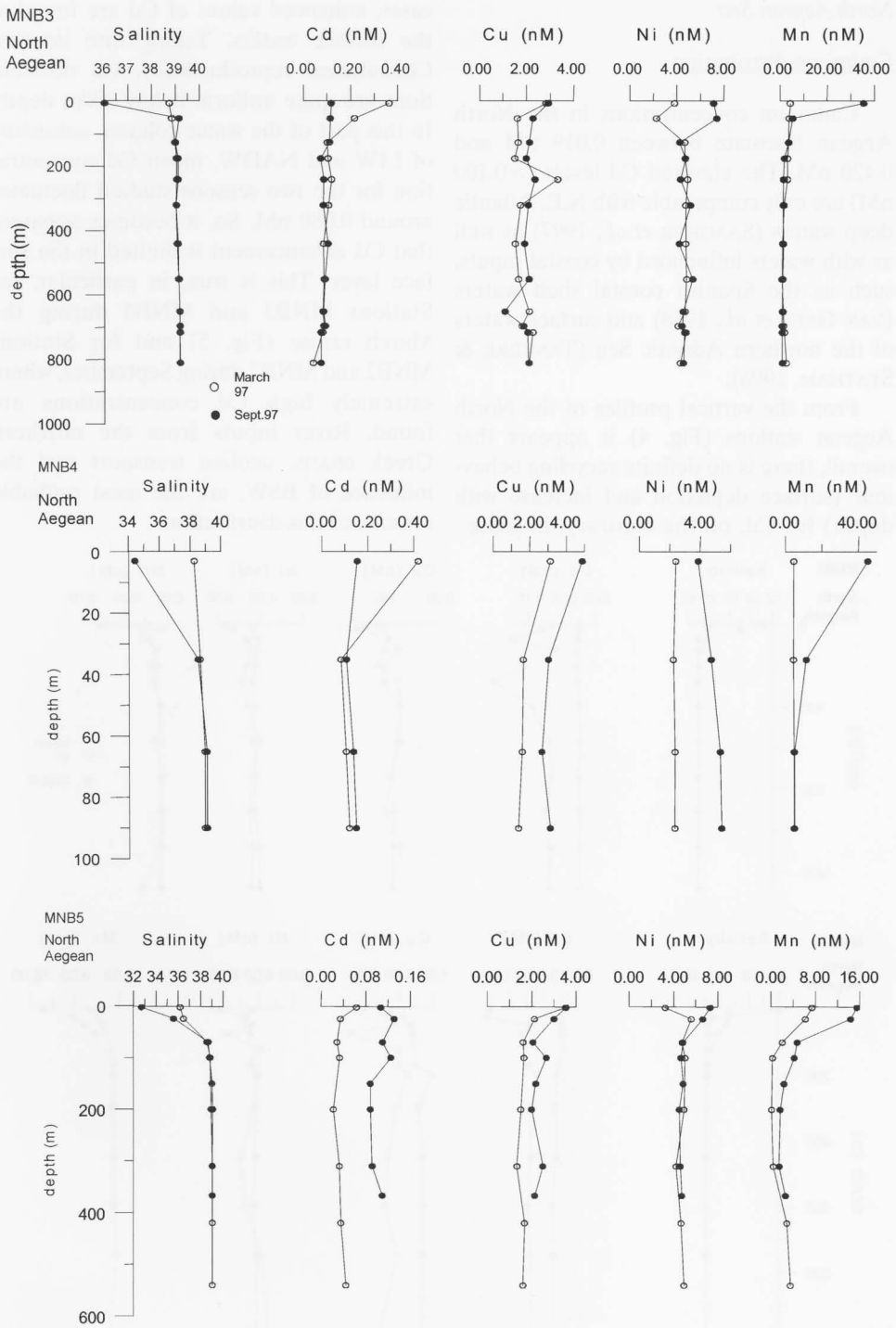

Fig. 4: (continued)

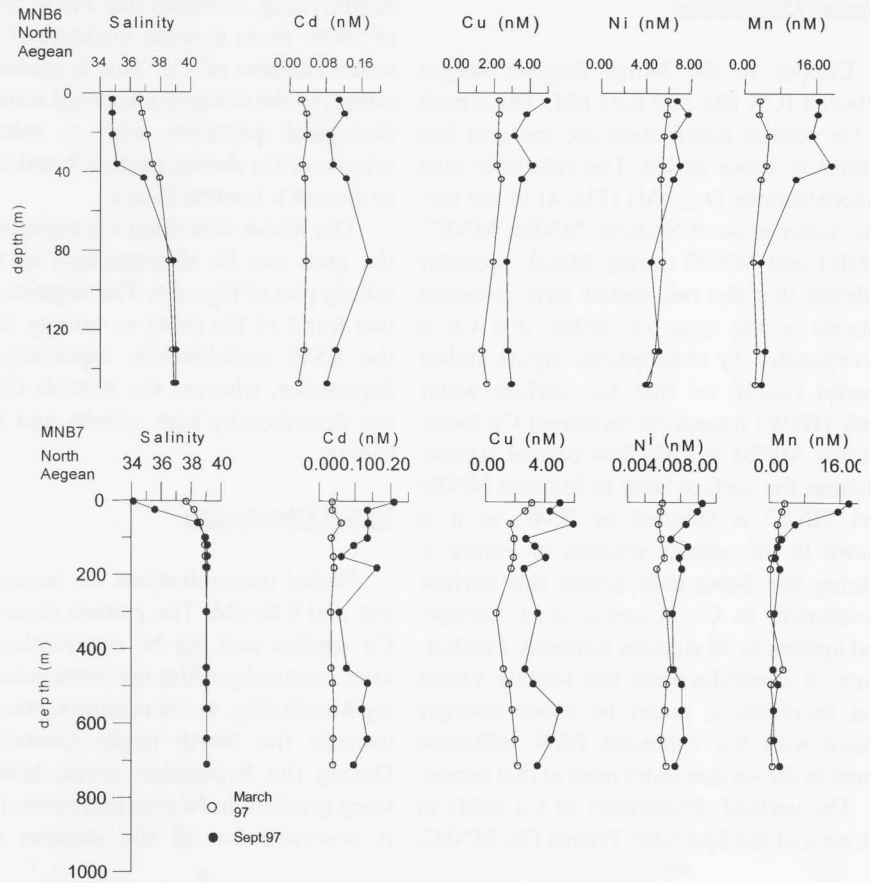

Fig. 4: (continued)

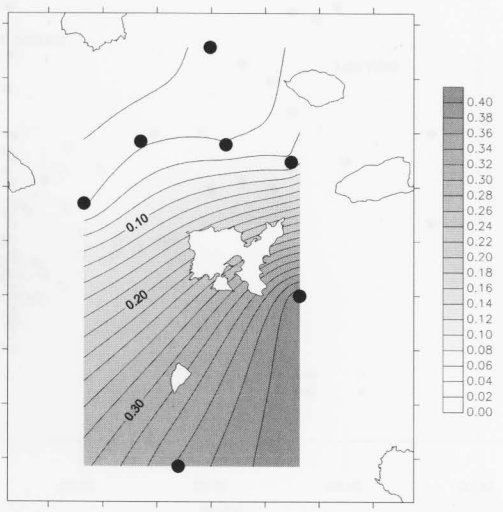

Fig. 5: Surface Cd (nM) distribution trends in the North Aegean during March '97.

Copper Distribution

Copper in the North Aegean ranges between 0.74 nM and 5.93 nM. The trends of Cu vertical distribution are more or less similar to those of Cd. The relatively high concentrations (>2 nM) (Fig. 4) in the surface water mass of Stations MNB5, MNB7, MNB4 and MNB3 during March probably indicate that the two metals have common sources in the area, i.e. either that Cu is incorporated by atmospheric inputs and/or coastal runoff, or that the surface water body (BSW) transports increased Cu loads. Station MNB4 is a shallow coastal station, whereas the surface layer of Stations MNB5 and MNB7 is affected by BSW, as it is shown in the salinity profiles of Figure 4. During the September cruise this surface enrichment in Cu becomes even stronger and applies to all stations sampled. Furthermore, it coincides with low salinity values and therefore it could be more strongly linked with the extended BSW influence found in the surface water mass at that period.

The vertical distribution of Cu (nM) in the area of the Sporades Trench (St. MNB2, MNB7) (Fig. 4) shows that below the depth of 500m there is some evidence of a deep water increase of Cu. This is probably due either, to the vertical downward transport of biological particles with a subsequent release of Cu during particle breakdown, or to some Cu benthic fluxes.

The above described Cu enrichments in the area can be distinguished in the Cu-salinity plot of Figure 6. The negative correlative trend of Cu (nM) vs salinity describes the BSW enrichments, especially during September, whereas the benthic Cu inputs are described by high salinity and high Cu values.

Nickel Distribution

Nickel concentrations lie between 2.22 nM and 8.46 nM. The picture described for Cu applies well for Ni distribution in the area. Vertical profiles are homogenous during March (Fig. 4). Increasing surface values towards the North imply coastal inputs. During the September cruise however, a steep gradient in Ni concentrations (>5nM) is observed for all the stations studied,

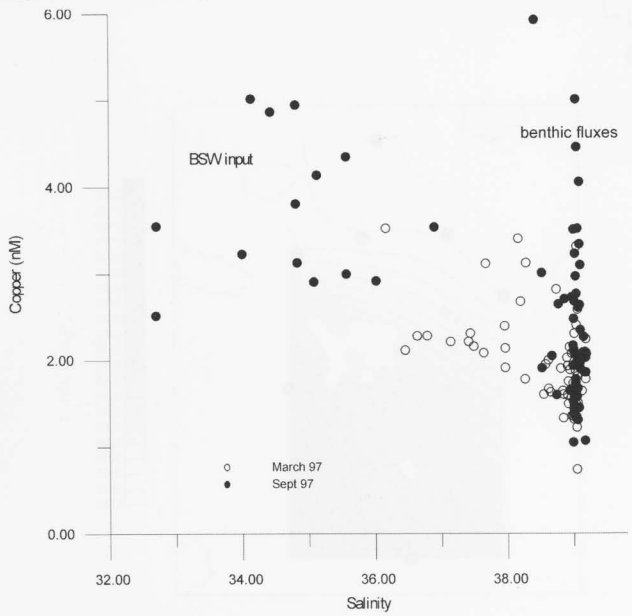

Fig. 6: Copper (nM) versus salinity in the North Aegean Sea.

which again is linked to BSW influence during that period. This trend is also shown in the vertical section of the area of the Sporades Trench in Figure 7.

As for Cu, benthic inputs contribute to Ni distribution in some cases too. It is apparent from the two metal-salinity plots (Figs 6 and 8) that Cu and Ni in the North Aegean have common enrichment sources, i.e. BSW entrainment and benthic inputs.

Manganese distribution

Manganese concentrations fluctuate between 0.07 nM and 44.98 nM. The scavenged character of this metal is obvious throughout the area studied during both seasons, with the exception of the very shal-

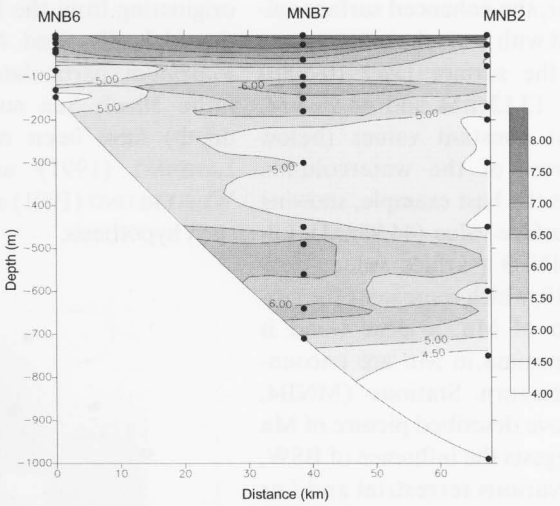

Fig. 7: Vertical distribution of Ni (nM) along the transect MNB6-MNB7-MNB2 during September

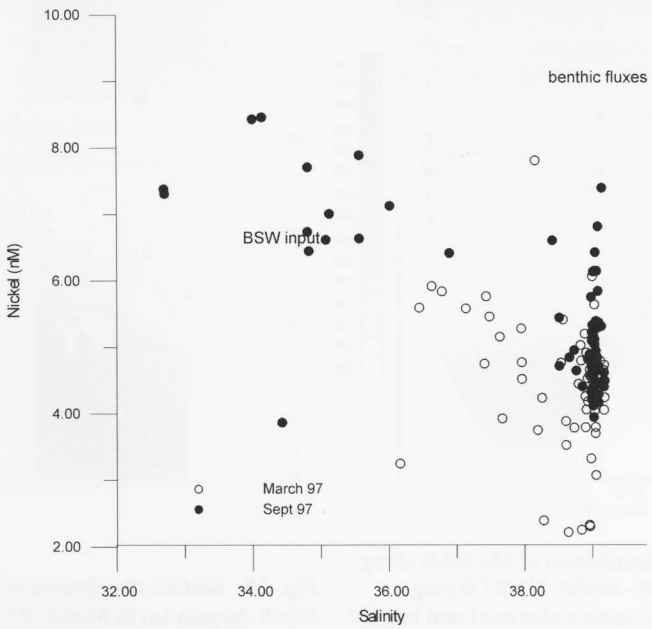

Fig. 8: Nickel (nM) versus salinity in the North Aegean Sea.

low Station MNB4. Elevated surface values until the depth of ~100m, rapidly decrease in the intermediate layer to around 0.5 nM and then in some cases (St. MNB1, MNB5, MNB7) increase slightly in the benthic layer, probably due to Mn remobilization from sediments (Fig. 9). Enhanced surface concentrations may reflect atmospherically transported material or riverine influence.

In September, the enhanced surface values are recorded with a much stronger way. Manganese in the surface layer (0-50m) ranges between 13.12 nM and 44.98 nM, reaching almost constant values (below 4nM) in the rest of the watercolumn. Station MNB4 is the best example, showing the maximum surface value (44.98nM), followed by St. MNB3 (surface value 35.49 nM). In Figure 10, which represents the surface distribution of Mn, a clear trend is depicted: The maxima in Mn are encountered in the eastern Stations (MNB4, MNB5). The above described picture of Mn distributions suggests the influence of BSW, apart from the various terrestrial and / or atmospheric sources of this metal. Since Mn is a scavenged metal with short residence times and in order to explain Mn enrichment in the BSW water mass, the following hypothesis was made: photochemical reactions which are stronger in the Aegean than in the Black Sea, may lead to dissolution of Mn hydroxides (SUNDA *et al.*, 1983; WAITE *et al.*, 1988; XYLA *et al.*, 1991) from particles originating from the Black Sea, resulting in the high dissolved Mn values measured. Maximum particulate Mn concentrations inthe Black Sea sub-oxic layers (~75m depth) have been reported by LEWIS & LANDING (1991) and HARALDSSON & WESTERLUND (1991) and may partly support such hypothesis.

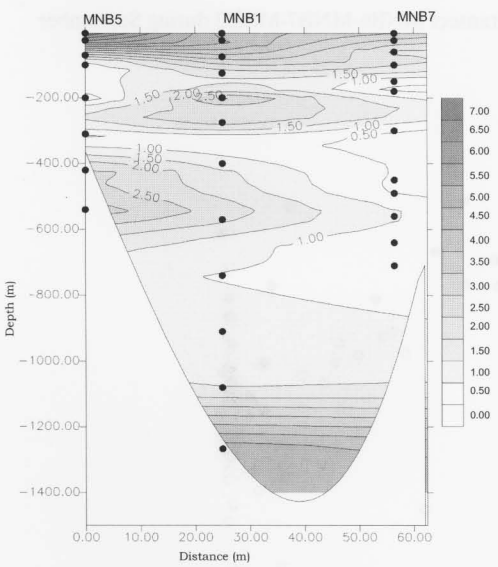

Fig. 9: Vertical distribution of Mn (nM) along the transect MNB5-MNB1-MNB7 during March '97. The scaenging character and benthic inputs are clearly depicted.

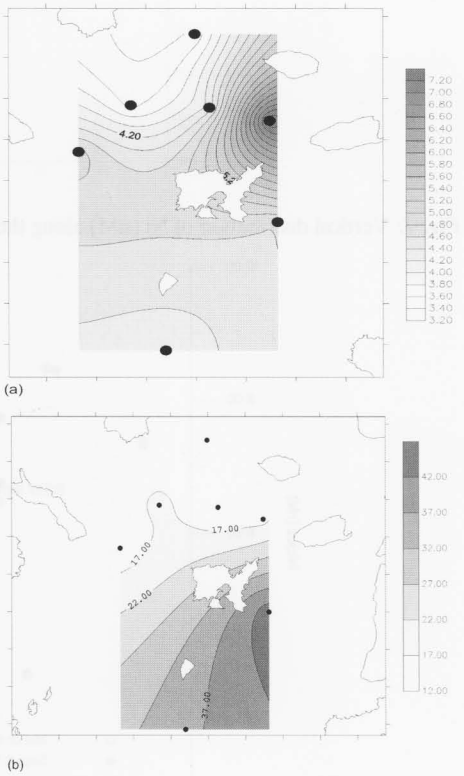

Fig. 10: Surface distribution of Mn (nM) in the North Aegean (a) in March '97, (b) in September '97.

South Aegean Sea

Cadmium Distribution

Cadmium in the South Aegean Sea ranges between <0.003 nM and 0.176 nM. The increased Cd levels observed in the North Aegean seawater were not recorded in the South Aegean. Stations MSB6, MSB7 and MSB1, in the eastern part, show somewhat lower concentrations throughout the watercolumn fluctuating around 0.050nM, whereas in the western part the values increase. This is clearly depicted in Figure 11. Furthermore, it is shown that Cd levels in 300m depth layer (TMW water mass) are in general lower. The fact that Cd is partly particle-reactive supports its lower concentration values in the "old" TMW water mass. Our analytical reproducibility for this metal, however, does not allow us to make any conclusions.

Evidence for some Cd benthic fluxes is shown from the vertical profiles of Stations MSB2, MSB3 and MSB4 (Fig. 12).

The nutrient-like character of this metal cannot be clearly distinguished. This is due to phenomena peculiar in the Mediterranean Sea, as already mentioned, i.e. atmospheric deposition, which tends to prevent surface depletion and vertical mixing of waters.

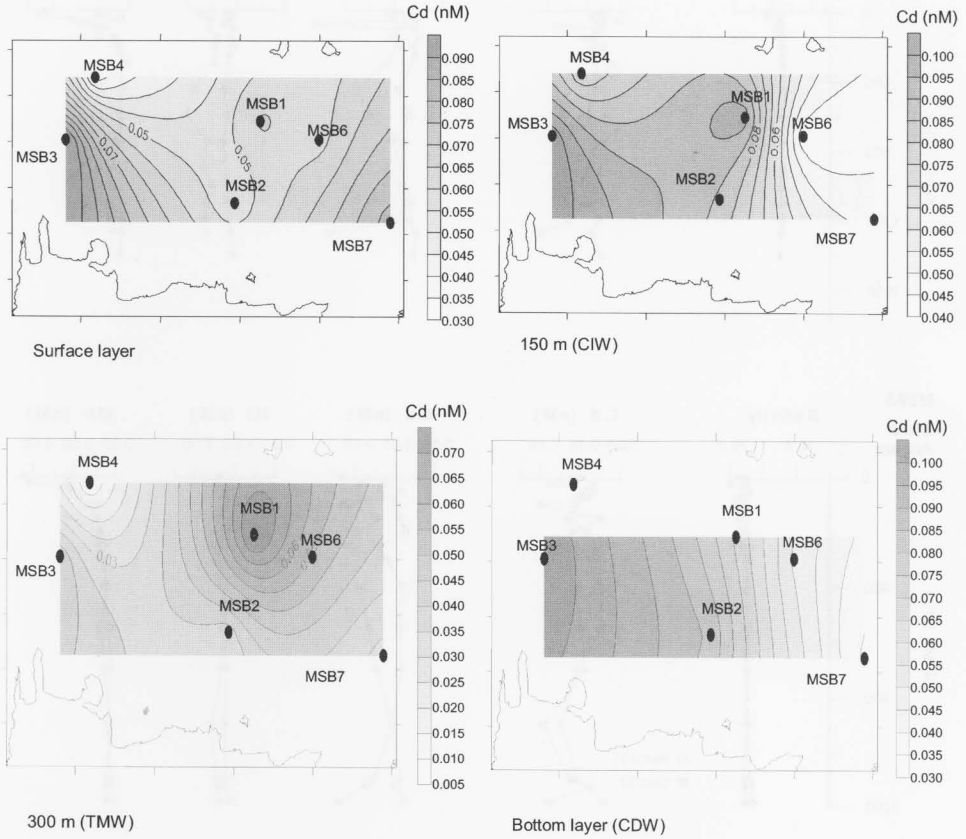

Fig. 11: Distribution trends of Cd (nM) in the various water masses present in the South Aegean. Cd levels in TMW are considerably lower.

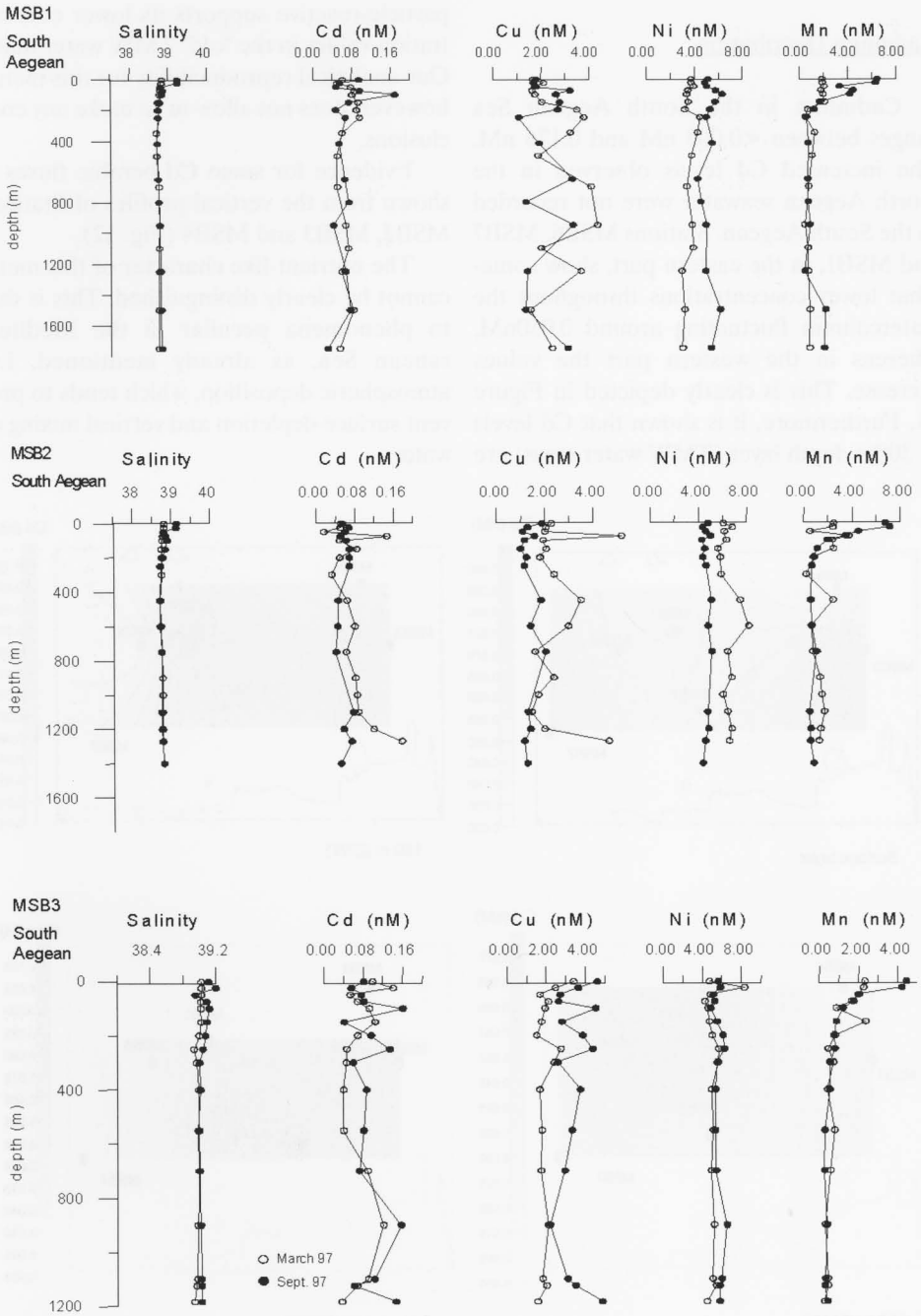

Fig. 12: Vertical profiles of salinity and trace metals in the South Aegean Sea.

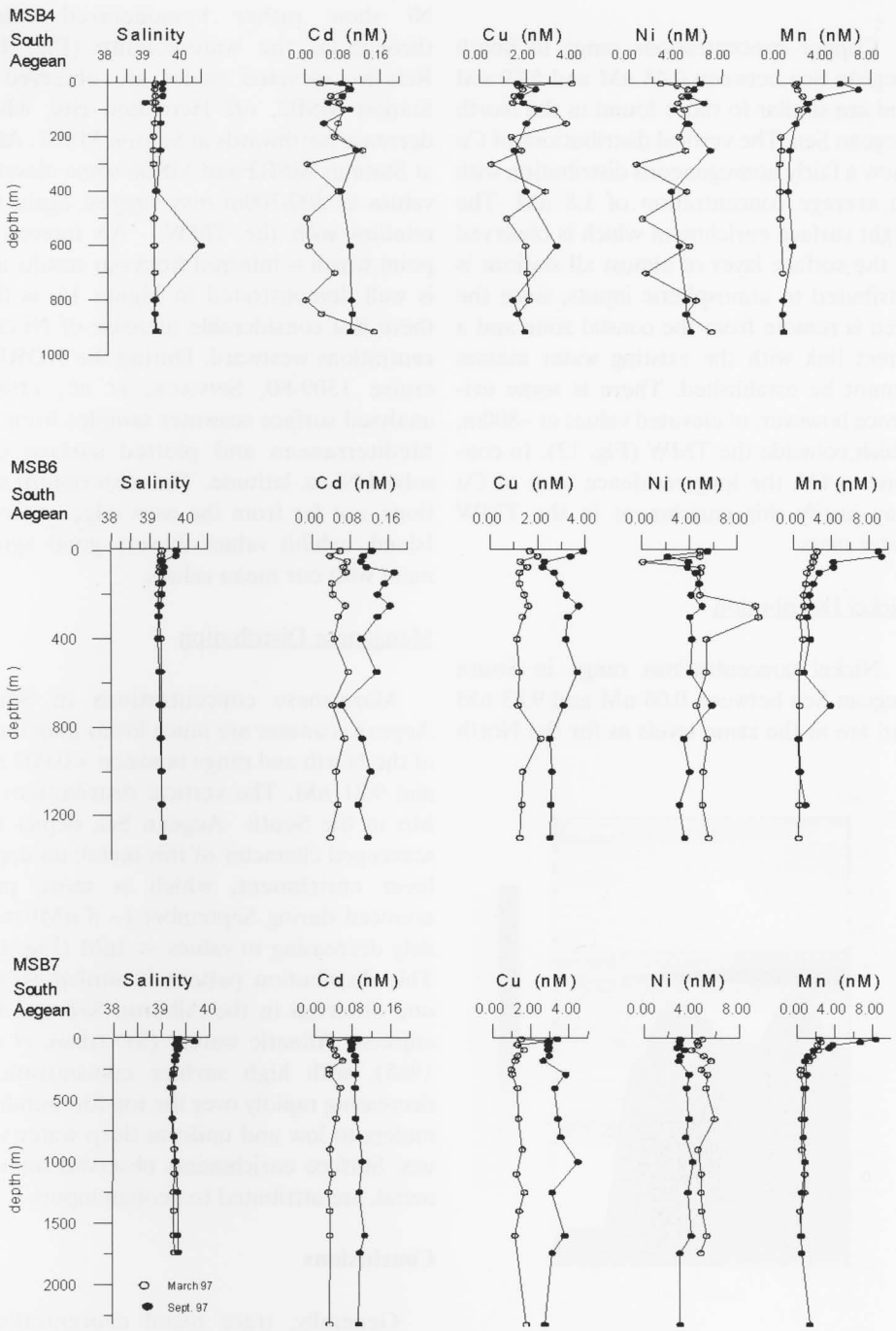

Fig. 12: continued

Copper distribution

Copper concentrations range in South Aegean Sea between 0.48 nM and 5.19 nM and are similar to those found in the North Aegean Sea. The vertical distributions of Cu show a fairly homogeneous distribution with an average concentration of 1.8 nM. The slight surface enrichment which is observed in the surface layer of almost all stations is attributed to atmospheric inputs, since the area is remote from the coastal zone and a direct link with the existing water masses cannot be established. There is some evidence however, of elevated values at ~800m, which coincide the TMW (Fig. 13). In contrast to Cd, the long residence time of Cu may justify this enrichment in the TMW water mass.

Nickel Distribution

Nickel concentrations range in South Aegean Sea between 0.08 nM and 9.83 nM and are at the same levels as for the North Aegean Sea. The vertical concentrations of Ni show rather homogenized values throughout the watercolumn (Fig. 12). Relative elevated values are observed at Station MSB2, off Heraklion city, which decrease northwards at Station MSB1. Also, at Stations MSB2 and MSB6 some elevated values at 300-700m may suggest again the relation with the TMW. An interesting point which is inferred from our results and is well demonstrated in Figure 14, is that there is a considerable increase of Ni concentrations westward. During the NORDA cruise 1309-80, SPIVACK, *et al.*, (1983) analysed surface seawater samples from W. Mediterranean and plotted surface dissolved Ni vs. latitude. The easternmost stations, not far from the west edge of Crete Island, exhibit values in very good agreement with our mean values.

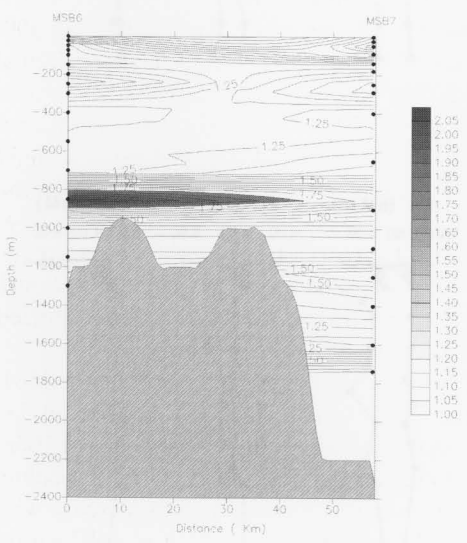

Fig. 13: Vertical distribution of Cu (nM) along the transect of stations MSB6 -MSB7 during March '97.

Manganese Distribution

Manganese concentrations in South Aegean seawater are much lower than those of the North and range between <0.002 nM and 9.31 nM. The vertical distributions of Mn in the South Aegean Sea depict the scavenged character of this metal: an upper layer enrichment, which is more pronounced during September (~ 8 nM) rapidely decreasing to values < 1nM (Fig. 15). This distribution pattern is similar to the one observed in the Alboran Sea and the adjacent Atlantic waters (STATHAM, *et al.*, 1985), with high surface concentrations decreasing rapidly over the top few hundred meters to low and uniform deep water values. Surface enrichments observed for this metal, are attributed to aeolian inputs.

Conclusions

Generally, trace metal concentrations determined in this study are similar to those reported for N.W. Mediterranean and the Straits of Sicily and Gibraltar.

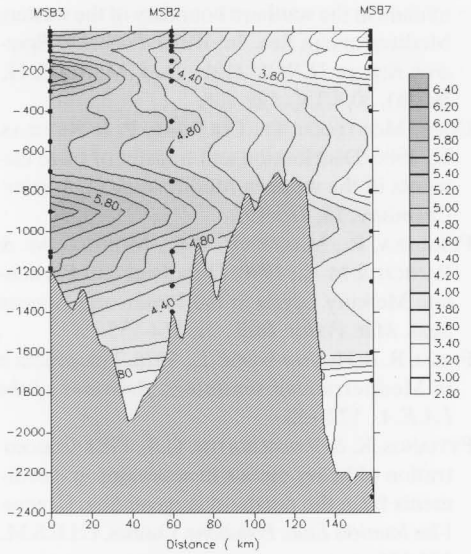

Fig. 14: Vertical distribution of Ni (nM) along the transect MSB3-MSB2-MSB7 during September '97.

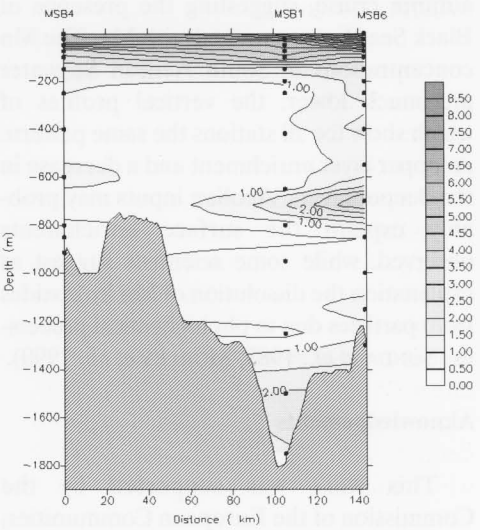

Fig. 15: Vertical distribution of Mn (nM) along the transect MSB4-MSB1-MSB6 during September '97.

North Aegean concentratrions are generally higher than South Aegean ones in the corresponding water depths. Also, all trace metal concentrations are clearly higher in all depths during the autumn cruise, probably due to stronger water mass inflow.

Cadmium, Cu and Ni distributions are quite uniform in the entire watercolumn and only minor variations, slightly enhanced values, are observed in the upper layer of certain North Aegean stations. These relatively high concentrations probably indicate that Cd, Cu and Ni have common sources in the area, i.e. atmospheric deposition, coastal runoff and influence of Black Sea Water. Hence, peculiar phenomena in the Mediterranean Sea tend to prevent surface depletion and "hide" the nutrient-like character of these metals. In the intermediate layer of North Aegean Sea slightly increased levels of Cu are found in the area of the North Sporades Basin. Furthermore, in this area and below the depth of 500m there is some evidence of a further concentration increase probably due either, to the downward transport of biological particles with a subsequent release during particle breakdown, or to Cu remobilization at the sediment-water interface. The vertical distributions of Cu in South Aegean Sea are fairly homogeneous. Neither surface depletion, nor deep enrichment is observed. There is some evidence of elevated values at 300-700m, which correspond to the Transitional Mediterranean Water. In the North Aegean Sea coastal Ni sources affect surface waters of the northern stations, and mask a slight recycling behaviour which is observed at the south-southeastern stations, with subsequent regeneration of Ni in the deep waters. The vertical concentrations of Ni in South Aegean Seawater show rather homogenized values throughout the watercolumn.

The scavenged character of Mn is obvious in all stations of the North Aegean, i.e. elevated surface values down to about 100m depth, rapidly decrease in the intermediate layer and then, in some cases increase with depth, probably due to Mn remobilization from sediments. Surface values one order of magnitude higher than those of the intermediate and bottom layers are recorded for the

autumn cruise, suggesting the presence of Black Sea Water enriched with Mn. The Mn concentrations in South Aegean Seawater are much lower, the vertical profiles of which show for all stations the same pattern: an upper layer enrichment and a decrease in the deeper layers. Aeolian inputs may probably explain the surface enrichments observed, while some scientists suggest as explanation the dissolution of Mn hydroxides from particles due to photochemical processes (SUNDA *et al.*, 1983; MORLEY *et al.*, 1990).

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