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THE BIOGEOCHEMISTRY AND DISTRIBUTION OF DISSOLVED TRACE METALS IN THE AEGEAN SEA

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In memory of Kristin Bruhn

ABSTRACT

Samples for the analysis of dissolved Mn, Co, Fe, Pb, Cu, Ni, Cd, Zn, nitrate plus nitrite, silicon and phosphate were collected at 7 stations in the northern and 6 stations in the southern Aegean Sea, eastern Mediterranean, in both March and September 1997. This represents the first extensive dissolved trace metal data set for this region. Additional samples were collected near hydrothermal vents in Milos, and across the Thermaikos Gulf. Trace metal distributions and concentrations were interpreted with respect to the particularly complex hydrography and circulation patterns of the Aegean Sea.

The results show elevated surface concentrations of Mn, Co, Fe, Pb, Cu, Ni and Zn which can be attributed to both atmospheric deposition in the southern Aegean and a combination of atmospheric deposition, the outflow of the Black Sea Water and potential coastal inputs within the northern Aegean. Spatial and temporal metal variability in surface waters was observed, with higher concentrations for all metals in the northern Aegean due to additional surface sources. In September 1997 the overall higher concentrations of Mn, Co, Pb, Cu, Ni and Zn are attributed to the shallowing of the thermocline located at approximately 100 m in March to around 50 m in September, although the possibility of enhanced aolian deposition is not excluded.

Elevated signatures of dissolved Mn, Co, Fe and Pb are associated with Black Sea Water and, to a lesser extent with Levantine Intermediate Water in the northern Aegean for March 1997. In the more complex hydrography of the south Aegean the elevated dissolved nitrate plus nitrite and silicon are associated with an intrusion of Transitional Mediterranean Water. In addition, dissolved trace metal results from Thermaikos Gulf and Milos do not suggest a significant input of metals from these sources into the Aegean Sea during the period of sampling.

Atmospheric metal fluxes for the central and north-western Mediterranean Sea were used to calculate the residence times in the Aegean surface waters. These fluxes were compared with metal fluxes from sediment traps and particulate metal data in the northern and southern Aegean during the period of sampling. Linear regression analysis was applied to Black Sea influenced surface water waters in the northern Aegean in order to estimate the concentrations of Mn, Co, Fe, Cu and Ni in the Straits of Dardanelles.

For the metals Mn, Fe and Pb the calculated short residence times in southern Aegean surface waters of 0.3 to 6.0 years reflect their high particle reactivity and scavenging onto particles and transport to depth. Co exhibits a similar cycling pathway to Mn but with longer surface residence times of 4 to 40 years. The vertical distributions of Ni, Cu, Cd and Zn do not resemble those of nutrients. Ni, Cu, and Zn exhibit surface elevation in the northern Aegean, and to a lesser extent in the southern Aegean, whereas Cd depth profiles were found to be homogenous. These profiles are the result of surface metal sources combined with the oligotrophic nature of the Aegean Sea. The present work suggests that the Aegean Sea, as well as the Mediterranean is not in a steady state with respect to Ni, Cu, Zn and Cd. Concentrations in the southern Aegean are overall comparable to recent high quality observations in the open Mediterranean. However, there appears to be an increase in dissolved Cu and Ni from the western to the eastern basins of the Mediterranean Sea due to continuous inputs to surface waters.

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ABBREVIATIONS (in alphabetical order)

BSW	Black Sea Water
CDW	Cretan Deep Water
CIW	Cretan Intermediate Water
CTD	Conductivity, temperature, depth
EMDW	Eastern Mediterranean Deep Water
LDW	Levantine Deep Water
LIW	Levantine Intermediate Water
LSW	Levantine Surface Water
MAW	Modified Atlantic Water
MSW	Mediterranean Surface Water
NAEGDW	North Aegean Deep Water
RT	Residence time
SD	Standard deviation
SPM	Suspended particulate matter
TMW	Transitional Mediterranean Water

CHAPTER 1

INTRODUCTION TO TRACE METALS IN THE MARINE ENVIRONMENT

1.1 INTRODUCTION

Since 1975 there have been major advances in the knowledge of trace metal concentrations and distributions in seawater (Brewer, 1975). Prior to this little was known other than that trace metal concentrations are very low (less than micromolar levels), with observed distributions exhibiting little relationship with biological, chemical and/or geochemical oceanographic processes. This oceanographic inconsistency was mostly due to lack of instrumental sensitivity and problems of contamination (Bruland, 1983). The 'quantum leap' in the understanding of trace metal distributions is primarily due to the advent of methodologies in the clean handling and analysis of samples, along with improvements in analytical methods. As a result nearly all trace metals were one to three orders of magnitude less than what had been previously estimated, whereas metal distributions indicated patterns consistent with oceanic processes, as demonstrated by the collection of papers by Wong *et al.* (1983). Thorough reviews have also been prepared by Bruland (1983), Whitfield & Turner (1987), Burton & Statham (1990) and Donat & Bruland (1995).

In the marine environment, where physical, biological and chemical processes inter-relate, a more complete understanding of the effects of sediment dynamics, biological activity, transport and formation of water masses, atmospheric and freshwater interactions and dissolved/particulate inorganic/organic marine chemistry, are required to fully comprehend the role of trace metals in the dynamics of the ocean.

This chapter reviews trace metal chemistry in rivers, estuaries and open oceans, along with boundary exchange and recycling processes for the metals under observation (Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn), with special attention to the Mediterranean Aegean Sea and the Black Sea.

1.2 TRACE METALS IN RIVERS AND ESTUARIES

Riverine runoff is a major source of dissolved and particulate trace metals to the shelf seas. Each river can vary considerably in size, altitude, gradient, flow regime, turbulence, temperature, substrate type, turbidity and water chemistry. Within each catchment the geographic location, rock type, vegetation, climatic regime and man's activities will influence the riverine flow and composition (Hart & Hines, 1995). This results in large variations of concentrations and fluxes of trace metals from the catchment area to the river or stream.

Natural sources of metals include the weathering of soils and base rocks, a slow process which is influenced by rainwater made slightly acidic through the solution of CO_2 from the atmosphere (Stumm & Morgan, 1981); and from the atmosphere, in both wet and dry precipitation. It has been observed in many parts of the world that an increase in the acidity of rain can accelerate the 'natural' weathering process in a number of catchments (Hart & Hines, 1995). Human activities, such as agriculture and anthropogenic discharges from industries, are the major contributors of trace metals to rivers. For this reason, environmental protection authorities in most countries are placing increasingly stringent requirements on the trace element concentrations allowed in effluents discharged directly into rivers.

In the riverine environment, physical, biological and chemical interactions control the behaviour of trace metals by abiotic or geochemical processes (such as for Cu, Pb, Zn, and Cd) or by both biological and geochemical processes, such as for Fe and Mn (Hart & Hines, 1995). Trace metals can exist in a number of physico-chemical forms in natural waters: free aquatic ionic forms; 'dissolved' inorganic or organic complexes; complexes with colloidal or particulate matter; and complexes associated with the biota (e.g. phytoplankton and bacteria). The speciation can have a major effect on the behavior, bio-availability and toxicity of a trace metal. For example, a free ionic form is more likely to become associated with sediments, suspended particulate matter (SPM) or colloids, than when it is already complexed to organic matter. Most studies of trace metals in aquatic systems assume that chemical equilibrium exists (Salomons & Förstner, 1984), although the kinetics will vary depending on whether the reaction is homogenous or heterogeneous and whether it is catalysed by organisms, light or surfaces. Sorption reactions involving colloidal matter, SPM and sediments are a significant influence on trace metal behaviour and can result in the removal from rivers by flocculation (Sholkovitz, 1978; Sholkovitz & Copeland, 1981).

Comparing the atmospheric and riverine contributions of trace metals to the western Mediterranean Sea, Guieu *et al.* (1997) calculated fluxes of Cd, Co, Cu, Fe, Mn, Ni and Pb from the Rhone and Evros. Concentrations were observed to vary greatly, with a tendency to decrease during increased river discharge. The particulate fluxes calculated were found to be greater than dissolved fluxes for all elements, indicating the importance of particles as a source of metals for the shelf seas and the ocean.

The behaviour of trace metals in rivers, as well as in the ocean, is widely accepted to be poorly understood and difficult to predict (Donat & Bruland, 1995; Hart & Hines, 1995). Much of the previously recorded data has been affected by contamination during sampling, and the real concentrations are recently shown to be far lower (Bruland, 1983; Donat & Bruland, 1995). In addition, most river studies (Hart & Hines, 1995) still use a simple separation method (based on membrane filtration using 0.4 μm filters) to separate the total element concentration into 'particulate' and 'dissolved' forms, when in fact a considerable fraction of colloidal material passes through the 0.4 μm filter.

Estuaries encompass the river-ocean interface, a region which is both chemically and physically dynamic. Pronounced biogeochemical reactivity, including sorption, flocculation and redox cycling of trace metals, is induced by sharp gradients in the estuarine variable of salinity, temperature, dissolve O_2, pH, and particle character and concentration that result from the mixing of fresh and saline end members (Martin & Whitfield, 1983; Millward & Turner, 1995). These processes drastically modify the riverine compositional signal to the oceans and must be fully understood to accurately determine trace metal fluxes.

The uniqueness of each estuarine system makes the generalisations concerning estuarine mixing difficult. The vertical salinity stratification of estuaries is controlled by circulation and mixing characteristics, which are dependant on the relative contributions of river and tidal flows. The flushing time (related to the river flow and salinity) has a significant role in estuarine trace metal reactivity. For the thermodynamic equilibria of *in situ* chemical reactions to take place, the flushing time of the estuary must be below a certain level as explained by Morris (1990).

The particulate phase plays a complex yet important role in the cycle of trace metals in estuaries, consisting of various mineral phases derived from the catchment and coastal erosion. In addition, discrete and biogenic phases are produced *in situ* through flocculation and biological activity respectively. The increase in salinity, along with increases in the concentration of the major sea-water cations, can lead to desorption, or flocculation and sedimentation of elements, such as Fe, which exist in river water mainly in a colloidal state. Transport of the particulate phase is highly non-conservative and particles, together with particle-reactive trace metals, may be subjected to many deposition-resuspension cycles in an estuary, thereby residing considerably longer than water. Residence times of suspended particles of 18 years have been calculated in the Humber Estuary and in the turbidity maximum zone of the Tamar estuary, to be 1.4 years (Millward & Turner, 1995). This has the effect of 'trapping' trace metals within the estuary before final transport to the shelf edge and oceans.

Some dissolved trace metals are simply diluted upon mixing of river and sea water (conservative behaviour), whereas others undergo dissolved-particulate reactions, which lead to their addition to, or removal from the dissolved phase (non-conservative behaviour). The behaviour patterns of each metal will be highly dependant on local conditions and can vary between (as well as within) each estuary. Sholkovitz & Copeland (1981) determined the percentage of trace metal removal from riverine water by flocculation, finding significant removal for Fe and Cu (80% and 40%), moderate for Ni and Cd (15%) and none for Mn and Co. Cu and Ni have competitive affinities with sea water cations and will therefore be removed, whereas Cd and Co form strong chloro-complexes in sea-water and are removed only to a small extent. In the Rhône and Evros estuaries in the Mediterranean, Co and Ni exhibit conservative behaviour (Zhang & Wollast, 1993). Millward & Turner (1995) compared the behaviour of trace metals in several estuaries and found that the axial distributions of each metal exhibited considerable inter-estuarine variability, with the exception of iron, consistently removed at low salinities (as a result of flocculation). Within the Gulf of Lions, seasonal variability of Mn, Co, and Pb between summer and winter also highlights changes in the regimes of solution and solid phase interactions in estuaries (Morley *et al.*, 1990).

1.3 TRACE METALS IN THE OCEAN

There have been major advances in the knowledge of trace metal concentrations and distributions in seawater since the mid 70s (Bruland, 1983; Whitfield & Turner, 1987; Burton & Statham, 1990; Donat & Bruland, 1995). It is now known that in the open ocean, dissolved trace metal concentrations are very low (down to nM and even lower), and such low concentrations have required improvements in analytical methods, sampling and sample handling.

The classification of trace metals according to their behaviour in the ocean has been well established. Bruland (1983) and Libes (1992) adopt a classification based on 7 types, whereas Whitfield & Turner (1987), Burton & Statham (1988), and Donat & Bruland (1995) reduce this to three major categories which will be discussed below.

1.3.1 CONSERVATIVE METALS

These metals behave conservatively, that is, they exhibit an essentially constant concentration with regards to salinity as a result of their low reactivity in seawater. This low geochemical reactivity is expressed in terms of a higher mean oceanic mixing time ($>10^5$ years) in comparison to the time scales of water mixing processes found in the ocean. These metals behave essentially like major constituents of seawater, but at far lower concentrations due to the lower levels in source materials such as crustal rock. The alkali trace metals lithium, rubidium and caesium fall into this category but they are not under review in this work, and they will not be discussed (see Burton and Statham, 1988).

1.3.2 RECYCLED METALS

The recycled metals (previously referred to as 'nutrient type') exhibit a close correlation in behaviour with the micronutrients phosphate, silicate and nitrate as a result of their involvement in the biogeochemical cycle. In addition, the concentrations of recycled metals in deep waters increase along the direction of the main advective flow of the deep water in the worlds oceans. Consequently, their concentrations in the deep North Pacific are higher than in deep North Atlantic waters (Bruland & Franks, 1983). This feature is due to the concentration build-up of elements which are transported into deep water, in association with biogenous particulates that undergo decomposition or dissolution processes that return material to the water column. The residence times of the recycled elements are intermediate (10^3 to 10^5 years) compared with conservative and scavenged elements (Donat & Bruland, 1995). Recycled metals include cadmium, zinc, nickel and copper.

Cadmium has been shown to have a nutrient type distribution in the ocean (Bruland & Franks, 1983), exhibiting a close correlation with phosphate. It has, however, an unknown biological function but it shows a strong affinity for biogenous particulate material (Burton & Statham, 1988). Although Cd has no biochemical function of its own, there is now strong evidence for its utilisation by phytoplankton in Zn-depleted surface waters, where Cd replaces Zn in some enzymes without loss of enzyme activity (Croot & Hunter, 1998). Typical depth profiles such as in the western North Atlantic (Bruland & Franks, 1983) exhibit marked depletion, with values less than 0.05 nM in surface waters followed by shallow water (<1000 m) regeneration. Maximum concentrations of 0.3 nM in the North Atlantic and 1.1 nM in the North Pacific have been observed (Bruland & Franks, 1983). This distribution is characteristic of phosphate and nitrate which are depleted at the surface and released due to oxidation and dissolution of soft tissue of sinking biogenic particulates. The cadmium:phosphate ratio is not constant between oceans, being significantly higher in the older deep waters of the Pacific. In addition, the actual metal and nutrient concentrations differ as a result of deep water circulation patterns of the oceans, with the highest values in the older deep waters of the Pacific.

Zinc also exhibits nutrient type behaviour, showing a close correlation with silicon (Bruland & Franks, 1983), and a long residence time of 50,000 years (Ruiz-Pino, *et al.*, 1991). Zinc is strongly depleted at the surface, with deep water regeneration and fairly constant concentrations below 2000m. This profile indicates that the major carrier phase is skeletal material. Deep water values are 1.7 nM and 9 nM for the North Atlantic and North Pacific respectively. The observed difference in the Zn:Si ratio in these two oceans indicate that carrier phases other than biogenous silica contribute to the down column transport of the metal (Burton & Statham, 1988).

Nickel in the ocean shows a considerable degree of nutrient-like behaviour, but with much less marked surface depletions than cadmium and zinc and less regeneration below 1000 m. Bruland & Franks (1983) observed surface concentrations of 2-5 nM in the North Atlantic and North Pacific, with concentrations of 5.7 nM and 10.4 nM between 1000 – 3000 m respectively. The nickel:nutrient ratio is highest in the North Atlantic. Saager *et al.* (1997) observed a closer relationship of Ni with phosphate and nitrate in the Atlantic, concluding that the biogeochemical cycles of Ni and Si are not related.

Copper has a shorter residence time (10^3 years) than nickel and zinc and the range of factors influencing its distribution is greater than the other metals considered here (Burton & Statham, 1988). Depth profiles show nutrient type behavior with surface depletion and gradual regeneration with depth, thought to be due to biological uptake within the surface mixed layer and significant diagenetic remobilization at the sediment water interface. The regeneration from sinking primary products is masked by scavenging onto fine particles. For scavenged metals, absorption onto particles cause the older deep waters of Pacific ocean to have lower concentrations than the younger Atlantic waters. However this is not the case for copper due to the significant source from the sediment water interface. The magnitude of the dissolved copper flux from depth depends on the sediment type i.e. red clays can contribute greater fluxes of Cu than carbonate dominated sediments.

1.3.3 SCAVENGED METALS

These metals are non conservative with very short residence times in the oceans ($<10^3$ year), reflecting their rapid removal onto particles by oxidative or hydrolic scavenging (Whitfield & Turner 1987). Concentrations will decrease significantly away from the source and, thus, North Pacific concentrations are lower than those in the North Atlantic. Examples of scavenged metals are manganese, cobalt, iron and lead.

Manganese distributions in sea water reflect their high particle reactivity and, hence, short residence times. A typical depth profile is characteristic of a single source to the surface layer coupled with oxidative scavenging onto particulate matter. Mn concentrations decrease with the age of deep water due to continuous scavenging (Landing & Bruland, 1987). The dissolved Mn(II) oxidises to insoluble Mn (III, IV) oxyhydroxide coatings, often quite amorphous and mixed with solid Fe (III) oxides (Landing & Bruland, 1987; Lewis & Landing, 1991; Saager *et al.*, 1997). These freshly formed ferro-manganese oxide coatings are deemed to be very efficient absorbers for additional Mn and Fe, as well as other metals from seawater. Given such efficient removal of Mn from the water column, local sources and sinks strongly influence the distribution of Mn (Saager, 1997). Deviations can occur associated with oxygen minimum zones and waters advected from active spreading centres (Burton & Statham, 1988). Atmospheric sources of manganese enhance the surface concentrations. Guieu *et al.* (1997) compared dissolved input from atmospheric and riverine sources for manganese, and observed that between 63 to 100% of dissolved Mn was derived from atmospheric origin.

Information on cobalt in the ocean is inadequate to enable interpretation of its geochemical behaviour, with concentrations generally below 100 pM. A strong correlation between Co and Mn has been found in the western Mediterranean Sea (Morley *et al.*, 1990) and English Channel (James *et al.*, 1993), indicating their similar sources to surface waters and geochemical behaviour. Moffett & Ho (1996) suggested that both elements are co-oxidised via the same microbial catalytic pathway and this is an important mechanism for the incorporation of Co into marine Mn oxides. The uptake mechanism of dissolved Co onto suspended particles is governed by the abundance and activity of Mn oxidising bacteria and the biological demand of Co as a micronutrient (Moffett & Ho, 1996).

Due to the sensitivity of iron to contamination during sampling and analysis (Bruland, 1983), there is relatively limited Fe data in the open ocean until the last decade (i.e. Landing and Bruland, 1987; Burton *et al.*, 1993; Witter & Luther III, 1998; Nolting *et al.*, 1998; Croot & Hunter, 1998; de Baar *et al.*, 1999). Iron distributions are effected by both recycling and scavenging processes with a behaviour similar to manganese, except that Fe(+II) is more rapidly oxidised. Studies in the open ocean show that the vertical distributions of dissolved iron are closely related to micronutrients (Croot & Hunter, 1998), with algal uptake in surface waters, settling of intact plankton and biogenic particles (e.g. faecal pellets) and bacterial remineralization of the settling particles at depth. However, deep water concentrations of iron are similar between the Atlantic and the 'older' waters of the Pacific, in sharp contrast to N and P. Fe accumulates in deep ocean waters, a behavior which is uncharacteristic for a highly reactive metal (Sunda, 1997). To solve these paradoxes, Johnson *et al.* (1997) proposed a model in which iron is taken up by phytoplankton at the surface and remineralized at depth, like major nutrients, and where it is held in solution in subsurface ocean waters by a solubilizing mechanism; most likely by the strong chelation of Fe by one or more organic ligands now known to be present in ocean waters at concentrations of 0.4-0.6 nM (Sunda, 1997). The high reactivity of dissolved iron towards particles is shown by the residence times with respect to removal in the upper 500 m in the Pacific ocean, ranging from 1 to 20 years (Landing & Bruland, 1987). Iron (+II) occurs in high concentrations in hydrothermal fluids, occurs in suboxic and anoxic environments and may be formed by reduction in the upper ocean. Since iron is the most important metal essential to phytoplankton, it may limit primary production in nutrient rich, oligotrophic oceans where atmospheric inputs are low (Donat & Bruland, 1995; de Baar *et al.*, 1999).

Ocean profiles of lead are dominated by the influence on the upper ocean of anthropogenic Pb through the atmosphere and the penetration of this material into subsurface waters. Oceanic concentrations can vary significantly due to the interaction of an atmospheric source, advection and differences in scavenging efficiency (Burton & Statham, 1988). Surface concentrations in the North Atlantic Ocean are higher than those in the North Pacific Ocean, though the trends in vertical profiles are similar (Schaule & Patterson, 1983) with surface enrichment followed by depletion with depth. This observed difference is attributed to the variations in atmospheric sources of lead to found in each region.

1.4 NON-RIVERINE TRACE METAL SOURCES TO THE OCEANS

Trace metals have two major external sources: i) atmospheric or riverine inputs of weathering products of the exposed continents; and ii) inputs resulting from the interactions of seawater with newly formed oceanic crustal basalt at ridge crest spreading centres and hydrothermal vents. In addition, benthic inputs of certain metals can be a major source.

1.4.1 ATMOSPHERIC SOURCES

Trace metals in the atmosphere, enter the oceans by precipitation (wet deposition), cloud or fog impaction (cloud deposition), or by impaction onto a surface in the absence of precipitation and clouds (dry deposition). Deposition over the worlds oceans are seen to vary regionally and can be ranked in the following order from the highest: North Atlantic > North Indian > South Atlantic > South Indian > South Pacific. This ranking highlights the elevated concentrations found in the northern. Rural and urban concentrations are also shown to range between 10 - 25 times and 35 - 150 times higher respectively, than for remote sites (Ross & Vermette, 1995). This demonstrates the importance of anthropogenic aerosols originating from industrialised regions for the trace metal input to the oceans.

Chester & Murphy (1990) compiled reports showing that the atmospheric flux of some metals (especially Pb, Zn, and Cd) to surface coastal waters can equal or exceed their riverine flux. Dust input to the nutrient-limited Mediterranean basin is one of the greatest in the contemporary ocean (Guerzoni *et al.*, 1999). Mean annual atmospheric mass fluxes were observed at Crete (21 g m^{-2}) and Israel (50 g m^{-2}), and were found to be the highest in the Mediterranean. In comparison to riverine discharge, 70% of insoluble particles in the Eastern Mediterranean were from the atmosphere, compared to 19% in the Western Mediterranean (Guerzoni *et al.*, 1999). Most metals have a relatively short residence time in the troposphere (between a few days and a few weeks). They are not well mixed and, thus, aerosols and rainwater are expected to exhibit strong spatial and temporal variability (Guerzoni *et al.*, 1999). In the north-western Mediterranean, Guieu *et al.* (1997) indicate that more than 50% of the dissolved metal input (Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn) originates from the atmosphere. The aerosols contain a significant anthropogenic component for each metal such as Pb and Cd, which are largely of man-made origin, even in 'Saharan' dominated aerosols. Iron was found at the highest concentrations, followed by Zn, Pb, Mn, Cu, Ni, and finally Cd and Co. For Pb and Cd, atmospheric entirely dominates the total external input of pollution-derived elements. The fate of an atmospherically-transported trace metal, once deposited at the sea surface, depends on its thermodynamic speciation in seawater, its speciation in the parent aerosol and the kinetics controlling any speciation change (Guerzoni *et al.*, 1999).

Significant atmospheric input of heavy metal contaminants which are transported in the prevailing westerly winds from sources in Europe, is suggested in the MEDPOL Programme (Windom *et al.*,1988) and from the results of recent research conducted as a part of the 1988 Black Sea Environmental Programme (Hacisalihoglu *et al.*, 1991).

1.4.2 HYDROTHERMAL ACTIVITY

Hydrothermal activity had been shown to exert a major influence on the chemistry of trace metals in seawater. It has been estimated that the entire ocean mixes through these hydrothermal vent systems, undergoing high temperature interaction with fresh basalt every 8-10 Ma, leading to the production of high temperature (350 °C), acidic, reducing, hydrothermal fluids (Bruland, 1983).

Seawater and sediment enrichment of metals (Fe, Mn, Cu and Zn) has been observed at hydrothermal vents along the Hellenic Volcanic Arc (Varnavas & Cronan, 1991; Varnavas *et al.*, 1993). Significant fluxes of Fe, Mn, Cu and Zn at the seafloor result from seawater-rock interaction processes similar to those described at mid-ocean ridges, were noted at Santorini and Milos (Varnavas & Cronan, 1991; Varnavas *et al.*, 1993). Variations in time and space in the composition of the hydrothermal solutions are due to changes in chemical composition of the rocks leached by seawater; temperature and pressure and the degree of mixing of hydrothermal solutions with seawater. Iron was observed to have the highest concentrations (800 to 22040 μg/l) in hydrothermal waters at Santorini, followed by Mn (142 to 1747 μg/l), Zn (5 to 59μg/l), Cu (1 to 46μg/l) and Ni (1 to 27μg/l) (Varnavas *et al.*, 1993).

1.4.3 BENTHIC SOURCES

Regeneration on, or beneath, the sea floor is one of the key processes in the cycling of elements through the oceans (Bruland, 1983). In the open ocean, the greater part of trace metal cycling takes place in the water column, although a significant diffusive contribution from pelagic sediments can exist. Within interstitial waters of sediments, micro-organisms use oxygen, thereby changing the redox potential of the sediment. This may result in trace metal mobilisation from sediments and permit diffusive transport to interstitial waters, and eventual release into the overlying water. Solubility and mobility of particulate-bound trace metals can be changed by five major factors in solid/interstitial water systems: lowering pH, increasing occurrence of natural and synthetic complexing agents, increasing salt concentrations, changing redox conditions, and decomposing organic matter containing trace metals (Hong *et al.*, 1995).

Enrichments in porewaters of coastal sediments of Cu, Cd and Ni have been investigated (Westerlund *et al.*, 1986). It was concluded that trace metal fluxes were dependant, in part, on oxygen concentration. Burton and Statham (1982) reviewed profiles from the Pacific ocean, all exhibiting significant increases in copper for bottom waters. These results indicate an input of copper due to the diagenic release from settled particles, which had previously taken up the element from the water column. Benthic fluxes will vary significantly with sediment type for different elements. In pelagic clays and siliceous ooze of the Pacific ocean, 88% of deposited Cu was returned to overlying waters, whereas less than 5% of Mn was regenerated (Hong *et al.*, 1995). This difference is attributed to the association of Mn with terrigenous particles, whereas the input of Cu was predominantly regulated by biogenic phases, such as organic matter, skeletal calcium carbonate, or silica. Cadmium also exhibits similar fluxes with biogenic phases (of about 80%) in Laurentian Trough sediments, due to the degradation of fresh organic matter. Migration of Mn under reducing sediments has also been documented (Hong *et al.*, 1995). In the Mississippi Delta, Mn^{2+} fluxes were greatest in the nearshore and inner delta (840 $\mu g\ cm^{-2}\ yr.^{-1}$), providing a potential source of Mn to the deep sea (Hong *et al.*, 1995).

1.5 RECYCLING AND REMOVAL OF TRACE METALS

The ultimate fate of most trace metals is to be removed from the oceans to marine sediments. However, before this they may undergo various degrees of recycling with particulate or biological phases with subsequent regeneration into the water column.

1.4.1 ABSORPTION AND SCAVENGING - PARTICLE INTERACTIONS

The term 'scavenging' was given by Golberg (1954), on discovering that low trace metal concentrations were the result of absorption of positively charged metal ions onto negatively charged marine particles or manganese nodules. As particles sink down through the water column, the associated trace metals are effectively being removed from the ocean. This was termed 'The Great Particle Conspiracy' by Turekian (1977).

Rapid removal of trace metals onto particles occurs via adsorption onto surfaces, precipitation and incorporation into biogenic particles. Suspended particulates play a major role in influencing dissolved trace metal concentration and distribution. In situ primary production in the surface layers of the ocean is the main source of particles which have an important role in the transport and cycles of trace metals in the water column (Tappin, 1988). This plant material is grazed upon by phytoplankton and zooplankton and the undigested residues are packaged into faecal pellets with sinking rates varying from a few meters to a few thousand meters per day (Bruland, 1983). The absorptive properties of marine particles are controlled by organic coatings. These humic substances are absorbed onto the particle surface in seawater (Murray, 1988). Hunter (1980) suggested that carboxylic acid and phenolic functional groups appear to be the major ionizable groups in such coatings. It is the large particles that sink rapidly (and not the slower small particles) that are responsible for the bulk of transport of materials to the deep sea (Bruland, 1983), whereas small particles are important for adsorption/desorption processes. This organic 'rain' to the sediment surface is the driving force for a characteristic sequence of diagenetic reactions, in which organic carbon is oxidised, during which concentrations of Mn^{2+} and Fe^{2+} and other trace metals associated with MnO_2 and Fe_2O_3 increase in pore waters. These dissolve metals migrate towards the surface of the sediment water interface and may be a source of metals to the water column. Some scavenged metals are reversibly scavenged onto sinking particles, whilst others are not. These latter metals are probably incorporated into the crystalline lattice of mineral phases, such as amorphous polymetallic oxyhydroxides. These precipitates form spontaneously in seawater as the majority of metal form insoluble oxides (Libes, 1992).

Price *et al.* (1999a) observed seasonal and spatial variations in particulate Fe and Mn in the Cretan Sea. Iron is closely related to Al, as most of its concentration is intimately bound within the structure of aluminosilicates. The ratio of Fe/Al was found to be higher in September than March 1994, especially in the upper 200 m of the water column, attributed to increased atmospheric inputs. Manganese concentrations in the photic zone are low compared to deeper waters and this is considered due to photoinhibition of MnO_x precipitation from Mn(II).

1.4.2 BIOLOGICAL CYCLING

There are a number of ways in which the activities of phytoplankton, zooplankton and bacteria can influence the cycling of trace metals. The assimilation of some trace elements is dependent on their function as micronutrients. Mn, Fe, Co, Ni, Cu and Zn are examples of elements that play an important role in metal requiring and metal activated enzyme systems which catalyse major steps in glycolosis, the triboxylic acid cycle, photosynthesis and protein metabolism (Bruland, 1983). Iron has reportedly the highest enrichment factor (Libes, 1992). The biological driven flux of an element through the ocean is determined not only by the concentration factor in phytoplankton but also by grazing and excretion of the phytoplankton crop by zooplankton.

The presence of metal complexing ligands in phytoplankton is discussed by Hudson and Morel (1993) and Donat & Bruland (1995). For metals such as Cu, Zn, Fe, Cd, Co and Ni, organic complexation may aid to keep the metal in solution, thus, retarding its adsorption onto particle and/or assist the assimilation by some species of phytoplankton (Donat & Bruland, 1995). In upwelling regions, Cu-complexing ligands may reflect strong selective pressure to detoxify Cu by lowering its free ion concentration. In addition, trace metals may act synergistically or antagonistically to influence growth limitation or toxicity. Organisms living in regions of high metal concentration, for example zinc in surface waters of the Alboran Sea, do not incorporate Zn to a greater degree than in metal depleted oligotrophic open ocean waters (Sherrell

& Boyle, 1988). This is consistent with auto-regulation of planktonic elemental compositions, either by metabolic controls or by simple chemical means.

As well as active uptake, much of the metal uptake is by binding to high surface ligands; this binding is passive and, therefore, will occur equally on dead organisms or be incorporated into faecal pellets (Murray, 1988). Finally trace elements are also associated with phases of plankton such as calcium carbonate and opal.

1.6 RECENT TRACE METAL DATA FOR THE MEDITERRANEAN AND THE BLACK SEA

Since the 1980's there has been a significant increase in trace metal research in the Mediterranean Sea. Several European Commission programmes have focused on different areas of the Mediterranean. These include 'PHYCEMED' (Laumond *et al.*, 1984; Copin-Montegut *et al.*, 1986; Ruiz-Pino *et al.*, 1991); 'EROS 2000', ('EROS 2000', Water Pollution Research Report, European Community, 1989; 1990; 1992; Morley *et al.*, 1997; Guieu *et al.*, 1997); 'EUROMARGE' in the Adriatic Sea (Tankere & Statham, 1996) and more recently 'PELAGOS' in the Cretan Sea (Varnavas & Voutsinou-Taliadouri, 1986). Additional trace metal research include Statham *et al.* (1985), Van Geen *et al.* (1988), Sherrell & Boyle (1988), Saager *et al.* (1993), Saager (1994) and Yoon *et al.*, (1999). A brief summary of some of the key findings on trace metal distributions and profiles will be given below.

Table 1.1 summarises the range of trace metal concentrations found in the Mediterranean Sea and North Atlantic Ocean. The first significant observation is that surface waters of the Mediterranean Sea have higher trace metal concentrations than open Atlantic waters (Statham *et al.*, 1985; Van Geen *et al.*, 1988; Ruiz-Pino *et al.*, 1991; Morley & Burton, 1993). The inflow of Atlantic water, via its exchange with deep Mediterranean water, is a major influence to the trace metal budget in the Mediterranean, with fluxes through the Strait of Gibraltar at 30 times higher than fresh water inflow (Van Geen *et al.*, 1988).

Table 1.1 Concentrations of dissolved trace metals found in the North Atlantic and Mediterranean Sea. (1) Statham *et al.* (1985), (2) Van Geen *et al.* (1988), (3) Morley *et al.* (1997), (4) Morley & Burton (1993).

	Atlantic		Western Mediterranean	
	Surface	Deep	Surface	Deep
Cd (pM)	20-40 (1)(2) 23-29 (3)	300-350 (1) 140 (2)	50-80 (1)	60-110(1)(2) 55-70 (3)
Co (nM)	0.037-0.057 (3)		0.084-0.139 (3)	0.039-0.046 (3)
Cu (nM)	1.3 (2) 0.85-1.13(3)	1.3 (2)	1.37-2.27 (3)	2 (2) 1.45-1.65(3)
Fe (nM)	0.81-0.93(3)		1.33-4.45(3)	1.0-2.7 (3)
Mn (nM)	1.3-1.6 (1) 0.5-1.03(3)	0.1-0.5 (1)	2.5-4.5 (1)	0.15-0.24 (1)(3)
Ni (nM)	1.8 (2) 1.65-2.01(3)	2.7 (2)	1.9-3.9 (3)	4.2 (2) 3.0-3.96(3)
Pb (nM)	0.044-0.071 (3)		0.078-0.321 (3)	0.064-0.121 (3)
Zn (nM)	0.8 (2)	1.5 (2)	2-18 (4)	5 (2)

The mixing of a number of water masses in the Mediterranean is an important key in controlling the distribution and concentration of trace metals in both surface and subsurface waters: 1) the inflow of North Atlantic Surface Water (NASW), typically low in dissolved metals; additional contributions to the Straits from the trace-metal enriched sources of 2) Gulf of Cadiz Water (GCW) and 3) subsurface Atlantic waters, identified as North Atlantic Central Waters (NACW) by Van Geen *et al.* (1991); and 4) from the eastern Mediterranean the Sicilian Strait Surface Water (SSSW) associated with low metal concentrations. This mixture forms the Mediterranean Surface Waters (MSW) below which the Levantine Intermediate Water (LIW) enters through the Straits of Sicily, forming a layer at 150-600 m, and contributes to elevated subsurface concentrations especially for Zn (Morley & Burton, 1993). LIW forms the major component of the Mediterranean Outflow water (MOW) (Morley *et al.*, 1997). Mediterranean deep waters are fairly homogenous in concentration (see Table 1.1) and exhibits profiles similar to Atlantic waters. In addition, river transport, mobilisation from shelf sediments, human activities and atmospheric inputs are potentially significant sources of trace metals to the Mediterranean (Statham *et al.*, 1985).

As a consequence of these various sources to the western Mediterranean, surface concentrations will vary in space (see Table 1.1). Zinc exhibits a surface maxima related to salinity throughout the Mediterranean, from west to east, with lower values in the central and eastern basins (although concentrations will vary with atmospheric and terrestrial sources, as well as seasonally). From the Straits of Gibraltar to the Straits of Sicily Ruiz-Pino *et al.* (1991) observed a subsurface minimum, corresponding to the low salinity of the NACW. A Zn intermediate maximum at about 200 m appears throughout the western Mediterranean, coinciding with the LIW layer. Tankere & Statham (1996) found Cu, Ni, Zn and Cd profiles in the Adriatic Sea to be similar to open Mediterranean profiles, with highest concentrations near the Po river and concluded that river inputs were not a significant source to the Adriatic Sea.

The Black Sea is the worlds largest stable anoxic marine basin with a strong oxic/anoxic interface which influences the quantities and distribution of dissolved trace metals. There is a potential risk of anthropogenic sources from poor polution control measures in Eastern European countries or those of the former Soviet Union, which comprise the major portion of the Black Sea watershed (Windom *et al.*, 1998). Furthermore , the likelyhood of significant atmospheric input of heavy metal contaminants transported in the prevailing westerly winds from sources in Europe, is suggested by the results of the MEDPOL Programme and as part of the 1988 Black Sea Expedition (Hacisalihoglu *et al.*, 1991). Recent trace metals research includes the 1988 Black Sea Expedition (Lewis & Landing, 1991; Tebo, 1991) and EROS 2000, (Tankéré, 1998). Overall the metal concentrations observed are greater than in the Mediterranean Sea, although there is much more variability within the Black Sea, above and below the chemocline.

1.7 AVAILABLE TRACE METAL DATA IN THE AEGEAN SEA

Up to 1983 relatively little research had been carried out on dissolved trace metals in the Aegean Sea. Distributions of Cd, Cu, Zn, Ni, Fe and Pb have been reported (Fukai & Huynh-Ngoc, 1976;1977; Romanov *et al.*, 1977; Huynh-Ngoc & Fukai, 1979; Aubert *et al.*, 1980; Fytianos & Vasilikiotis, 1983). They found variable concentration ranges of most metals, with depth, geographical location and season, and they also made the first steps in understanding the processes governing trace metal distribution in the Aegean sea. Romanov *et al.* (1997) observed interseasonal variation in copper samples collected in the northern Aegean during 1974-1975, which he attributed in part to the seasonal change in the flux of low salinity Black Sea Water through the Dardanelles. The problems associated with low trace metal concentrations were observed by Fukai & Huynh-Ngoc (1977) and Huynh-Ngoc & Fukai (1979), finding approximately half the Cu and Cd data were below the detection limit.

The CEC/MAST project 'PELAGOS' provided the first extensive trace metal (Cu, Cd, Pb, Ni, Co, Mn, Cr and Fe) database for the southern Aegean Sea (Varnavas & Voutsinou-Taliadouri, 1986). Concentrations were found to be of a similar range to Mediterranean waters (see Table 1.1), as reported by Martin *et al.* (1993) and Tankere *et al.* (1994). Distinct spatial and temporal variations were observed to be linked to climatological conditions, circulation of water masses and particulate/dissolved interactions. Data was collected in June, September and December 1994, from the Cretan Sea and Kirthira Straits in the east to the Rhodes Straits in the west. Maximum concentrations were observed in the summer and in the eastern Straits (except Cu); whilst lowest concentrations were observed in winter and in the Cretan Sea. Vertical profiles were reported to exhibit a three-fold maxima: at the surface, at 500-600 m and in deeper waters of around 1100m (related to the creation of Cretan Dense Water, CDW). Elevated concentrations in dissolved and particulate metals were linked to southwards fluxes of Black Sea Water (BSW), Levantine water (LIW), Transitional Mediterranean Water (TMW), with its characteristic low oxygen content, increases in chlorophyll and the presence of an anticyclone in the Cretan Sea.

When considering the distribution of trace metals, it is important to note that the Aegean is one of the most seismically active regions on earth and has the highest seismic activity in Eurasia (Dando *et al.*, 1995). Seawater and sediment enrichment of metals (Fe, Mn, Cu and Zn) has been observed at hydrothermal vents along the Hellenic Volcanic Arc at Nisiros and Kos (Varnavas & Cronan, 1991) and Santorini and Milos (Varnavas *et al.*, 1993). These seawater rock interaction processes are similar to those described from mid-ocean ridges.

With the growing awareness of the potential pollution to the marine environment by anthropogenic activities, the rivers and bays of the Aegean have also been a focus of research for trace metals. Elevated levels due to pollution of dissolved and particulate trace metals have been observed in the Gulfs of Thessaloniki and Kavala (Fytianos & Vasilikiotis, 1983); the Evoikos Gulf (Scoullos & Dassenakis, 1983;

Dassenakis *et al.*, 1996); the rivers Axios, Aliakmon (Samanidou & Fytianos, 1987) and Acheloos (Dassenakis *et al.*, 1997).

1.8 OBJECTIVES

The primary objectives of this work fall within those of the Mediterranean Target Programme (MTPII) MATER programme during which all samples and analysis were carried out. That is to 'identify the main sources of the different trace elements and their spreading pathways in the northern Aegean Sea. Also to understand the mechanisms which are responsible for the trophic differentiation between the north and south ecosystems (oligotrophic in the North and extremely oligotrophic in the South), combining the trace metal data with other physical and chemical parameters.'

Considering the lack of information on dissolved trace metals in the Aegean Sea and the predetermined station positions, the initial objective was to obtain an overview of the biogeochemistry and distribution of dissolved trace metals in the Aegean Sea. Based on the existing knowledge of trace metals in the Mediterranean and the general knowledge of the Aegean Sea, the key areas the present work focuses on include: the influence of atmospheric, coastal and riverine and hydrothermal sources on metal concentrations and distributions; the relationship of trace metals with the complex circulation and hydrography of the Aegean; the spatial and temporal variability of dissolved trace metals and their causes; the oligotrophic nature of the Aegean and the relationship between dissolved nutrients and metals; residence times of metals in the Aegean; and finally the comparison and potential influence of the Aegean Sea on the distribution of metal concentrations in the Mediterranean.

CHAPTER 2

THE HYDROGRAPHIC AND BIOGEOCHEMICAL BACKGROUND OF THE AEGEAN SEA

2.1 GEOMORPHOLOGY OF THE AEGEAN SEA

The Aegean Sea (Figure 2.1) is globally the third major sea, and one of the most oligotrophic areas of the Eastern Mediterranean. It is an almost enclosed sub-basin, located between the Greek and Turkish coasts and has an area of approximately 1.81×10^5 km ^{2} (Carter, 1972) with a volume of 7.4×10^4 km ^{3} (Hopkins, 1978).

To the north-east, the Aegean exchanges flows with the Black Sea via the Sea of Marmara, an almost completely enclosed depression, with a surface area of 11,500 km^2 and a total volume of 3378 km ^{3} (Region *et al.*, 1991). The Sea of Marmara is connected to the Aegean via the Dardanelles Strait (with a width of 4 km and a sill depth of 55 m) and to the Black Sea via the Bosporus Strait (with a width of 0.7-3.5 km and an average depth of 35m)

To the south, the Aegean Sea is linked with the Ionian Basin through the Elafonisos Straits (depth 180 m, width 11 km), the Kithira Straits (depth 60 m, width 33 km) and the Antikithira Straits (depth 700 m, width 32 km), and with the Levantine Basin through the Kassos Straits (depth 700 m, width 67 km), the Karpathos Straits (depth 550m, width 43 km), and the Rhodos Straits (depth 350 m, width 17 km) (Poulos *et al.*, 1997).

The Aegean region is a geologically complex area located within the Alpine-Himalayan orogenic system, with an irregular bathymetry, a varied coastline and over 2000 small and large islands (Theocharis *et al.*, 1993). There are three major basins: the North Aegean Trough (maximum depth 1600 m), the Chios Basin (maximum depth 1160 m) in the central region and the Cretan Basin in the south (maximum depth 2529 m). There are three main shelf areas: the Samothraki and Limnos Plateaux in the north and the Cyclades plateaux extending between the Chios Basin and the Cretan Sea.

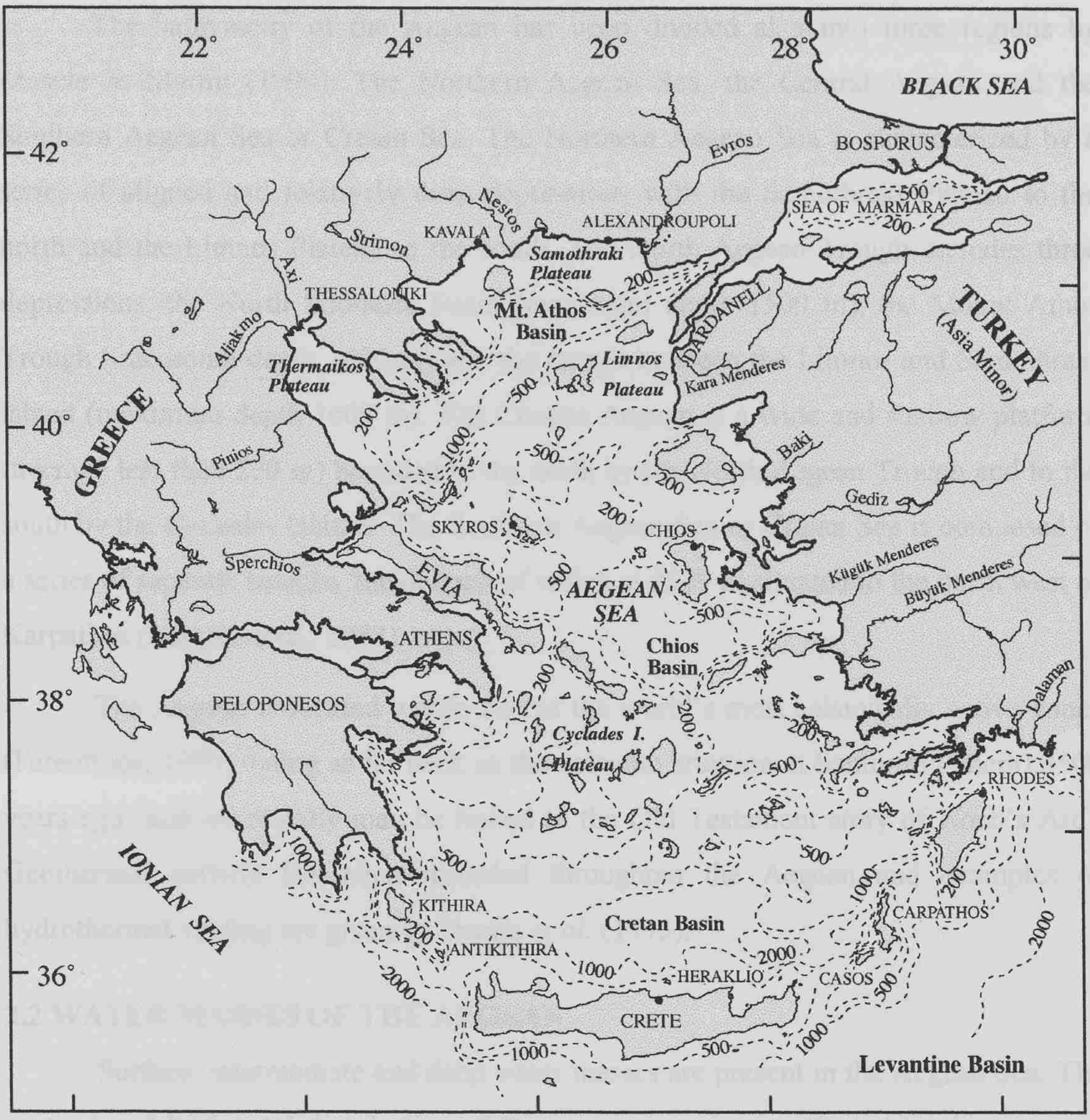

Figure 2.1 The Aegean Sea.

The bathymetry of the Aegean has been divided also into three regions by Mascle & Martin (1990): The Northern Aegean Sea, the Central Aegean and the Southern Aegean Sea or Cretan Sea. The Northern Aegean Sea is characterized by a series of aligned and relatively deep depressions with the Samothraki Plateau to the north and the Limnos Plateau to the south. The North Aegean Trough includes three depressions: the North Sporades Basin (maximum depth 1500 m), the Mount Athos Trough (maximum depth 1000 m) and the trough between the Limnos and Samothraki island (maximum depth 1600 m). The Central Aegean is a wide and shallow platform (average less than 200 m) bounded to the north by the North Aegean Trough and to the south by the Cyclades Islands. The Southern Aegean Sea or Cretan Sea is composed of a series of separate troughs, the deepest of which at 2529 m situated to the north west of Karpathos (Bartole *et al.*, 1983).

The Aegean is located within one of the world's most seismically active zones (Ferentinos, 1990) dating as far back as the volcanic eruption at Santorini (Thera) 3500 years ago (and historically may be linked to the Old Testament story of Noah's Arc). Geothermal activity has been recorded throughout the Aegean and examples of hydrothermal venting are given by Dando *et al.* (1995).

2.2 WATER MASSES OF THE AEGEAN

Surface, intermediate and deep water masses are present in the Aegean Sea. The vertical and horizontal distribution of these water masses is affected by the temporal and spatial variability in this region. This variability is reflected not only in the complex circulation of these waters and positioning of mesoscale features, such as fronts and eddies, but also in the characteristics of the deeper water formed in the Aegean.

The major water masses in the Aegean are: the Black Sea Water (BSW), the North Atlantic Water (NAW), the Levantine Intermediate Water (LIW), the Cretan Intermediate Water (CIW), and dense waters formed in the north, central and southern basins. A brief summary of these water mass characteristics are given below.

2.2.1 SURFACE WATERS

The Black Sea Water (BSW) flows into the Aegean through the Dardannelles and is characterised by its surface salinity minimum (salinity of 21-35), although there is great seasonal variability in the magnitude of the signal because of changes in water flows from the Turkish Straits. Freshwater input into the Black Sea is greater in the summer than the winter (Ünlüata *et al.*, 1990) resulting in lower salinities observed in the summer (24-26) than in the winter (31-35). This water mass has been identified almost throughout the Aegean, (Zodiatis, 1993; Balopoulos *et al.*, 1996) decreasing southwards to 38.0 - 38.5 when leaving the Aegean (Lascaratos, 1993b).

North Atlantic Water (NAW), or alternatively Modified Atlantic Water (MAW), enters the Cretan Sea through both the western and eastern Cretan Straits in the surface and subsurface layers, although predominantly through the Antikithira Strait (Balopoulos *et al.*, 1996), and can be identified by a subsurface salinity minimum throughout the Cretan Sea. This salinity minimum can vary from 38.5 to 39.0 (Lascaratos, 1993b), due to the interannual variability in local meteorological and oceanographic conditions which influence its entry into the Aegean as well as to those factors governing the quantity of NAW entering through the Strait of Gibraltar.

Warm and saline (~39.5) Levantine Surface Waters (LSW) are observed in most regions of the eastern Mediterranean during the warm period of the year and are considered to be the product of intense evaporation (Theocharis *et al.*, 1999).

2.2.2 INTERMEDIATE WATERS

The Levantine Intermediate Water (LIW) is formed in the Rhodes region where in winter, cold and dry continental winds cause sea surface cooling, which results in a density increase of the surface water and consequent sinking of this water mass. More recently, the formation of LIW is thought not be restricted to one unique region, but instead forms simultaneously in more than one place, i.e. the southern Aegean and the northern regions of the Levantine basin (Klein *et al.*, 1999). By the end of winter a deep mixed layer (150 m to 200 m) with a temperature of 15.5 °C and a salinity of 39.1 is formed (Lascaratos, 1993b). This water mass sinks to ~300 m and following a path from the formation region to the western basin, exits from Gibraltar and spreads at 1000 - 1500 m, forming the well-known salty water tongue of the Mediterranean Outflow Water of the northern Atlantic.

Cretan Intermediate Water (CIW) formation has been observed in the Cretan Sea, particularly in the east. Georgopoulos *et al.* (1989) observed high surface densities following a period of strong, cold and dry north winds, with 4 to 5 days of low air temperature, which subsequently cause these water masses to sink and spread along isopycnal surfaces. At depths of 200 to 250 m, just below the LIW, the water mass salinity was found between 38.99 to 39.01, with a temperature range of 15.25-15.30 °C. Over recent years there has been an apparent decrease in the formation of CIW corresponding to an increase in the formation of deep water masses (Klein *et al.*, 1999). The reduction of CIW has raised the vertical density gradient at the base of the LIW and brought mid-depth waters in direct contact with LIW. This has affected a dilution of LIW through upwelling and/or mixing by up to 30% (Roether, *et al.*, 1998), causing lower salinities, lower CFC and higher nutrient concentrations.

Transition Mediterranean water (TMW) can be identified by a temperature and salinity minimum layer throughout the Cretan Sea between 300 to 400 m, and it can be observed during late spring/early summer (Theodorou *et al.*, 1994). This water mass is a mixture of LIW and Eastern Mediterranean Deep Water (EMDW) (Balopoulos *et al.*, 1996), originates from outside the Aegean, and exhibits a characteristic low oxygen and high nutrient content (Theocharis *et al.*, 1993).

2.2.3 DEEP WATERS

The Aegean Sea has been described as one of the most dense seas in the world (Yüce, 1995) and deep-winter vertical convection processes forms these deep waters whose properties are dependent on the regional characteristics of the formation waters.

North Aegean Deep Water (NAEGDW) formation has been observed over the Samothraki and Limnos plateau, promoted by the hydrological regime during severe winter meteorological conditions. This water mass is characterised by a high oxygen content (5 - 5 ml l^{-1}) and cold temperatures (Theocharis & Georgopoulos, 1993). The relatively warmer and more saline waters of Levantine origin propagate northwards along the Eastern Aegean, encounter the less saline and colder BSW over the Limnos Plateau and form a strong permanent thermohaline front. Intermittent intrusions of the warm and high salinity waters during winter form a succession of cold, less saline and warm, high saline patches over the Samothraki Plateau. Mesoscale eddies enhance the presence of warm and saline waters at the surface. These intrusions and mesoscale eddy activity are important elements for dense water formation over the Samothraki Plateau.

The newly formed dense waters then flow along isobaths to deeper layers, thus, contributing to the ventilation of the deep waters of the North Aegean basins. Below 400 meters advection and mixing is limited due to the presence of shallow sills in the area (Georgopoulos *et. al.*, 1998) which cause the 'trapping' of water masses between basins and troughs.

Central Aegean Deep Waters are generally warmer with characteristic temperature and salinity values in the summer of 14.05 °C and 38.8 and 14.0 °C and 38.7 respectively in the winter at 1000 m depth (Lascaratos, 1993a).

Cretan Sea Deep Water (CDW) can be characterized by its relatively high temperature, salinity and density values (T = 13.9-14.5 °C, S= 38.7–39.0, $\sigma\theta = 29.2$) at depths of >700 m (Theocharis, *et al.*, 1993); the highest values of these parameters are observed in the eastern depression of the Cretan Sea. The mechanism for CDW formation involves i) an increase in surface water salinity up to the point where its density increases above that of the underlying waters, ii) convection would result, involving waters of higher salinity and slightly higher temperature, 3) as deep waters become progressively denser, the surface waters must become colder in order to sink (Tsimplis *et. al.*, 1999).

Deep Mediterranean Waters are found at 500 - 800 m where these waters flow into the Aegean Sea with a temperature and salinity of approximately 15 °C and 38.9 respectively (Lascaratos, 1993b). This flow has been observed through the Kassos strait to the south-east and the Antikithira strait to the south-west of Crete. The main source of Eastern Mediterranean Deep Water (EMDW) was up to 1987 the Adriatic Sea, whereas in recent years EMDW formation has also been observed in the Aegean Sea (Theocharis, *et al.*, 1999), with uniform salinity (38.7) and temperature (13.6 °C) basin-wide.

2.3 GENERAL CIRCULATION OF THE AEGEAN SEA

2.3.1 NORTHERN AEGEAN

In the winter a cyclonic gyre has been identified in the northern basin with a northerly flow along the eastern boundary (Turkish coastline) and southerly flow along the western boundary (Greek coastline) (Theocharis & Georgopoulos, 1993), Therefore, waters of Levantine origin propagate northwards along the Eastern Aegean and encounter BSW over the Limnos Plateau, whilst BSW is observed in the Cretan Sea and south-east Ionian Sea. In the summer, there is a general flow of surface waters to the south (Poulos, *et al.*, 1996). This flow is induced by the prevailing wind climate, dominated by the Etesians, and cause divergence and subsequent upwelling along the eastern boundary, whilst downwelling occurs on the western boundary.

2.3.2 SOUTHERN AEGEAN

The general circulation in the South Aegean is complex, with cyclonic and anti-cyclonic gyre and eddies are interconnected by currents and jets variable in space and time (Theocharis, *et al.*, 1999). The Cretan Cyclonic Gyre and Western Anticylonic Gyre dominate, along with the Mirtoan West Cretan Cyclone in the Mirtoan Sea. The Ionian Sea region is characterized by an anticyclonic flow, and the north-western Levantine by the Rhodes Cyclonic Gyre and Ierapetra Anticyclone. (Theocharis, *et al.*, 1999). Modified Atlantic Water (MAW) enters the South Aegean from the Ionian Sea within surface or sub-surface layers transported by the Mid-Mediterranean Jet (MMJ). On the other hand, the Asia Minor Current (AMC) carries towards the south Aegean the surface saline waters of Levantine origin, promoting the formation of highly saline intermediate waters (CIW) within the Cretan Sea. TMW enters through the Cretan Arc Straits, and forms an intermediate layer throughout the Cretan Sea. BSW generates a distinct surface layer (25 to 50 m), following the cyclonic general circulation of the Aegean to the Southern Aegean, occasionally detectable down to the Kitherian Straits (Theocharis, *et al.*, 1993).

Klein *et al.* (1999) proposed the name Cretan Sea Overflow Water (CSOW) for the overflow of CDW from some of the sills of the Cretan Arc into the Levantine and Ionian basins. Until recently it was thought that the contribution of CDW to the creation of the East Mediterranean Deep Water was small; however new evidence suggests that since 1987 there has been a considerable increase in the CDW outflow (Roether *et al.*, 1996), accompanied by an increase in salinity and density, and a decrease in temperature (Theocharis *et al.*, 1998). These changes are associated with changes in thermohaline circulation in the Cretan Sea.

2.4 FRESHWATER INPUTS TO THE AEGEAN

Various rivers discharge into the Aegean along the Greek and Turkish coastlines (Figure 2.1). The main inputs are: i) the rivers Axios, Aliakmon, Gallikos, Pinios which discharge into Thermaikos Gulf; ii) the river Sperchios, along the western coastline; iii) the rivers Evros, Strimon and Nestos along the northern Greek coast, and vi) the smaller rivers K. Menderes, Bakir, Gediz, Kuguk Menderes and Bujuk Menderes discharging along the Turkish coastline. The annual discharges of the main rivers are shown in Table 2.1. Along the Greek coastline, high levels of fresh water discharge occur between December and April, whilst along the Turkish coastline maximum discharge occurs from October to March.

Table 2.1 Major riverine inputs into the Aegean Sea. River water discharge data for Greek (1962-1972) and Turkish (1978-1982) rivers abstracted from Therianos (1974) (after Poulos *et al.*, 1997).

Rivers	Drainage Area (km^2)	Annual Discharge ($m^3 s^{-1}$)	Annual Runoff ($m^3 10^6$)
GREECE			
Axios	22450	159	5031
Aliakmon	6075	73	2292
Pinios	7081	81	2529
Sperchios	1158	62	743
Evros	27465	103	3250
Nestos	4374	58	1819
Strimon	10937	110	3440
TURKEY			
Kara Menderes	1586	11	345
Bakir	16463	7	204
Gediz Nehri	15617	9	283
Kuzuk Menderes	3255	1	33
Bujuk Menderes	19596	31	370

Sewage effluent also contributes a major source of 'freshwater' from numerous cities such as Athens which discharges some 219×10^6 m^3 $yr.^{-1}$ of waste (Theodorou, 1992). The total amount of fresh water input to the Aegean is approximately 2×10^{10} m^3 $yr.^{-1}$ (Poulos *et al.*, 1997) when rivers and torrents are incorporated into the total water discharge of the main rivers presented in Table 2.1.

2.5 CLIMATE OF THE AEGEAN

The Aegean Sea has atypical Mediterranean type of climate with two distinct periods: a cool and rainy season from November to March; and a hot and rather dry season from May to September (Poulos *et al.*, 1996).

2.5.1 WINDS

The predominant winds over the Aegean are northerly, dry and cold and are generated by the outbreak either of the Arctic or the Polar continental air masses (Poulos *et al.*, 1996). South-southwesterly winds occur during Spring, whilst diurnal sea breezes occur along the Greek and Turkish coasts during summer.

The northerlies occur at two periods during the year; a primary maximum during winter (December to February) and a secondary maximum from July to August. During winter these strong cold dry northerlies are funneled through the valleys of the Axios, Strimon and Evros rivers, towards the Aegean Sea (Theocharis and Georgopoulos, 1993).

In summer the northerly Etesian winds influence greatly the climatic conditions in the Aegean Sea (Lascaratos, 1993b); these winds are associated with clear skies which persist for extended periods, and often reach gale force strength. The pressure gradients associated with Etesian winds are: i) the low pressure system of the deep Asiatic low, which extends over the Levantine, ii) the high pressure system of the Azores, which extends to south-east Europe and the Balkans, and iii) the high pressure systems of western Russia and of north-west Europe. The most important factors are the Asiatic low and the Azores high, either of which can generate Etesian winds. Influence of these winds can be felt in both the north-west Levantine basin and south of the Peloponnisos and west of Crete. The Etesians cause upwelling on the eastern boundary and downwelling on the western boundary of the Aegean. The Etesians disappear in late autumn followed by violent cyclonic storms.

2.5.2 AIR TEMPERATURE

The mean annual air temperatures over the Aegean Sea varies between 16.0 °C and 19.5°C, increasing towards the south (Polous *et al.*, 1996). From a 16 year data set (1975-1990) the lowest mean monthly winter values varied from 4.8 °C to 12.0 °C, whereas in summer the mean monthly values varied between 24.0 °C and 26.5 °C. Air temperature is the main factor affecting sea surface temperature, which appears to lag that of the air by the order of a month (Polous *et al.*, 1996).

2.5.3 EVAPORATION

A mean annual evaporation over the Aegean Sea of 4.2 m d^{-1} has been calculated from a four year data set (1980-1983), and is in agreement with other estimations (Jakovides *et al.*, 1989 as cited in Polous *et al.*, 1996). Evaporation fluctuations follow that of air-temperature, precipitation and wind speed, with minimum evaporation in late spring and Autumn and maximum in February and July/August when evaporation is expected to exceed precipitation and river runoff (Theocharis, *et al.*, 1993). Minimum evaporation values in spring may be the result of reduced wind speeds and sea surface temperature, whereas in autumn minimum values can be attributed to a reduction in Etesian winds and the lack of depressions during this period.

2.5.4. PRECIPITATION

Annual precipitation over the Aegean varies between 400 and 700 mm $yr.^{-1}$, with a mean relative humidity of between 65% and 75% (Polous *et al.*, 1996). In general rainfall is limited or absent during the summer period.

2.6 OLIGOTHROPHIC STATUS OF THE AEGEAN SEA

The Mediterranean Sea is well known to be one of the world's oligotrophic sea due to the limited nutrient supply to its surface waters both from its lower layers and from external sources (the Atlantic inflow, riverine discharges and atmospheric input) (Yimaz, & Tugrul, 1998). According to estimates of Bethoux and Copin-Montegut (1988), the Atlantic inflow through Gibraltar accounts for only 20% of the nutrients exported from the Mediterranean via the strait undercurrent; the rest is compensated by terrestrial and atmospheric inputs. The annual primary production in the western basin is in the order of 80 g C/m^2, comparable to open ocean values, whereas the estimates for the south and north-eastern Mediterranean is as low as 18 g C/m^2 (Berman *et al.*, 1984) due to very limited inputs from external sources.

The nutrient regimes of the eastern Mediterranean and the Aegean Sea have been studied extensively in recent years (Kucuksezgin *et al.*, 1995; Souvermezoglou, 1996; Souvermezoglou *et al.*, 1998; Yilmaz, & Tugrul, 1998; Kress & Herut, 1999; Vukadin *et al.*, 1999; Yilmaz *et al.*, 1999). The Aegean Sea is regarded in general as the most oligotrophic sea in the Mediterranean, with nutrient concentrations that decrease from the western to the eastern Mediterranean (Kucuksezgin *et al.*, 1995). Profiles show surface depletion of nutrients in waters above the euphotic zone with regeneration at depth, almost throughout the year (except when mixing or upwelling bring deep water nutrients to the surface). Surface water concentrations are governed by sources (i.e. water mass type, coastal and atmospheric inputs) versus sinks (i.e. phytoplankton production), and remain generally very low (see Table 2.2), therefore limiting primary production. In the Aegean, phosphate is responsible for limiting pelagic productivity with mean N/P values of 21.5, for the north and 20.9 for the south, with highest values observed at the surface (Kucuksezgin *et al.*, 1995 and Souvermezoglou *et al.*, 1998).

Table 2.2 Nutrient concentrations observed in the Eastern Mediterranean and Aegean Sea. (1) Kucuksezgin *et al.*, (1995), (2) Souvermezoglou, 1996, (3) Yimaz & Tugrul, 1998, (4) Civitarese *et al.*, 1998, (5) Tankere, 1996

	Surface Waters			Deep Waters		
Nutrient concentration (µM)	$N0_2$+$N0_3$	Si	$P0_4$	$N0_2$+$N0_3$	Si	$P0_4$
North Aegean (1)	< 1.2	< 1.0	< 0.05	<2.8	<3.8	<0.16
South Aegean (1)(2)	<1.5	0.6-2.2	<0.05	1.0-6.0	2.0-6.0	<0.14
Levantine Sea (3)	<1.0	<2.0	<0.05	1.0-6.0	2.0-11.0	0.10-0.22
South Adriatic (4)	0.5-3.0		<0.05	1.0-6.0		0.10-0.22
North Adriatic (5)	1-74		<0.15	1.0-10.0		0.05-0.25

Surface water masses in the eastern Mediterranean include Black Sea Water (BSW), Atlantic Water (AW), Modified Atlantic Water (MAW), and Levantine Surface Water (LSW) as described in Section 2.2.1. Black Sea Water, entering the north Aegean through the Straits of Dardanelles can carry elevated nutrient concentrations (Polat &

Tugrul, 1995; Polat *et al.*, 1999; Yilmaz *et al.*, 1999). During mixing and upwelling events, nutrient rich deep waters supply surface waters, resulting in the potential for increased primary production. Cyclonic gyres such as the Rhodes gyre (RG) and over the Mirtoan Sea (western Cretan Sea), bring the nutricline above the euphotic zone leading to areas of increased biological activity, as observed in the Cretan Sea (Souvermezoglou, 1996) and the Levantine Basin (Yimaz, & Tugrul, 1998). Anticyclones observed in the Cretan Sea (Souvermezoglou, 1996) and Levantine Basin (Yimaz, & Tugrul, 1998) have the reverse effect, lowering the nutricline and, thus, reducing biological activity. Intermediate and deep waters masses include Cretan Deep Water (CDW), North Aegean Deep Water (NAEGDW), Levantine Deep Water (LDW), Central Aegean Deep Water and Transitional Mediterranean Water (TMW) (see section 2.2.3). Each water mass has differing characteristics. CDW has high concentrations of oxygen (~ 5 ml/l) and low nutrient concentrations ($N0_3 \sim 3$ µM), similarly LIW has low nitrate (<3 µM). In contrast, TMW observed in the Cretan Sea between 200-600 meters exhibits elevated nutrients and low oxygen concentrations ($N0_3 \sim 5.6$ µM and $O_2 < 4.4$ ml/l) (Souvermezoglou, 1996) along with LDW ($N0_3 = 5.5$, $Si = 9.7$ and $P0_4 = 0.2$ µM) (Yimaz, & Tugrul, 1998). In addition to influences of water mass type, circulation, coastal and atmospheric sources, and biological activity, the nutrients in the Aegean have been observed to vary spatially, interannually and with season, being lowest at the surface in summer (Souvermezoglou, 1996. Yimaz & Tugrul, 1998).

CHAPTER 3

SAMPLING AND ANALYTICAL PROCEDURES

3.1 THE DATABASE FOR THE STUDY

Sampling took place in the Aegean Sea on the National Centre for Marine Research, Athens (NCMR) RV Aegeo during two separate cruises; March (late winter) and September/October (late summer) 1997 as part of the EU MTPII MATER programme. Sample stations and numbers of samples collected are summarised in Table 4.1, and station details and data are tabulated in Appendix 2. The locations of the 14 main CTD sampling stations are given in Figure 3.1 Additional CTD stations and surface pole sites are included in more detailed maps of the South Aegean (Figure 3.2) and the North Aegean (Figure 3.3). Additional CTD casts and samples were obtained for the September 1997 cruise, down to 250 dbars, enabling an accurate study of an east to west transect across the Cretan Sea to be made.

The data base includes dissolved trace metals (Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn), dissolved nutrients (nitrate plus nitrite, silicon and some phosphate) and salinity. With each CTD cast data is available for salinity, temperature, density (courtesy of NCMR, Athens), at sample depths, and also at 1 m intervals for θ/S plots. Fluorometry data was collected for the September 1997 cruise only in the Northern Aegean, with calibration courtesy of NCMR. Particulate Si_{bio}, Fe, Mn, Cu, Zn and Pb data for the northern (MNB) and southern (MSB) stations of the Aegean Sea was collected in March and September 1997, along with particulate metal fluxes (Mn, Fe, Cu, Pb and Zn) from sediment traps (500 m and 35 mab) at stations MNB1, MNB2, MNB3, MSB1 and MSB2 (renamed MNT and MST respectively) for the period of 1/4/97 to 31/3/98, courtesy of Professor Brian Price of the University of Edinburgh, U.K.

Table 3.1 Summary of CTD and surface (S) pole sample sites in the Aegean Sea.

Main Stations	Position	Depth (meters)	Number of depths sampled	
South Aegean			March 1997	Sept./Oct. 1997
MSB1	36°.04,50 N 25^{0}.17,00 E	1775	16	16
MSB2	35°.44,70 N 25°·06,00 E	1363	16	16
MSB3	36°.00,00 N 23°.53,60 E	1191	16 + S	16
MSB4	36°.15,00 N 24°.06,30 E	911	16 + S	12
MSB5	36°.11,60 N 24°.41,00 E	1235	N/A	8
MSB6	36°.00,00 N 25°.42,30 E	1286	16 + S	16
MSB7	35°.40,00 N 26°.13,00 E	2273	16 + S	16
North Aegean				
MNB1	40°.14,90 N 25°.12,00 E	1258	12 + S	12 + S
MNB2	40°.04,65 N 24°.36,20 E	976	12 + S	12
MNB3	39°.13,45 N 25°.00,00 E	806	12 + S	14
MNB4	39°.47,10 N 25°.31,50 E	96	4 + S	4
MNB5	40°.12,65 N 25°.28,50 E	560	8 + S	8
MNB6	40°.34,70 N 25°.08,00 E	152	8 + S	8 + S
MNB7	40°.16,60 N 24°.50,50 E	728	12 + S	12
Additional Stations	**Position**	**Depth (meters)**	**Number of depths sampled**	
South Aegean			March 1997	Sept./Oct. 1997
MSB34	36°.07,62 N 23°.59,60 E	873	N/A	8
MSB45	36°.13,73 N 24°.23,27 E	614	N/A	8
MSB51	36°.07,66 N 24°.59,10 E	1321	N/A	8
MSB16	36°.02,20 N 25°.30,44 E	1413	N/A	8
MSB67	35°.49,86 N 25°.57,72 E	988	N/A	8
Milos S5	36°.39,70 N 24°.30,45 E	33	S	3 + S
Milos S6	36°.41,40 N 24°.33,04 E	53	S	N/A
S7	37°.12,00 N 24°.17,50 E	440	S	N/A
North Aegean				
MT4 (S8)	39°.21,87 N 23°.36,71 E	1170	S	N/A
T1	40°.22,00 N 24°.32,00 E	155	N/A	5
MT3 (S9)	39°.29,30 N 23°.14,70 E	395	S	N/A
MT2 (S10)+M2	39°.40,76 N 23°.15,63 E	410	S	N/A
M2M2	39°.42,00 N 23°.13,00 E	160	N/A	4 + S
M2M3	39°.48,00 N 23°.24,50 E	317	N/A	3 + S
MT1 (S11)	39°.52,11 N 23°.27,31 E	395	S	N/A
M2M4	39°.54,50 N 23°.34,50 E	400	N/A	S
S12	39°.56,00 N 24°.03,00 E	690	S	N/A
S19	39°.30,95 N 25°.16,96 E	165	S	N/A
		Total	**184**	**231**
			415	

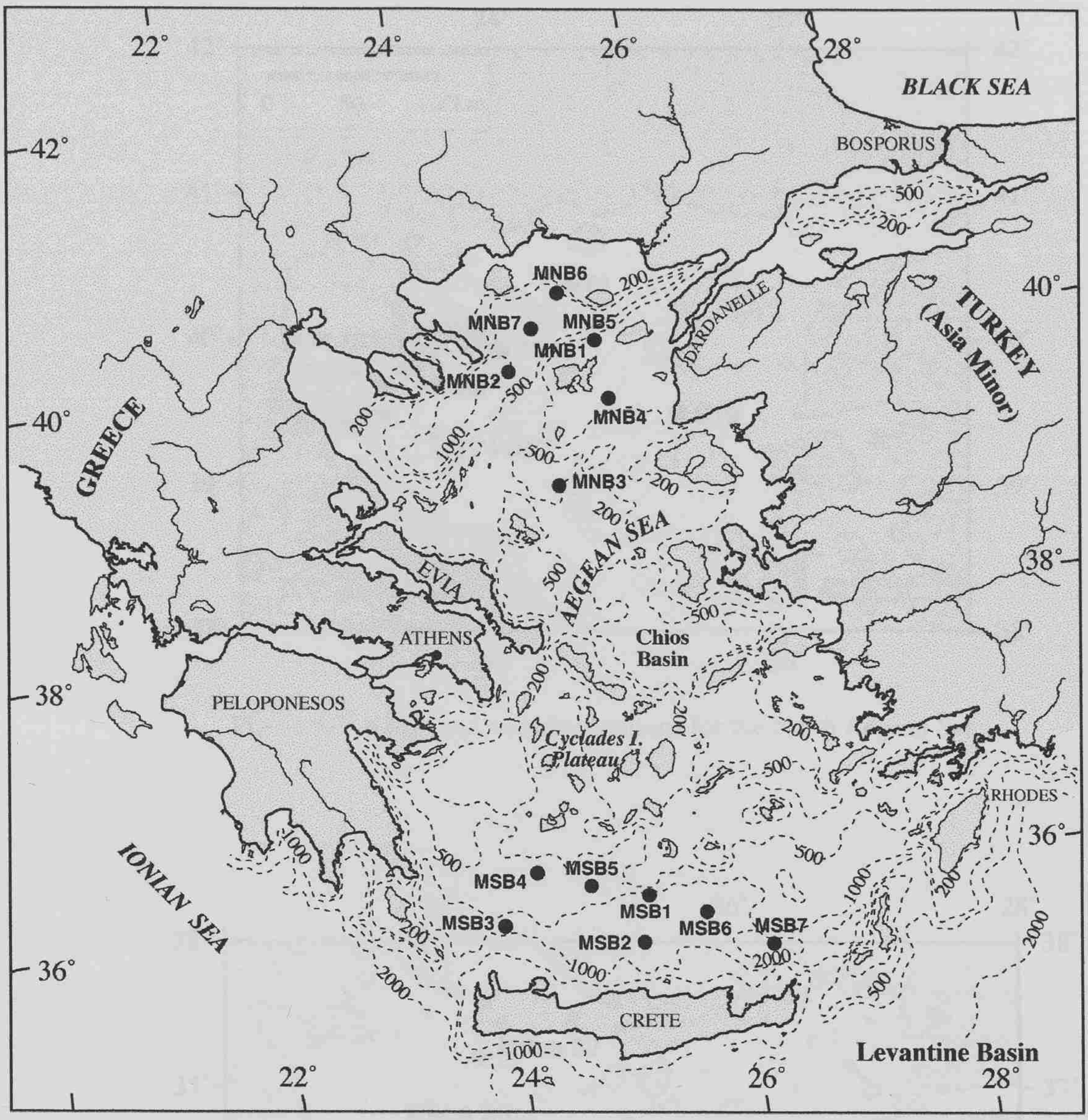

Figure 3.1 Mater sampling stations for the Aegean Sea.

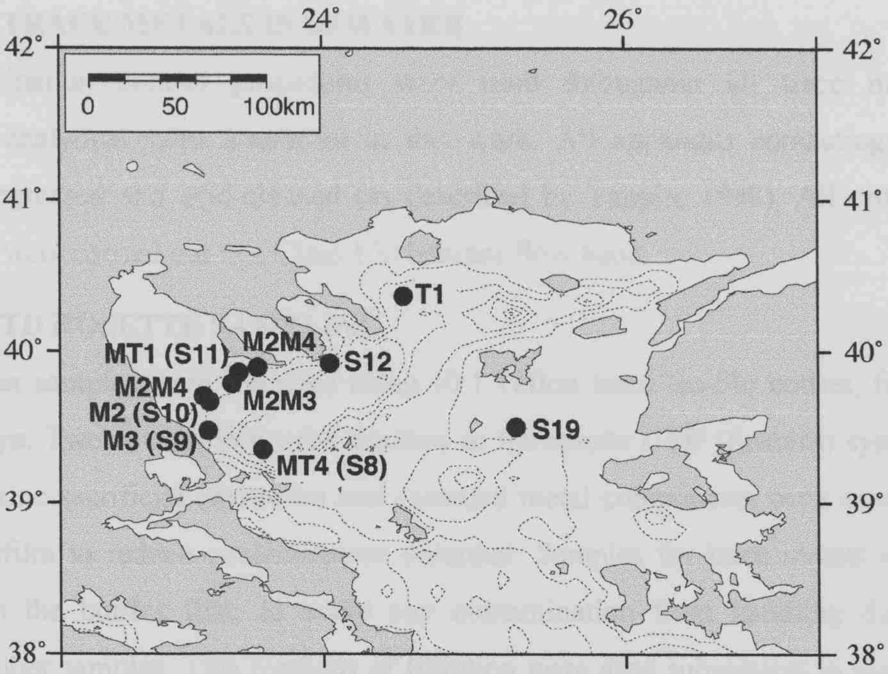

Figure 3.2 Additional sampling stations for the North Aegean Sea.

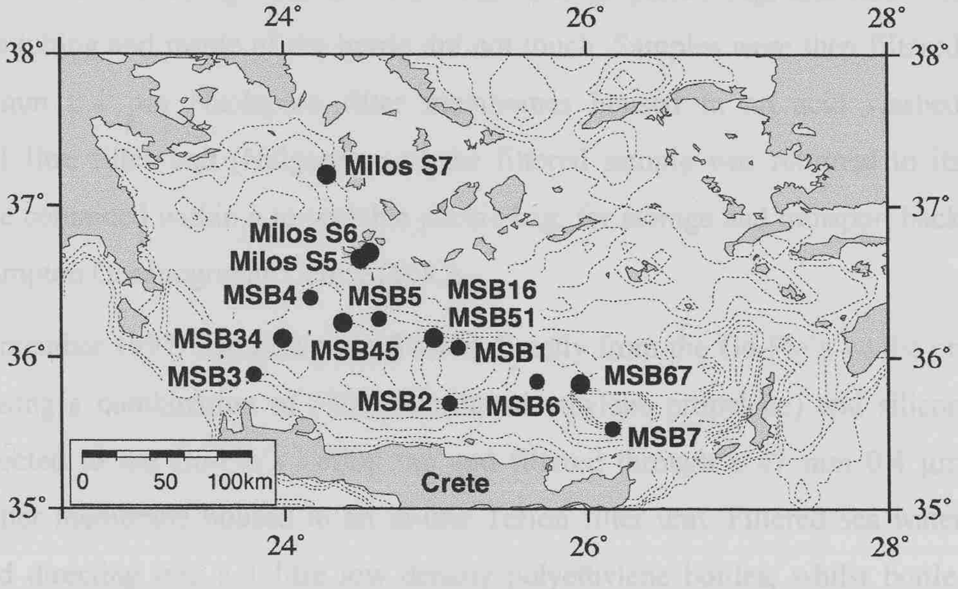

Figure 3.3 Sampling stations for the South Aegean Sea.

3.2 SAMPLING AND HANDLING OF SEAWATER SAMPLES FOR DISSOLVED TRACE METALS IN SEWATER

Contamination control procedures were used throughout all trace metal sampling and analytical steps employed in this work. All apparatus contacting the sample was degreased and acid-cleaned (as described by Tappin, 1988). All critical handling steps were carried out in a Class 100 laminar flow hood.

3.2.1 CTD ROSETTE SAMPLING

Seawater samples were collected using 10 l Teflon lined Go-Flo bottles, fitted with Teflon taps. Twelve Go-Flo's were attached to the rosette CTD (Seabird) system, with exposed zinc sacrificial electrodes and corroded metal components were covered in plastic parafilm to reduce contamination potential. Samples for trace metals were collected from the bottles first, to avoid any contamination from handling during collection of other samples. Two methods of filtration were used subsequent to sample collection:

i) March 1997. A cleaned silicon rubber tube was attached to the tap and water was collected in 1 litre low density polyethylene bottles (Nalgene). To minimise sample exposure, the bottle and tubing were all held within a large plastic bag, and care was taken that the tubing and inside of the bottle did not touch. Samples were then filtered through 47 mm 0.4 μm Nuclepore filter membranes housed in an acid washed polysulfone 1 litre filter unit (Nalgene), and the filtered sample was returned to its original bottle contained within a re-sealable plastic bag, for storage and transport back to the Southampton Oceanography Centre (SOC).

ii) September 1997. Samples were filtered directly from the Go-Flo's whilst on the rosette using a combination of FEP (fluorinated ethylene propylene) and silicon tubing, connected to the Go-Flo's Teflon tap and filtered through a 47 mm 0.4 μm Nuclepore filter membrane housed in an in-line Teflon filter unit. Filtered sea water was collected directing into a 1 litre low density polyethylene bottles, whilst bottle, filter unit and tubing were covered within a plastic bag (to minimise exposure). Go-Flos were pressurised using nitrogen gas, connected by silicon tubing (via an air filter) and a series of FEP taps connected in turn to each Go-Flo. The 1 l sample was then contained within a re-sealable plastic bag, for storage and transport back to the SOC.

3.2.2 POLE SURFACE SAMPLING

Surface samples were collected directly into an acid cleaned 1 litre low density polyethylene bottle held in a polypropylene frame, attached to the end of a 5 meter wooden pole. The sampler was dipped into the water whilst the ship was moving slowly (at approximately 2 knots) into the oncoming wind/tide, and samples were collected at approximately 3 meters away from the ship, reducing the potential contamination from the vessel. From this 1 litre bottle, sub-samples were taken for salinity, nutrients and trace metals, Trace metal samples were filtered through 47 mm 0.4 μm Nuclepore filters, using the polysulphone vacuum system.

Within 1 week of collection, all samples were acidified with sub-boiling distilled nitric acid to a pH of about 2 (1 ml of acid per litre of sample).

3.3 DEVELOPMENT OF ANALYTICAL PROCEDURE FOR TOTAL DISSOLVED TRACE METAL ANALYSIS: ^{54}MN ADDITIONS TO SEAWATER TO CALCULATE EFFICIENCY OF CHLOROFORM EXTRACTION METHOD.

Despite recent advances in instrumental techniques and sensitivity, the direct measurement of dissolved trace metals at concentrations found in open ocean and shelf waters remain difficult, although possible. (Tappin, 1988). The requirement is still to pre-concentrate, and in doing so separate from the salt matrix trace metals prior to measurement. Solvent extraction has been widely used (Statham 1985; Tappin 1988 and Nolting & de Jong 1994) and is shown to achieve high efficiencies in the extraction of trace metals.

A variation on the previous method of Statham (1985) and Tappin (1988) was required for the current study due to restrictions of Freon after the Montreal protocol, and awareness of damage to the ozone layer, Freon was replaced by Chloroform for the solvent extraction procedure.

The efficiency of chloroform for the extraction of trace metals was examined, using the addition of ^{54}Mn to seawater. This was done in order to reduce the thorough cleaning stages of equipment and reagents required for stable trace metal work. Two methods of back extraction were examined in order to ascertain the efficiency of each.

The methods used are based on a hybrid of methods for trace metal extraction described by Tappin (1988) and Nolting & de Jong (1994). All work was carried out in designated radioisotope laboratory, following guidelines of the Radioactive Substance Act, 1960.

3.3.1 GENERATION OF REAGENTS AND NECESSARY APPARATUS

From the ^{54}Mn stock, a working solution of 33 nCi/ml in 5 ml of 0.1 M HCl was made up. The radioactive activity was estimated from the rate of ^{54}Mn decay, using a scalar (Ratemeter SR3) gamma detector. To obtain reproducible values, a count value of over 10,000 (measured over a 100 second period) was achieved by adding 200 µl of the working standard to 5 ml of 0.1 molar HCl to make the ^{54}Mn standard solution.

Apparatus

Scalar (Ratemeter SR3) gamma detector with setting:
  HV, Potential setting = 480 (i.e. max. peak for Mn)
  Energy = 0.84
  Measurement Time = 100 second period
500 ml FEP separatory funnels (2)
125 ml FEP separatory funnels (2)
250 ml, 25 ml and 10 ml polyethylene measuring cylinders
pH probe
Micropipettes and tips
Stand to hold separatory funnels
10 ml Teflon beaker

Reagents

Chloroform (AR Grade)
Complexant: 2% (w/v) Ammonium pyrrolidine dithiocarbamate (APDC) and 2% (w/v) diethylammonium diethydithiocarbamate (DDDC)
Concentrated Nitric acid (AR Grade)
1 molar Nitric acid (AR Grade)
Isothermally Distilled Ammonia solution: 2 molar i.e. 5 ml in 35 distilled water (AR grade)

3.3.2 METHOD 1

To a 500 ml FEP separatory funnel, 210 ml of low metal seawater was transferred, and 200 µl of working standard was added. The addition of ammonia to bring the pH to the desired range 6.5 and 8 for maximum extraction efficiency, was unnecessary, as the pH of the seawater used, when checked fell within this range. Next was the addition of 12 ml of complexant followed by 5 mls of chloroform. The separatory funnel was then shaken for 5 minutes. After allowing a short interval for the phases to separate, the chloroform was collected in a count vial, counts were measured (see Table 3.2) and chloroform was transferred to a 125 ml separatory funnel. The count vial was then rinsed with 1 ml chloroform and this was measured and added to the 125 ml separating funnel. A further 5 ml of chloroform was added to the seawater sample and the procedure as described above is repeated.

To the 125 ml separatory funnel 78 µl of nitric acid was added. After shaking for 5 minutes, 2 ml of distilled water was added and is shaken for a further 5 minutes. The aqueous phase was then removed and made up to 5 ml in the count vial with 1 molar HCl. After the counts have been measured, the procedure was repeated.

3.3.3 METHOD 2

To a 500 ml FEP separatory funnel 210 ml of low metal seawater was transferred, and 200 µl of working standard was added, along with 12 ml of complexant and 5 ml of chloroform as described in 3.3.2. The separatory funnel was then shaken for 5 minutes. After allowing a short interval for the phases to separate, the chloroform was collected in a 10 ml Teflon cup. A further 5 mls of chloroform was added to the separating funnel, rotated for 5 minutes and as before the chloroform was transferred to the original Teflon beaker.

The Teflon beakers containing chloroform, were then transferred to a corrosion protected hot-plate, where samples were dried overnight at a low temperature. To each Teflon beaker, 100 µl of sub-boiling distilled concentrated nitric acid was added, to oxidise matrix components. The solution was left to dry. The procedure was repeated once more, and the sample was re-dissolved in 2 ml of 1 molar sub-boiling distilled HNO_3. This gives a concentration factor of 105. The volume was made up to 5 ml with 1 molar HCl and counts were measured.

3.3.4 RESULTS

Efficiencies for both methods were calculated (Table 3.2), taking into account counter blanks and standards (see Appendix I). These results show that although chloroform was efficient at extracting Mn in the forward extraction step, the nitric back extraction (Method 1) was far less efficient than the evaporation technique (Method 2).

Table 3.2 The recovery efficiencies of Manganese-54 in seawater by pre-concentration: comparing back extraction vs. evaporation methods. Efficiency [1] was taken during forward extraction, and efficiency[2] was taken from the back extraction (method 1) or after evaporation stage (method 2).

	Efficiency [1]	Efficiency [2]
Method 1 Back Extraction (based on 4 experiments)	98.30 (±0.733)	86.36 (±2.77)
Method 2 Evaporation (based on 5 experiments)	N/A	98.71 (±2.71)

On the basis of these results, evaporation instead of back extraction into nitric was the method chosen for the preconcentration of trace metals in seawater in this work.

3.4 ADAPTED METHOD FOR TOTAL DISSOLVED TRACE METAL ANALYSIS IN SEAWATER

Chelation-solvent extraction was used to concentrate trace metals and remove the salt matrix interference from the samples. Ammonium pyrrolidine dithiocarbamate (APDC) and diethylammonium diethydithiocarbamate (DDDC) are used as chelating agents to form metal-carbamate complexes, due to their non-selective complexing properties over a relatively broad pH range. Chloroform was chosen as the organic solvent for its low solubility in water and high efficiencies in extracting metals.

3.4.1 GENERATION OF REAGENTS AND NECESSARY APPARATUS

The apparatus and reagent requirements in the procedure described below are sufficient for the extraction of 8 blanks, 6 standard additions, 2 open ocean seawater reference (NASS4) and 60 to 80 samples.

Apparatus:

500 ml FEP separatory funnel (5)
2000 ml FEP screw-capped bottles (2)
1000 ml FEP screw-capped bottles (3)
500 ml FEP screw-capped bottles (2)
100 ml FEP screw-capped bottles (3)
10 ml polyethylene measuring cylinders
2 ml screw capped polyethylene vials (1 per sample)
pH probe
micropipettes, 10-100µl (1), 100-1000 µl (2) and 500-5000 µl (1)
polyethylene tips for micropipettes
polypropylene stand to hold 4 x 500 ml separatory funnels
polypropylene rotating table (holds 4 separatory funnels) for extraction
15 ml PTFE vials for back extraction
corrosion protected hot-plate (1)
polypropylene holder for 2 ml snap shut polyethylene vials

Reagents:

APDC (Ammonium pyrrolidine dithiocarbamate)
DDDC (Diethylammonium diethyldithiocarbamate)
Cleaned chloroform
Sub-boiling distilled (SBD) water
SBD concentrated nitric acid
SBD nitric acid, 1 molar in SBD water (i.e. 63 ml nitric in 1000 ml SBD water)
Isothermally distilled ammonia solution
Low metal seawater (LMS), acidified to pH 2

Reagent preparation:

Complexant (4% w/v APDC and DDDC)

20 gms APDC and DDDC are dissolved in 500 mls of SBD water, within a 1000 ml FEP bottle. The complexant is then filtered through a Whatman no 1 filter to remove particles and transferred to a separate FEP bottle. Aliquots (125 ml) are transferred to four 500 ml separating funnels with approximately 30 ml of cleaned chloroform. The complexant and chloroform are mixed for 5 minutes on the rotating table, and once separated the chloroform is drawn off to a disposal bottle. This procedure is repeated four times, and after the last chloroform has been removed, the complexant is transferred to a 500 ml FEP bottle and stored in the fridge, within a re-sealable plastic bag until use. The life time of the complexant is 3 to 4 days.

Chloroform

Around 300 ml of chloroform is transferred to each of the four 500 ml separatory funnels. Approximately 30 ml of SBD water is added to each funnel and is rotated for 5 minutes. The chloroform is collected in a 500 ml FEP bottle leaving the aqueous phase to waste. The chloroform is returned to original funnel and a new aliquot of SBD water is added. Procedure is repeated 10 times. The clean chloroform is then transferred to a 2000 ml FEP bottle for storage.

SBD water

Highest purity water is prepared from Milli-Q water using a sub-boiling still and is stored in a 2000 ml FEP bottle.

SBD concentrated nitric acid

Sub boiling distillation using 16N AR grade nitric acid.

Isothermally distilled ammonia solution

Isothermal distillation of 0.880 S.G. AR grade ammonia solution. Equilibrate over several days with sub-boiling distilled water and store in an FEP bottle.

Metal Standards

A series of metal standards are required for standard additions to seawater to be extracted, and for calibration during analysis on the graphite furnace.

From spectroscopic grade 1000 ppm (1000 μg/l) the following 2 stages of dilution's were prepared:

(A) Dilute spectroscopic grade metal standards to make a mixed standard of 100 µg/ml for Mn, Ni, Zn, Cu and Fe with 10 µg/ml for Co, Cd and Pb in a 50 ml LDPE bottle with 1 molar SBD nitric acid;

(B) dilute standard a) by 100 to give metal concentrations of 1,000 µg/l (for Mn, Ni, Zn, Cu and Fe) and 100 µg/l (for Co, Cd and Pb) in a 100 ml LDPE bottle with 1 molar SBD nitric acid.

Mixed metal standard for standard additions

Standard (B) was diluted with 1 molar SBD nitric acid to give a mixed standard of 100 µg/l (for Mn, Ni, Zn, Cu and Fe) and 10 µg/l (for Co, Cd and Pb).

Mixed metal standard for graphite furnace calibration

Using standard (B) the following standards were prepared (in 1 molar SBD nitric acid):

(i) 100 µg/l (for Mn, Ni, Zn, Cu and Fe) and 10 µg/l (for Co, Cd and Pb).
(ii) 75 µg/l (for Mn, Ni, Zn, Cu and Fe) and 7.5 µg/l (for Co, Cd and Pb).
(iii) 50 µg/l (for Mn, Ni, Zn, Cu and Fe) and 5 µg/l (for Co, Cd and Pb).
(iv) 25 µg/l (for Mn, Ni, Zn, Cu and Fe) and 2.5 µg/l (for Co, Cd and Pb).
(v) 10 µg/l (for Mn, Ni, Zn, Cu and Fe) and 1 µg/l (for Co, Cd and Pb).

3.4.2 PROCEDURE

To a 500 ml separating funnel (supported on a balance) 200 gms of acidified sample is weighed. A predetermined volume of isothermally distilled ammonia solution is added to the sample using a 1000 µl pipette to adjust the pH to between 7 and 9. Then 5 ml of complexant (using a 1-5 ml pipette) and 5 ml of chloroform (using a 10 ml polyethylene measuring cylinder) are added. The separatory funnel is then rotated (~1 rps) for 5 minutes. After a few minutes when the phases have separated the chloroform is drawn off into a 15 ml PTFE vial and a fresh aliquot of 5 ml of chloroform is added to the funnel. This procedure is repeated twice more until 15 ml of chloroform have been added to the sample and collected in the PTFE vial for evaporation on a hotplate (set at 60 °C). 50 µl of concentrated SBD nitric acid is added to the chloroform (using a 10-100 µl pipette) to break down any organic component present.

Once the solvent and acid have evaporated, 50 µl of concentrated SBD nitric acid is added to the residue and is left once more to evaporate. The final residue is redissolved by adding 100 µl of concentrated SBD HNO_3, followed by 500 µl of SBD water. This acid is collected from the PTFE evaporation vial using a 100-1000 µl pipette and is transferred to a 2 ml polyethylene vial. Two more additions of 500 µl of SBD water to the evaporation vial ensure that no residue is left behind. The final volume in the 2 ml polyethylene vial is 1.6 ml (at a concentration of 1 molar HNO_3). The concentration factor of the extract is 125 times the original seawater sample.

Extraction blanks are obtained by using 100 ml of SBD water, with 200 µl HNO_3 and a predetermined volume of ammonia, followed by the addition of complexant and chloroform as described above. To ascertain the efficiency of the method, standard additions to low metal seawater (LMS) are carried out. LMS is first extracted as before, and then to 200 gms of LMS, a mixed standard of 100 µg/l (for Mn, Ni, Zn, Cu and Fe) and 10 µg/l (for Co, Cd and Pb)(as described in 3.1.4.1) is added to achieve the following concentrations: 25, 50, 100 and 250 ng/l. Isothermally distilled ammonia solution, complexant and chloroform are added and the procedure is carried out as described above. To ascertain the accuracy of the method a certified reference material (NASS-4) was extracted by this method. Sample replicates were extracted to calculate precision, with standard deviations for each metal given in Table 3.4. Between samples the separatory funnels are rinsed to prevent any carryover of metals from one extraction to the next. This is essentially a blank, with the chloroform and complexant discarded after a single 5 minute rotation.

3.4.3 MEASUREMENT BY ATOMIC ABSORPTION SPECTROMETRY

A Perkin-Elmer 1100B Atomic Absorption Spectrometer fitted with a HGA graphite furnace and a AS-70 autosampler is used. The extracts are analysed for Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn. The instrument runs with a background correction and two replicate measurements of the absorption peak area. The conditions and parameters for the setting up of the instrument are based on the manufacturers recommendations (see Table 3.3). Mixed metal standards for instrument calibration were analysed along with a 1 molar HNO_3 blank. An extract volume of 100 µl (using a 20-200 µl pipette) was transferred to polyethylene cups for measurement, with all cups and pipette tips cleaned and rinsed as described by Tappin (1988).

Table 3.3 Standard conditions for GFAAS

Element	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Wavelength (nM)	228.7	240.7	324.7	248.3	279.4	232.0	216.9	213.8
Slit (nm)	0.7	0.2	0.7	0.2	0.2	0.7	0.7	0.7
Lamp current (mA)	5	13	5	12	7	10	8	10
Injection temperature (T°C)	100	20	100	60	100	80	80	100
Injection volume (µl)	10	50	10	15	10	10	30	10
Dry 1 (T°C)	150	130	150	120	120	130	130	120
Ramp (s)	5	15	5	10	10	5	10	10
Hold (s)	10	30	10	10	10	1	1	20
Dry 2 (T°C)		150	250	180	600	600	150	
Ramp (s)		20	5	5	10	15	10	
Hold (s)		15	10	5	10	5	1	
Dry 3 (T°C)		180					170	
Ramp (s)		10					10	
Hold (s)		15					1	
Ash (T°C)	500	1400	1250	1250	1100	1000	700	700
Ramp (s)	10	15	5	10	5	10	10	10
Hold (s)	20	15	10	5	1	10	10	10
Atomisation (T°C)	1600	2500	2300	2400	2200	2300	1900	1800
Ramp (s)	0	0	0	0	0	0	0	0
Hold (s)	4	3	5	3	3	3	2	3
Burn (T°C)	2300	2650	2800	2700	2800	2550	2400	2200
Ramp (s)	1	2	1	1	1	1	1	1
Hold (s)	4	5	3	5	3	3	3	3
Standard 1 (µg/l)	10.0	10.0	100	100	100	100	10.0	100
Standard 2	7.5	7.5	75	75	75	75	7.5	75
Standard 3	5.0	5.0	50	50	50	50	5.0	50
Standard 4	2.5	2.5	25	25	25	25	2.5	25
Standard 5	1.0	1.0	10	10	10	10	1.0	10

3.4.4 CALCULATION OF SAMPLE CONCENTRATION AND METHOD PERFORMANCE

The concentration of metals in nM are calculated from the extract concentration (µg/l) using the following equation:

$$\text{Metal concentration in sample (nM)} = \frac{1000 \times V \times (E-B)}{W \times M} \times 1.025$$

E = Extract concentration(µg/l)
B = Blank (µg/l)
V = Extraction volume (1.6 ml)
W = Weight of original sample (≈ 200 gms)
M = atomic weight of the measured element
1.025 = the SG of seawater

Table 3.4 gives values for typical blanks, detection limits, recovery efficiencies and NASS-4 values for the metals analysed. The detection limit is calculated as three times the standard deviation of the mean blank given in nM. Open Ocean seawater reference (NASS-4) was analysed with each batch of sample, and results (Table 3.4) indicate accuracies within 10 % of the certified values, with the exception of Pb at ~50% error, also observed by Tankere (1996).

Table 3.4 Typical blanks, detection limits, standard deviations (SD) and spike recoveries.

Element	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn.
Blank (nM)	0.001	0.003	0.097	0.21	0.02	0.04	0.01	0.09
Detection limit (nM)	0.001	0.009	0.126	0.014	0.011	0.028	0.001	0.021
Replicate seawater samples (nM) (n=4)	0.055	0.085	2.049	1.546	0.850	5.39	0.110	5.796
Mean SD of replicates (nM)	0.002	0.003	0.066	0.064	0.030	0.433	0.013	0.256
NASS (Certified value)	0.14 (0.142)	0.11 (0.153)	3.43 (3.58)	1.95 (1.88)	6.49 (6.92)	3.66 (3.88)	0.03 (0.063)	1.67 (1.76)
Spike Recovery (%)	110.0	91.0	97.6	107.0	99.5	94.3	106.0	105.0

3.5 AUXILIARY DATA

3.5.1 SALINITY

Samples for salinity measurement were collected in 300 ml glass bottles, sealed tightly with an insert inside the cap of the bottle, to prevent any evaporation during transit. The bottle was rinsed three times with sample before collection. Salinity samples were analysed using an Autosal 8400A salinometer, calibrated with Ocean Scientific International IAPSO standard seawater.

3.5.2. NUTRIENTS

Nutrient samples were collected in 60 ml clean low density polyethylene bottles, which had been rinsed thoroughly with the sample before being filled; 200 µl of 3% w/v mercuric chloride was then added to prevent changes in the nutrient concentrations during transport and storage.

Samples were analysed onshore using a Chemlab AAII type Auto-Analyser, coupled to a Digital-Analysis Microstream data capture and reduction system. Precision and detection limits are given in Table 3.5. For the analysis of silicon the standard AAII molybdate-ascorbic acid method with the addition of a 37°C heating bath was used (Hydes, 1984). In order to sensitise the system so that a linear response was obtained from the colorimeter over a range of 0 to 10µM of silicon, the colorimeter was fitted with a 50 mm flow cell and a 660 nm optical filter was used. The standard AAII method using sulphanilamide and naphthylenediamine-dihydrochloride was used for nitrate analysis (Grasshoff, 1976) with a Cadmium-Copper alloy reduction column (Hydes & Hill, 1985). A 15 mm flow cell and 540 nm filter were used. For phosphate analysis the standard AAII method was used (Hydes, 1984), with a 50 mm flow cell and 880 nm filter.

Table 3.5 Nutrient detection limits and precision.

	Nitrate plus nitrite	Silicon	phosphate
Detection limits (µM)	0.1	0.1	0.01
Precision	±5%	±5%	±7%

CHAPTER 4

HYDROGRAPHIC AND CHEMICAL SETTING: RESULTS

4.1 INTRODUCTION

In order to aid interpretation of the trace metal data, it is important to understand the hydrographic and chemical settings during the period of sampling. Trace metal concentrations in seawater are determined predominately by their sources and biogeochemical cycling. Primary production and nutrient concentrations will have a strong influence on those metals associated with biological cycling (i.e. Cd, Ni, Zn and Cu). In addition, riverine and Black Sea Water (BSW) are potential metal sources and such masses have been noted for their associated trace metal signatures. Hence the circulation and water masses in the Aegean may in part control the distribution of metals.

4.2 THE NORTH AEGEAN

The north Aegean is influenced by riverine sources and the outflow of BSW, as well as water masses from the Levantine Basin and the Mediterranean Sea. It is also an area of deep water production and of low biological activity (i.e. oligotrophic).

4.2.1 SALINITY, TEMPERTURE AND DENSITY: WATER MASSES AND CIRCULATION

The north Aegean is composed of three major waters masses in March and four water masses in September 1997 of differing characteristics. Black Sea Water (BSW) enters the north Aegean from the Black Sea via the Straits of Dardanelles and occupies a low salinity layer at the surface between 20-100 m (Figures 4.1, 4.2 and 4.3); its distribution can be identified by the depth of the 38.70 isohaline as its lower limit (Yüce, 1994). In late summer salinities are lower and temperatures higher in the upper 3 m, compared to the late winter 1997 (Table 4.1). This corresponds with the increased warmer freshwater output from the Straits of Dardanelles in summer (Ünlüata *et. al.*, 1990). However there is some variability in the temperature of surface waters in September 1997. A sub-surface increase in temperature (at 25 m) is observed at MNB1 and MNB5. Whereas at MNB3 surface temperature decreases in the upper 25 m, followed by a subsurface increase at 52 m.

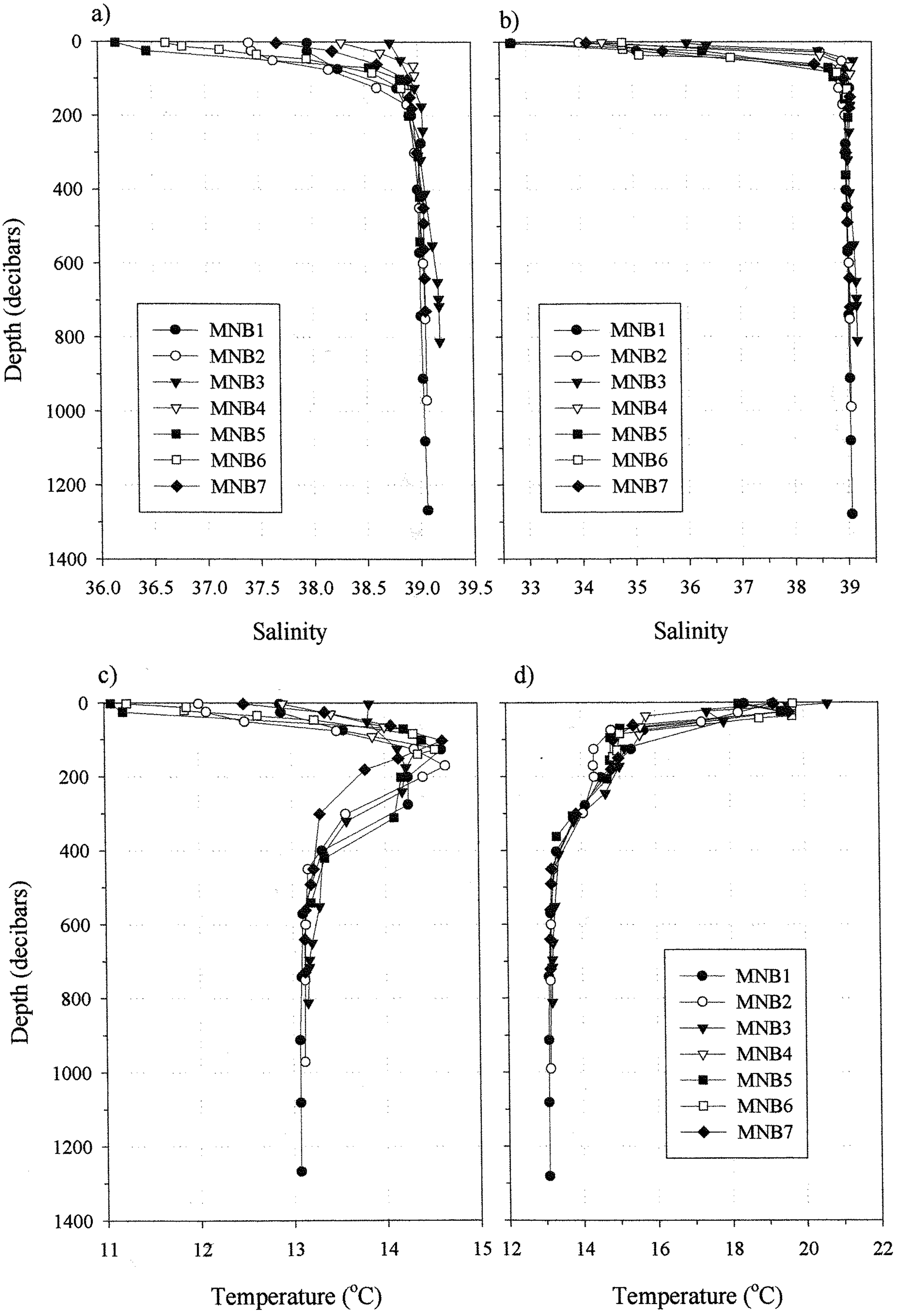

Figure 4.1. Salinity and temperature depth profiles for the north Aegean in a), c) March and b), d) September 1997. Note: The x-scales are different between the two seasonal plots.

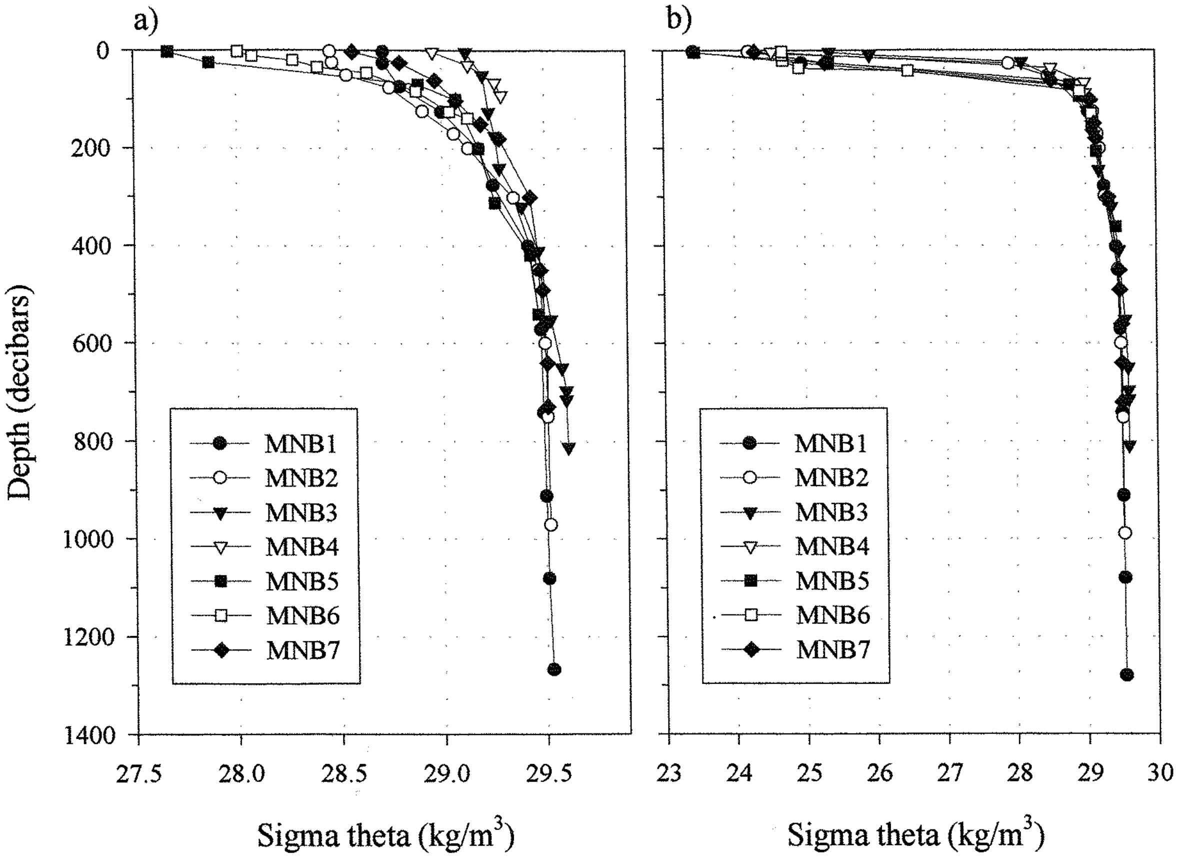

Figure 4.2. Density depth profiles for the north Aegean in a) March and b) September 1997. Note: The x-axis are different between the two seasonal plots.

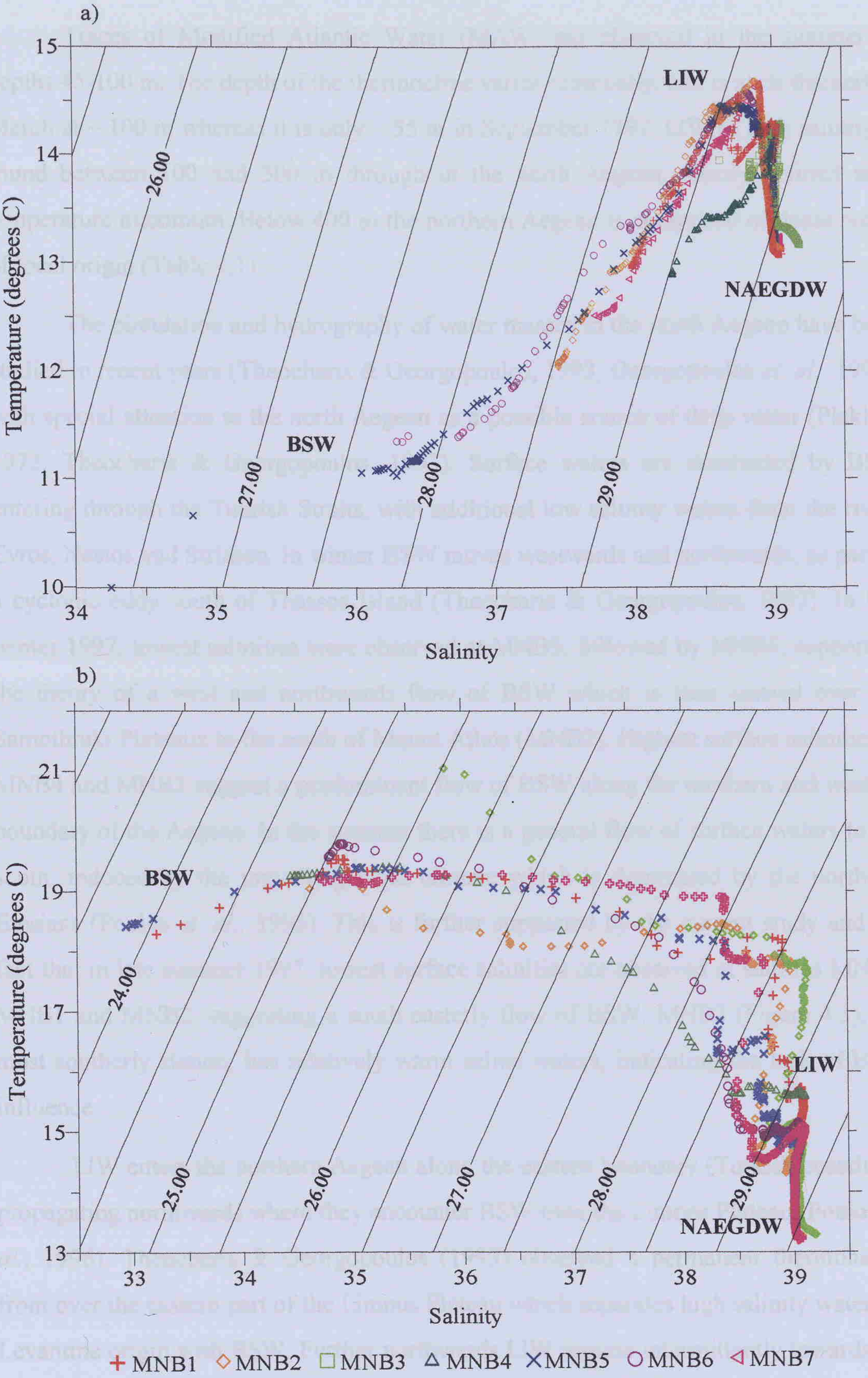

Figure 4.3. Salinity versus temperature plots for a) March and b) September 1997 in the north Aegean Sea. Note: Axis are not to the same scale.

Traces of Modified Atlantic Water (MAW) are observed in the summer at depths 45-100 m. The depth of the thermocline varies seasonally, and is at its thickest in March at ~ 100 m whereas it is only ~ 55 m in September 1997. LIW of high salinity is found between 100 and 300 m throughout the north Aegean, clearly defined as a temperature maximum. Below 400 m the northern Aegean is comprised of dense water of local origin (Table 4.1).

The circulation and hydrography of water masses in the north Aegean have been studied in recent years (Theocharis & Georgopoulos, 1993; Georgopoulos *et. al.*, 1998), with special attention to the north Aegean as a possible source of deep water (Plakhin, 1972; Theocharis & Georgopoulos, 1993). Surface waters are dominated by BSW entering through the Turkish Straits, with additional low salinity waters from the rivers Evros, Nestos and Strimon. In winter BSW moves westwards and northwards, as part of a cyclonic eddy south of Thassos Island (Theocharis & Georgopoulos, 1993). In late winter 1997, lowest salinities were observed at MNB5, followed by MNB6, supporting the theory of a west and northwards flow of BSW which is then carried over the Samothraki Plateaux to the south of Mount Athos (MNB2). Highest surface salinities at MNB4 and MNB3 suggest a predominant flow of BSW along the northern and western boundary of the Aegean. In the summer there is a general flow of surface waters to the south, induced by the prevailing wind climate which is dominated by the northerly Etesians (Poulos *et. al.*, 1996). This is further supported by the current study and the fact that in late summer 1997, lowest surface salinities are observed at stations MNB5, MNB1 and MNB2, suggesting a south-easterly flow of BSW. MNB3 (Figure 4.3), the most southerly station, has relatively warm saline waters, indicating the lack of BSW influence.

LIW enters the northern Aegean along the eastern boundary (Turkish coastline), propagating northwards where they encounter BSW over the Limnos Plateau (Poulos *et. al.*, 1996). Theocharis & Georgopoulos (1993) observed a permanent thermohaline front over the eastern part of the Limnos Plateau which separates high salinity waters of Levantine origin with BSW. Further northwards LIW intrude intermittently towards the Samothraki Plateau in the form of projecting tongues as seen at MSB1 with two intrusions of LIW. Examination of the bathymetry in the region reveals that there is free communication between various basins and troughs of the northern Aegean above 300 m depth (Georgopoulos, *et. al.*, 1998), whilst water movement below that level is hindered by shallow sills, which limit advection and mixing. In addition, the θ/S characteristics in the deep waters of the north Aegean (Figure 4.3) show that there are small but significant differences between sub-basins. This fact signifies that the communication between the deep waters of neighbouring basins, if any, is hindered. The densest waters are observed at MNB3, south-east of the Limnos Plateau in the Skyros basin, as also observed by Theocharis & Georgopoulos (1993). Georgopoulos *et. al.* (1998) suggest the Chios Basin as a possible site for deep water formation.

4.2.2 NUTRIENTS

Nutrient concentrations (Figure 4.4) exhibit significant variations with both season and depth. Profiles are generally characterised by surface depletion in waters above the euphotic zone and regeneration at depth, almost throughout the year, typical of oligotrophic regions. Similar concentrations have been observed in the eastern Mediterranean by Yimaz & Tugrul (1998) and in the Aegean (Kucuksezgin *et. al.*, 1995; Souvermezoglou, 1996). Although phosphate data was limited due to analytical problems and concentrations below the detection limit; however N/P values were calculated for September and March 1997.

Depth profiles of nitrate plus nitrite (Figure 4.4) for both March and September 1997 exhibit low surface concentrations (< 1 μM). In March, there is higher variability than in September, especially at MNB5, where concentrations decrease from 0.8 μM (at the sub-surface) to 0.1 μM (at 3 m), corresponding to the lowest salinities observed. On the other hand, September surface concentrations are more consistent (0.4 - 0.6 μM). In March the nutricline is not clearly defined due to surface variability and the intrusion of low nutrient LIW below. In September the nutricline is found between 36 and 90 m, and shallowest at MNB4, where we also encounter shallow bathymetry (90 m) and deepest at MNB5.

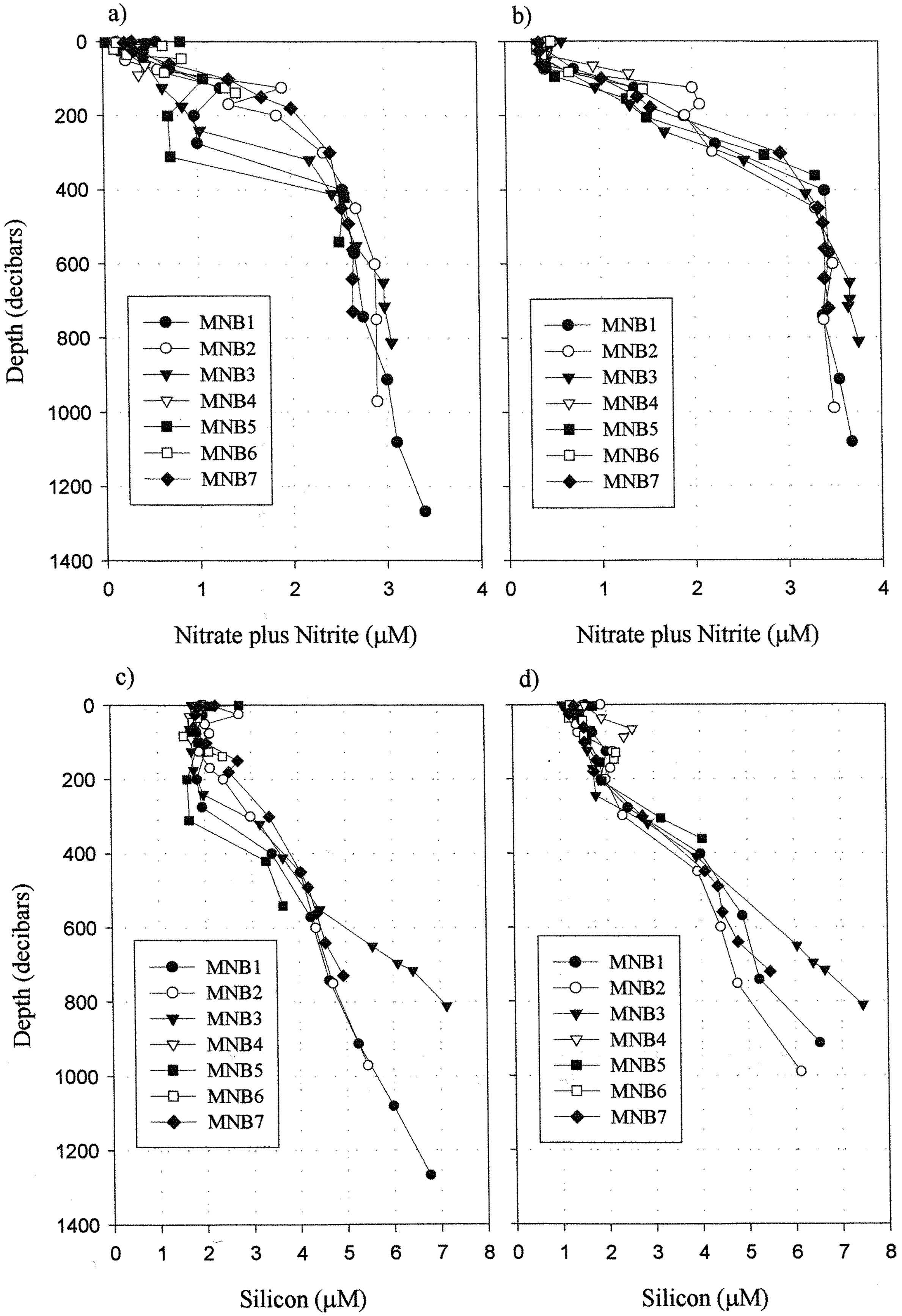

Figure 4.4. Nitrate plus nitrite and silicon depth profiles for the north Aegean in a), b) March and b), d) in September 1997. Note: Symbol size represents +/- 1 SD estimate for each measurement.

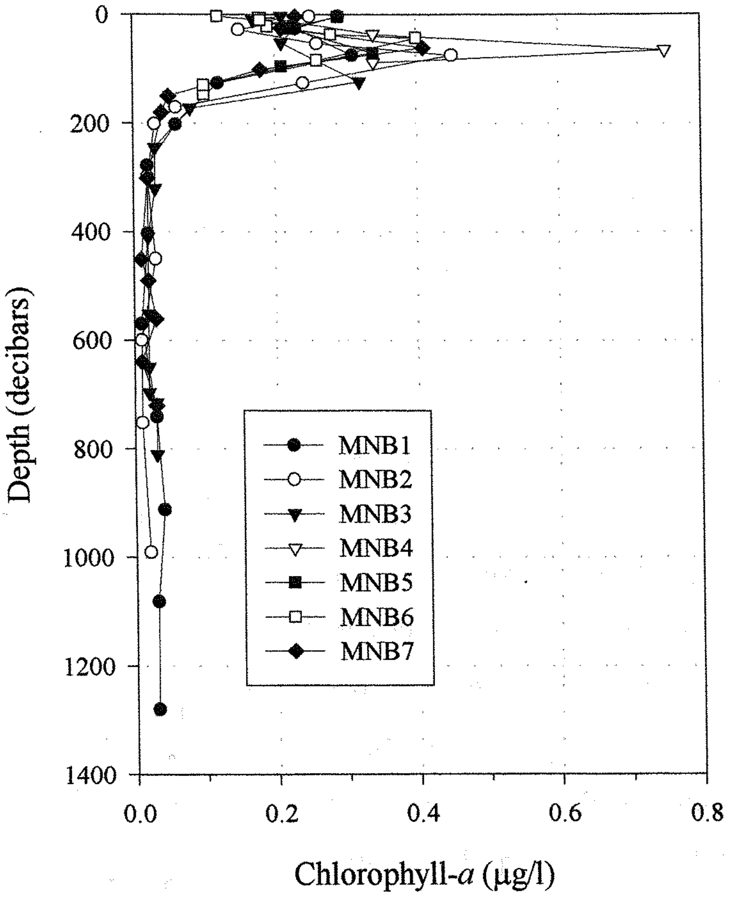

Figure 4.5 Chlorophyll-*a* depth profiles for the north Aegean Sea in September 1997 only.

Below the nutricline, regeneration from sinking particles results in an increase of nitrate plus nitrate to maximum concentrations in deep waters, with the exception of a band of lower nutrient water observed in March 1997 at MNB5 (0.7 μM) and MNB1 (1 μM) between 200 and 311 m. This band corresponds to an intrusion of LIW waters, carried north along the eastern boundary of the Aegean Sea from the Levantine Sea. In September 1997 the slightly higher nitrate plus nitrite concentrations between 125 and 200 m (Figure 4.4) correspond to MAW. Deep water concentrations are slightly higher in September (3.5 - 3.8 μM) than in March (2.5 - 3.4 μM) with similar concentrations (relative to depth) with the exception of MNB3. This station is situated on the eastern edge of the Limnos plateau, in the Chios Basin, exhibits denser and more saline deep waters than the others stations, and is indicated as a formation site for NAEGDW.

N/P values of 21.4 in March and 25.8 in September suggest that the productivity is phosphate limited, more so in late summer due to phytoplankton blooms. Kucuksezgin *et. al.* (1995) observed similar N/P values in the northern Aegean.

Silicon exhibits depth profiles similar to that of nitrate (Figure 4.4). Surface concentrations are slightly lower in September (1.1 - 1.9 μM) than in March 1997 (1.9 - 2.8 μM). In March 1997, lower silicon concentrations at MNB5, MNB1 and MNB3 are associated to the presence of LIW at 200 - 311 m. Regeneration occurs with depth and the highest concentrations are found in deep waters. MNB4 is an exception, with a distinct sub-surface maximum of 2.6 μM at 66 m, where high chlorophyll-*a* can also be observed. MNB3 deep waters exhibit the highest concentrations (as for nitrate plus nitrite) for both seasons, corresponding to a deep water mass of differing characteristics than the other more northern stations (7.1 and 7.5 μM for March and September 1997, respectively).

4.2.3 CHLOROPHYLL A

Chlorophyll-*a* data was collected for September 1997 only, however chlorophyll-*a* samples were analyzed by Ignatiades, *et. al.* (1998) during the same period, therefore enabling some overall conclusions to be made.

In September 1997, chlorophyll-*a* (Figure 4.5) exhibits typically low concentrations as a result of nutrient limitation thus demonstrating the oligotrophic nature of the Aegean Sea. Surface waters range between 0.12 and 0.29 μg/l, with a well developed deep chlorophyll maximum at 40-75 m (0.30 - 0.75 μg/l) near the base of the euphotic zone, at all stations. Maximum concentrations at MNB4 (at 66 m), also correspond to elevated nitrate plus nitrite and silicon concentrations at the same depth. MNB4 is the shallowest station in the north Aegean (90 m), where nutrient rich deep waters follow the bathymetry and are carried up into the euphotic zone. Between 200 m and bottom waters, concentrations are uniformly low (0.01 - 0.03 μg/l). Ignatiades, *et al.* (1998) observed higher concentrations of chlorophyll-*a* and primary production in March than in September 1997.

4.3 THERMAIKOS GULF

The Thermaikos Gulf, in the north-west region of the Aegean, receives riverine water from the Axios, Aliakmon, Gallikos and Pinios rivers and contributes the largest discharge into the north Aegean. Within the drainage area, there are densely populated and industrialised regions, including the city of Thessaloniki, second largest in Greece after Athens. Samples were collected during both seasons, to ascertain the influence of the Gulf on nutrient and trace metal concentrations in the north Aegean. In March 5 pole samples were collected and, therefore, bottle salinity and nutrient data is available only, whereas in September two CTD casts (M2M2 and M2M3) were collected along with 3 pole samples. Station T1 (September 1997) is also discussed although it is situated outside the Gulf (Figure 4.2), on the shelf edge and close to the river Strimon.

4.3.1. SALINITY, TEMPERATURE AND DENSITY: WATER MASSES AND CIRCULATION

Hydrographic data (Figure 4.6) show a significant difference in surface salinity between seasons, with lower salinities in September (S = 35.9 - 36.1) than in March 1997 (S = 38.1 - 38.6), as also observed in BSW at northern stations. However, temperature profiles (Figure 4.6) for September suggest different water mass characteristics, with higher surface temperatures than observed for BSW. Below 30 m traces of MAW are observed and LIW is found between 100 - 300 m. Deep waters (below 300 m) are similar in characteristic to central northern Aegean deep waters (MNB).

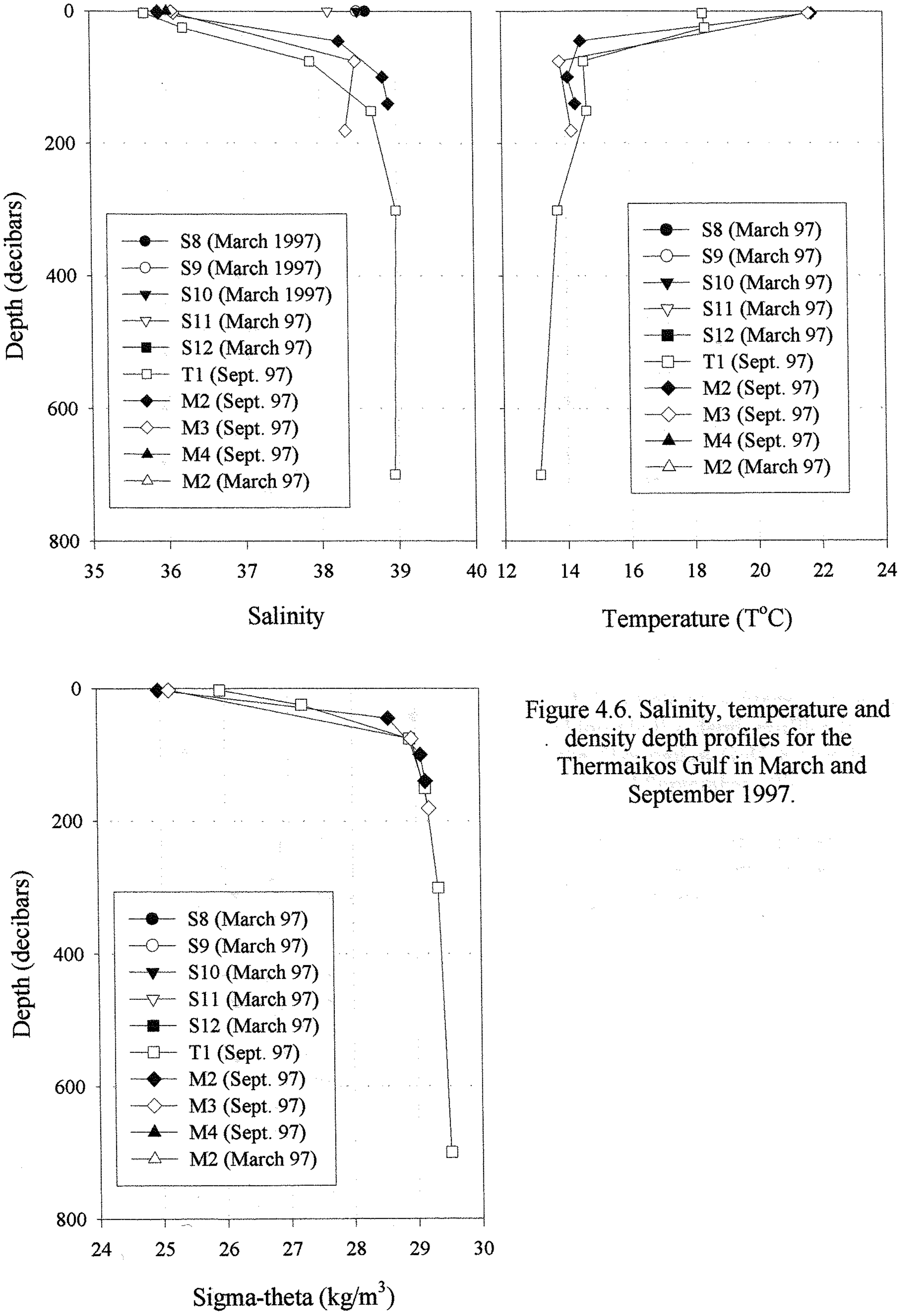

Figure 4.6. Salinity, temperature and density depth profiles for the Thermaikos Gulf in March and September 1997.

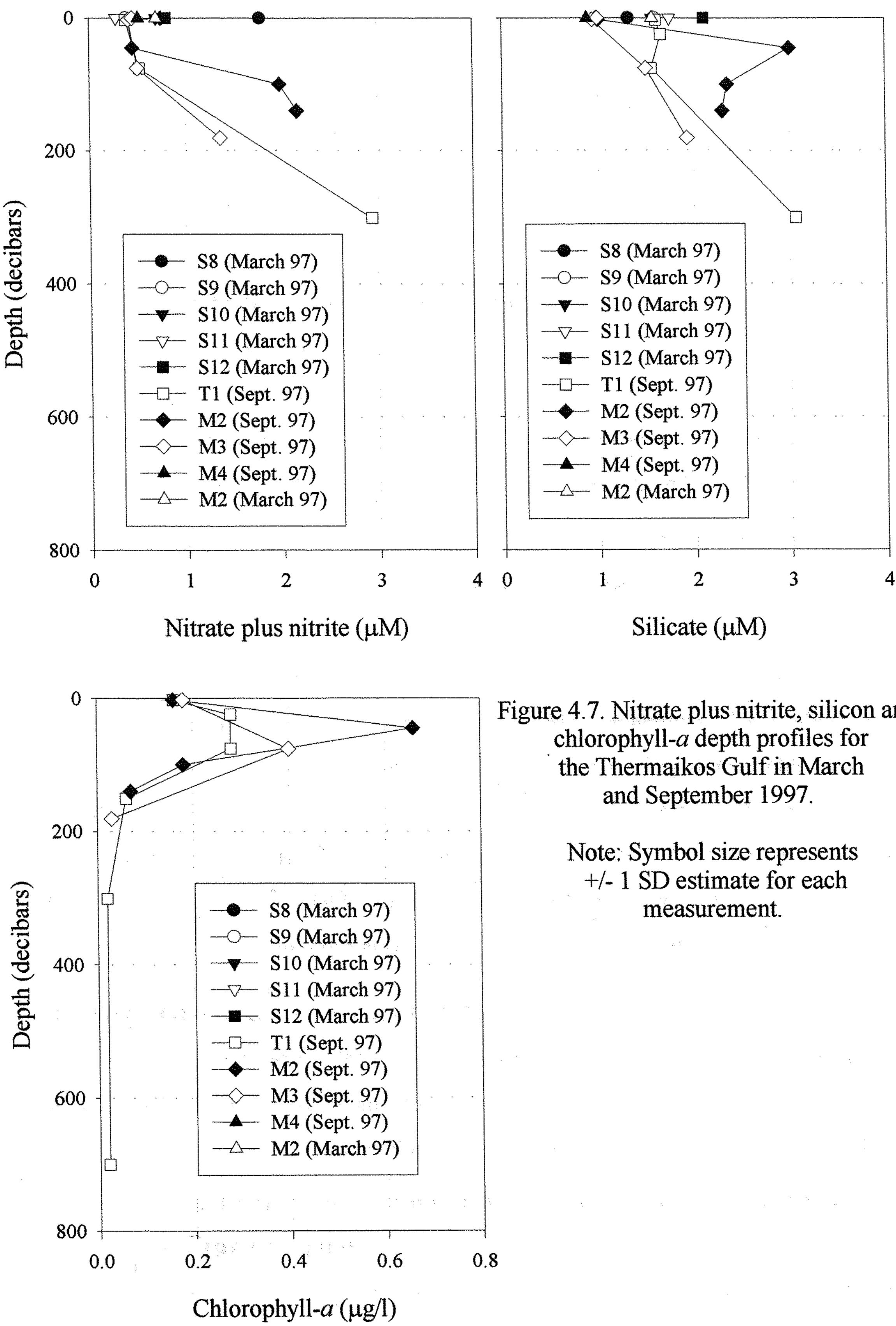

Figure 4.7. Nitrate plus nitrite, silicon and chlorophyll-*a* depth profiles for the Thermaikos Gulf in March and September 1997.

Note: Symbol size represents +/- 1 SD estimate for each measurement.

In March high surface salinities indicate the lack of either riverine and/or BSW influences, with values similar to station MNB3 which is the furthest from the Straits of Dardanelles.

Station T1 exhibits salinities similar to MNB and Thermaikos surface waters, with slightly lower temperatures as seen at MNB2. LIW is observed between 100 and 300 m and deep waters as in MNB stations.

4.3.2 NUTRIENTS AND CHLOROPHYLL A

Depth profiles of nitrate plus nitrite (Figure 4.7) show low surface concentrations (0.3 - 0.8 μM) similar to MNB stations. Below the nutricline (45 - 100 m) concentrations increase with depth, with higher concentrations (relative to depth) at M2M2. Overall deep water concentrations are lower those found at MNB stations.

Silicon depth profiles (Figure 4.7) exhibit low surface concentrations, with higher values in March (1.3 - 2.1μM) than in September (0.9 - 1.0 μM). September surface waters in Thermaikos are lower than the central MNB stations. Station T1 exhibits higher surface Si values, similar to MNB stations. The silicon concentrations increase with depth, with the exception of M2M2 (September 1997) where a sub-surface maximum (3.1 μM) is observed at 45 m, corresponding to high chlorophyll-*a* at this depth (0.66μg/l), as also observed at MNB4. As with nitrate plus nitrite, silicon deep water concentrations are lower than observed at central MNB stations (Figure 4.4). Chlorophyll-*a* data is available for September 1997 only (Figure 4.7) with profiles and concentrations similar to those encountered at central MNB stations.

4.4 THE SOUTH AEGEAN/CRETAN SEA

During September 1997, in the southern Aegean (also termed Cretan Sea), additional CTD casts were obtained in-between the main stations, down to 250 m depth (at 1 m intervals) and are presented in an east west transect contour plot (Figure 4.11).

4.4.1. SALINITY, TEMPERATURE AND DENSITY: WATER MASSES AND CIRCULATION

The Cretan Sea is regarded as an area of complex hydrography and circulation, variable in space and time, exchanging water with the northern Aegean, Ionian and Levantine Seas. Theocharis *et. al.* (1999) as part of the EU MTP II ‘PELAGOS’ programme extensively surveyed the south Aegean between March 1994 and January 1995; their results are used in this report to substantiate the present limited study. Unlike the north Aegean, there are many water masses present in the south Aegean as seen in depth profiles of salinity, temperature and density (Figures 4.8, and 4.9) and θ/S plots (Figure 4.10).

Deep waters (below 680 m) are composed of two types of water masses, in both March and September 1997. At central and eastern stations MSB1, MSB2, MSB6 and MSB7, cold and dense waters characteristic of Cretan Deep Water (CDW) are observed (Table 2). At western stations MSB3 and MSB4 deep waters are less saline and dense, and may originate from the Mirtoan Basin (Theocharis, 1999). Above CDW in March 1997 only, a variable water mass can be distinguished between 420 and 777m. This water mass is observed at all south Aegean stations, with higher salinities and temperatures in western MSB3 and MSB4 than in the central MSB1, MSB2 and MSB6. This water mass is identified as the Eastern Mediterranean Deep Water (EMDW) (Theocharis, *et al.*, 1999).

Above CDW and EMDW lies Transitional Mediterranean Water (TMW), a low salinity water mass seen throughout the south Aegean (Theocharis, *et al.*, 1999). In March 1997 it is observed between 225 and 350 m, at its thickest, 100 m, and with lowest salinities at MSB3 and MSB2 (S = 38.93). TMW increases in salinity to the east to MSB7 (S = 38.97). In September 1997 TMW is observed at slightly deeper depth of 321 to 550 m.

Intermediate waters exhibit spatial and seasonal variability, composed of a mixture of Levantine Intermediate Water (LIW) and Modified Atlantic Water (MAW). In March 1997, intermediate waters from 220 m up to 15 m consist of one (as seen at MSB6) or several low and high salinity peaks composed of LIW and MAW. Less saline MAW is observed in patches at all stations, except MSB6, with lowest salinities in the east (MSB3) at 184 m (S = 38.97). MAW increases in salinity eastwards to 39.99. Overall in September 1997, surface and intermediate waters are warmer than in late winter.

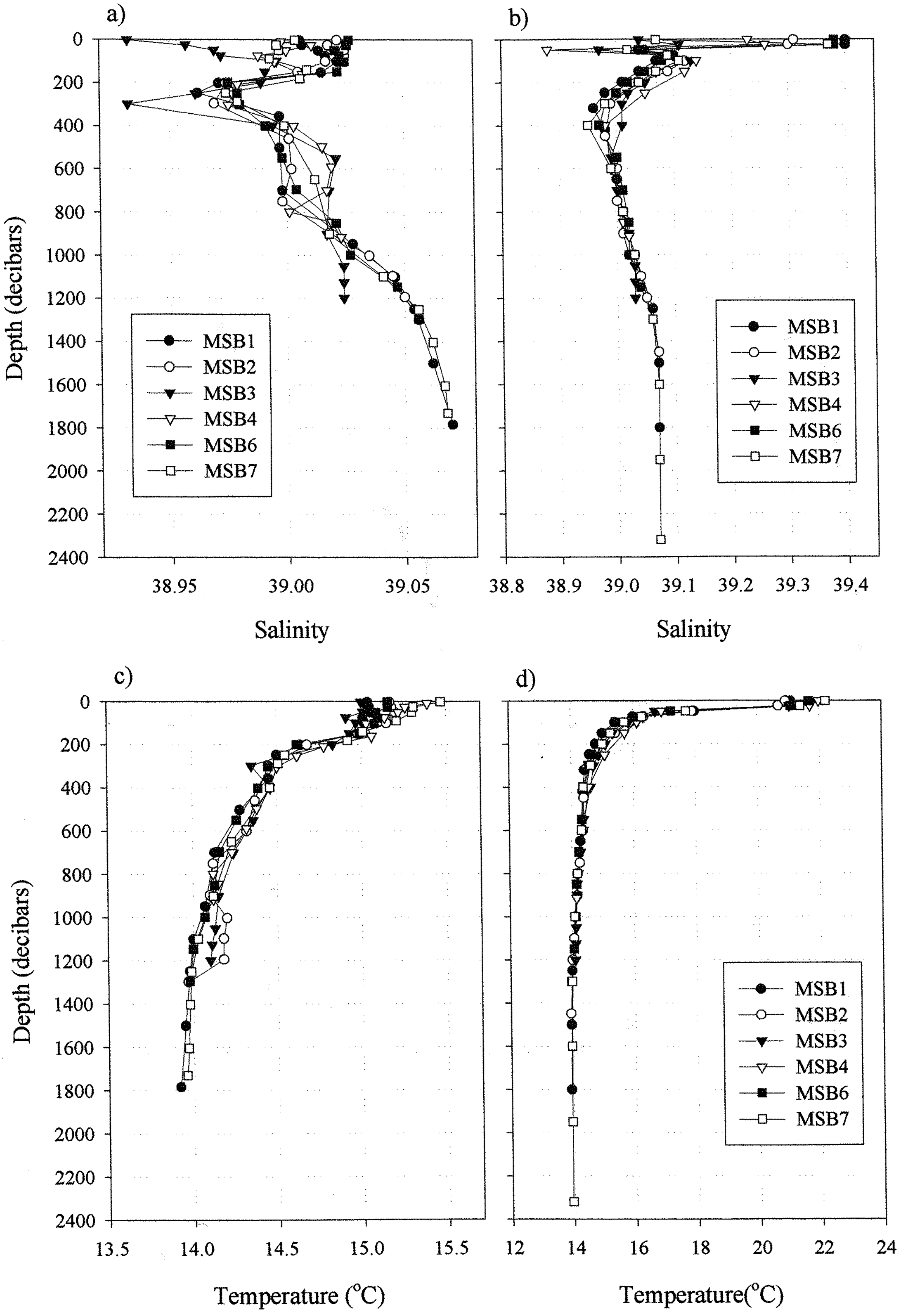

Figure 4.8. Salinity and temperature depth profiles for the south Aegean in a), c) March and b), d) September 1997. Note: The x-axis are different between the two seasonal plots.

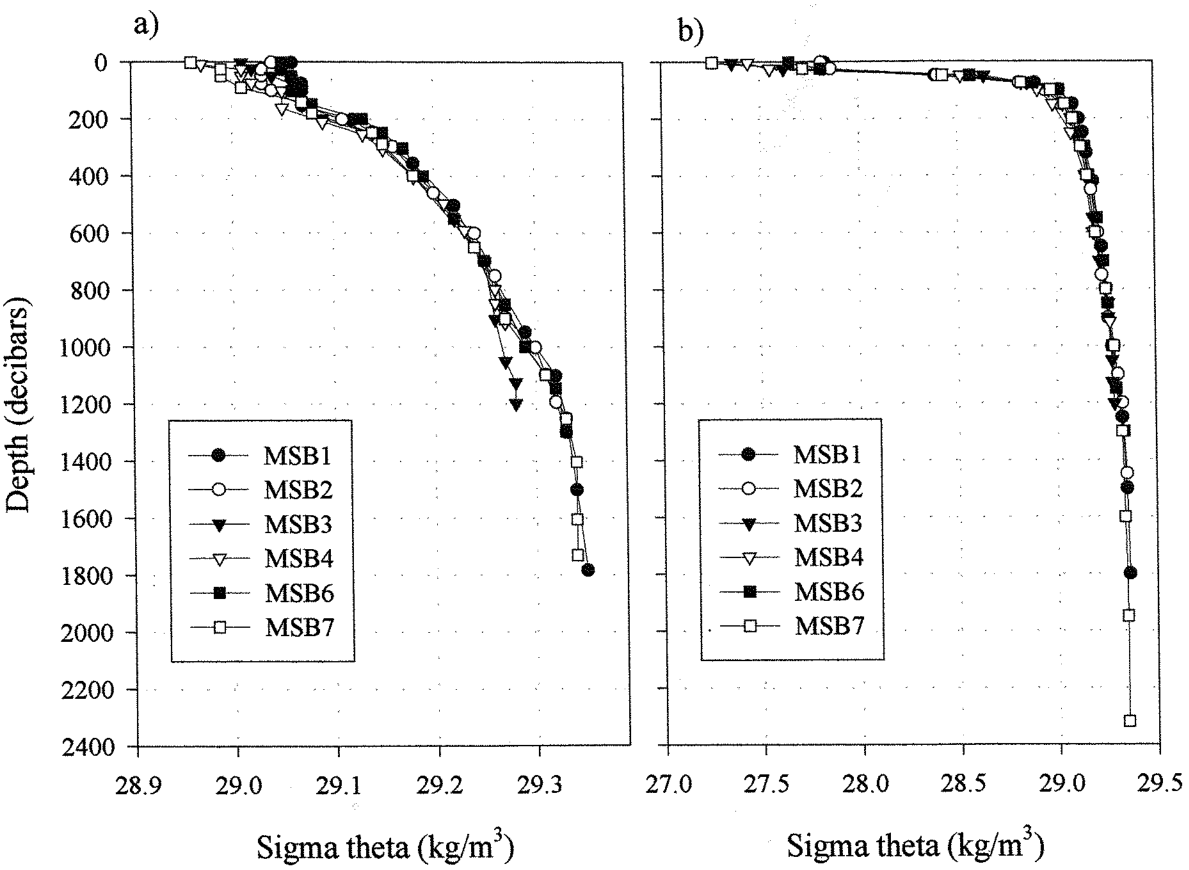

Figure 4.9. Density depth profiles for the south Aegean in a) March and b) September 1997. Note: The x-axis are different between the two seasonal plots.

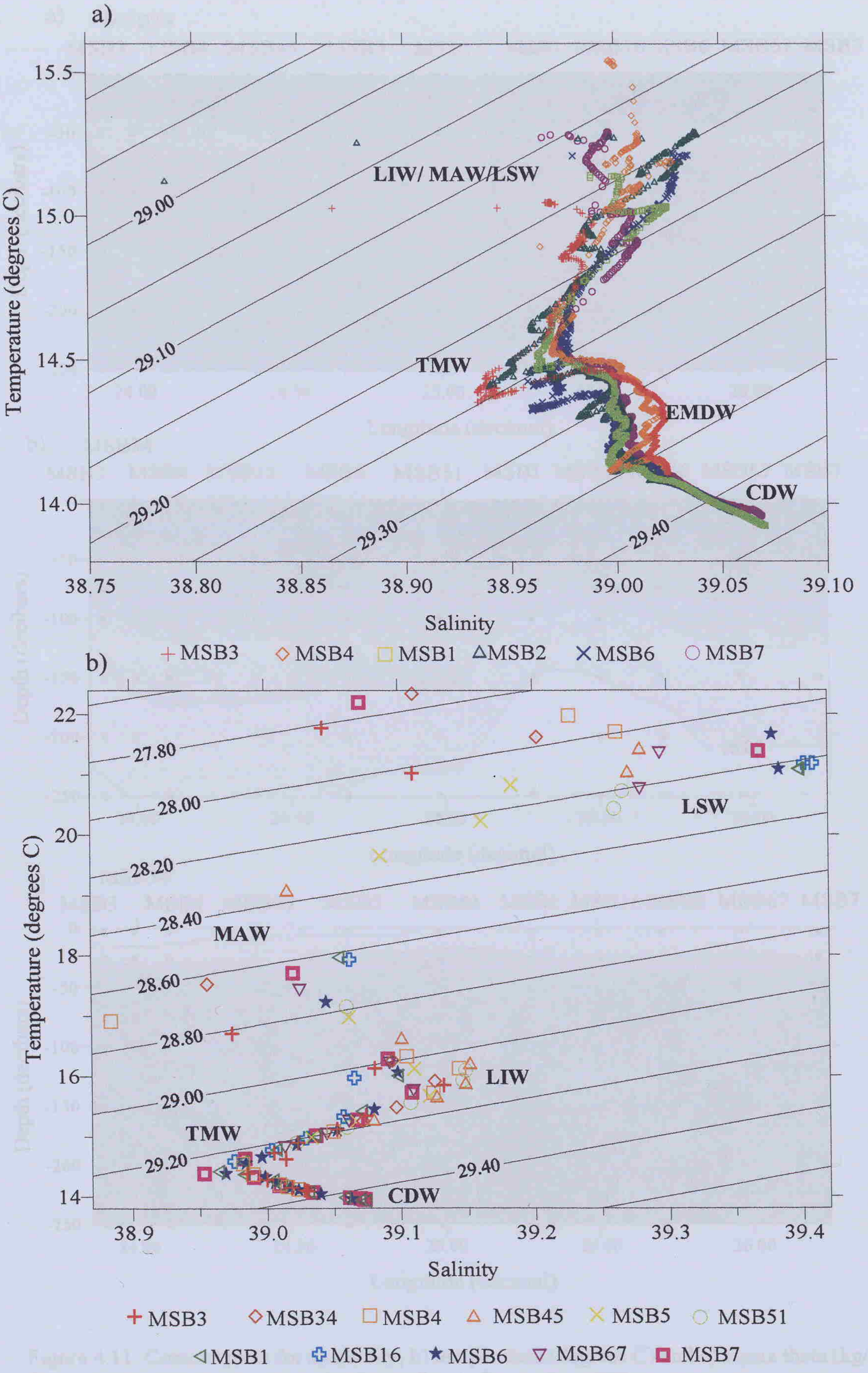

Figure 4.10. Salinity versus temperature plots for a) March and b) September 1997 in the south Aegean Sea. Note: Axis are not to the same scale.

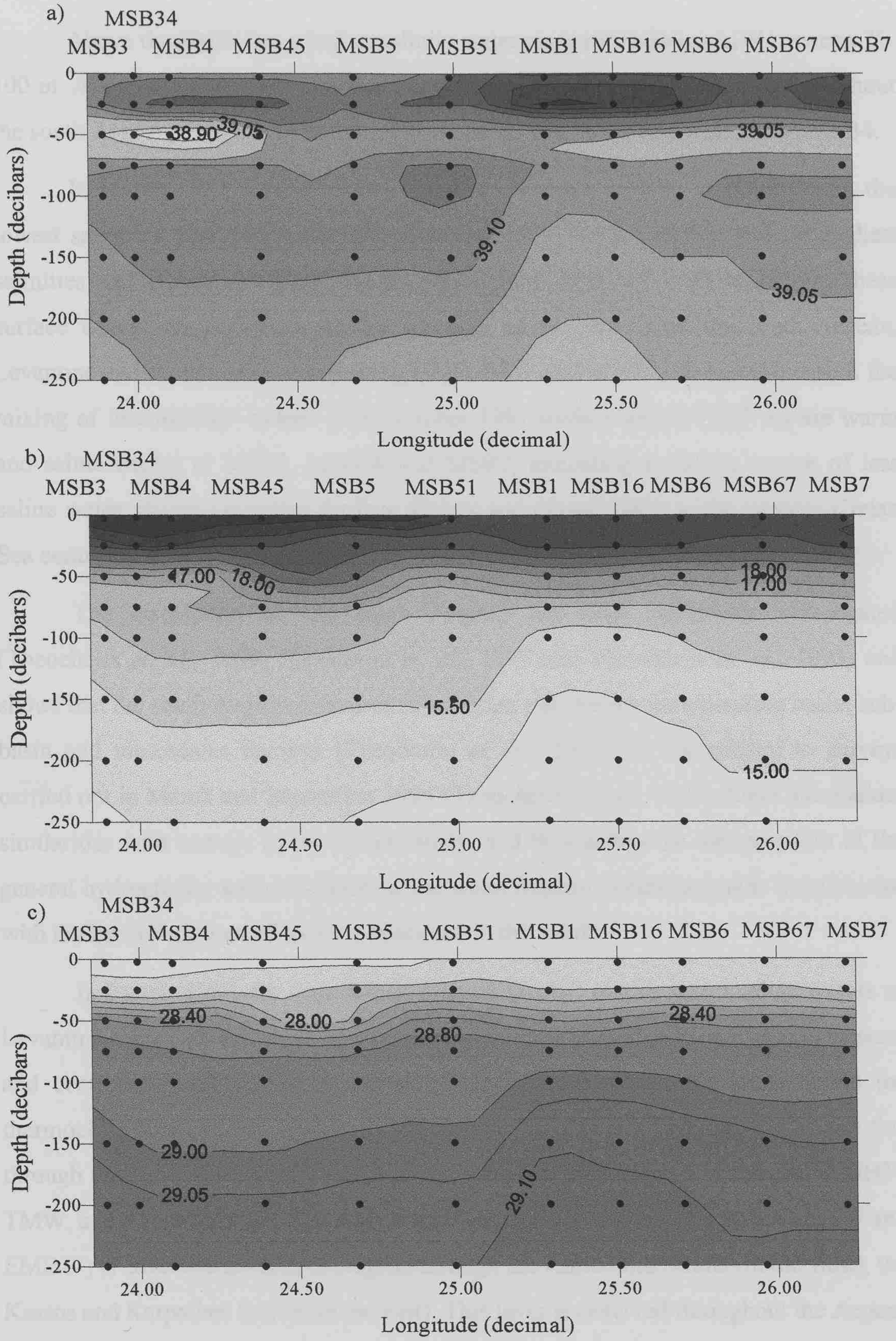

Figure 4.11. Contour plots for a) salinity, b) temperature (degrees C) and c) sigma theta (kg/m3) for an east-west transect across the Cretan Sea in September 1997.

Above the TMW lies a higher salinity water mass identified as LIW between 75-100 m. Above LIW, at 50-75 m lower salinity MAW forms a distinct layer throughout the south Aegean, with lowest salinities at western stations MSB3, MSB34 and MSB4.

In March 1997, surface waters (1-10 m) decrease slightly in salinity with the lowest salinities observed at MSB2 and MSB3 ($S = 38.78 - 38.87$), and the highest salinities were found at MSB7, MSB6, MSB1 and MSB4 ($S = 38.96$-38.99). These surface waters are dependent on the complex circulation within the south Aegean, Levantine and Ionian Sea's transporting LSW, BSW and MAW and combined with the mixing of intermediate waters. In September 1997 surface waters (3-25 m) are warm and saline except at MSB3, MSB34 and MSB7, indicating a surface source of less saline water. Saline Levantine Surface Waters and diluted BSW in the western Cretan Sea control the characteristics of surface waters within the south Aegean.

The circulation of the south Aegean has been previously investigated (Theocharis *et. al.*, 1999, Theodorou *et. al.*, 1997 and Theocharis *et. al.*, 1993) and shows that the south Aegean is an area of complex circulation, incorporating basin, sub-basin and mesoscales features (Theodorou *et. al.*, 1997). In comparison to surveys carried out in March and September 1994 (Theocharis, *et. al.*, 1999), there are marked similarities with surveys in the present study, and thus aiding the interpretation of the general hydrography and circulation of the south Aegean, otherwise made inconclusive with the limited amount of stations examined in this work.

In March 1997, the Asia Minor Current (AMC) carries warm saline waters of Levantine origin the north-eastern Cretan Sea, with the highest salinities seen at western and central stations. MAW (a sub-surface salinity minimum) is found above the thermocline between 34 - 184 m as patches and is observed entering the Cretan Sea through the Antikithira Strait, where lowest salinities are observed in the east (MSB3). TMW, a low salinity water mass (corresponding to transitional waters between LIW and EMDW) is advected towards to Aegean through the Antikithira Straits (in the west), the Kassos and Karpathos Straits (in the east). This layer is observed throughout the Aegean between 225-350 m, at its thickest and with lowest salinities at MSB3, followed by MSB6, indicating a predominant source from the west. EMDW is also likely to be advected from the west, where highest salinities are observed, decreasing towards to east. CDW, found at central and eastern stations, outflows from the Aegean through the Antikithira and Kassos Straits due to strong thermohaline gradients and, being denser than EMDW, immediately sinks into the Levantine and Ionian basins. Theocharis *et. al.* (1993, 1999) observed a central cyclonic and a western anticyclonic eddies in the Cretan Sea, which although they may shift in space and extent between seasons, they appear stable over time and affect the vertical and lateral distribution of intermediate and surface waters. Within the central cyclonic eddy homogenisation of salinity down to 150 m is observed at MSB1 and MSB6, where waters of intermediate depths are transported to the surface. Temperature and density profiles (Figures 4.8 and 4.9) indicate upwelling at MSB6.

In September 1997 a contour plot (Figures 4.11) highlights the variation of salinity, temperature and density from east to west across the Cretan Sea in the upper 250 m. A number of features can be distinguished relating to water exchanges between the Levantine and Ionian basins, exchanges within the Aegean Sea, Cretan Sea circulation and the presence of cyclonic and anti-cyclonic features. In September 1997, surface waters are warm and saline, indicating strong thermocline coupling between the Aegean and Levantine Basins. LSW enters the Cretan Sea from the Levantine Sea via the Kassos Straits, where it follows surface meandering currents and it is observed at both western (MSB7) and central (MSB1 and MSB16) stations. Lower salinities are observed in the upper 3 m at MSB3 in the east, and MSB7 in the west. MAW enters through the Antikithira Strait and spreads eastwards forming a low salinity intrusion across the Cretan Sea at 50-75 m (i.e. above the thermocline), with a possible secondary source of MAW via the Kassos Strait. In the central Cretan Sea, within the central cyclonic circulation, the presence of MAW disappears as LIW is found up to sub-surface waters. Theocharis *et al.* (1993) observed a similar disappearance of MAW at the centre of the Pelops and Rhodes gyres, due to its dilution in the anticyclonic cell and its displacement in the cyclonic dome, respectively. The variability of MAW in both seasons, is attributed to spatial variability of circulation features. Upwelling due to the cyclonic eddy can be observed as a dome of salinity, temperature and density at stations MSB1 and MSB16 (Figure 4.11). Below MAW, LIW is also influenced by circulation and the presence of gyres in the Cretan Sea. In September 1997 LIW is observed at MSB45 and MSB4 down to 150 m, and < 50 m at MSB16. TMW and CDW masses remain characteristically similar throughout both seasons, except TMW is observed across the Cretan Sea at slightly deeper 321 to 550 m than in March 1997.

4.4.2 NUTRIENTS

Depth profiles (Figure 4.12) for nitrate plus nitrite exhibit a well defined nutricline for both March and September, above which surface concentrations are very low, and below which concentrations are governed by a combination of regeneration with depth and the complex hydrography and circulation of the Cretan Sea. Surface concentrations are more variable and slightly higher in March (0.2 - 0.8 μM) than September 1997 (0.1 - 0.4 μM). The nutricline varies in depth with season, as does the thermocline, at ~ 150 m in March and ~ 75 m in September 1997. Additional stations were sampled in September 1997 and a contour plot across the Cretan Sea down to 250 m (Figure 4.13) shows an elevation of nutrient isolines at stations MSB1 and MSB16, indicating the upwelling of deeper nutrient-rich waters. This feature corresponds to a cyclonic eddy, previously examined (Figure 4.8). At intermediate depths of 225 - 350 m in March and 321 - 550 m in September 1997, a layer of nutrient-rich water occurs throughout the Cretan Sea, with greater concentrations than in deep waters. This corresponds to TMW entering the Cretan Sea from the Levantine and Ionian Basins. Highest concentrations are observed at MSB3 (4.5 μM) and MSB7 (4.0 μM) in March and MSB7 and MSB1 (3.9 μM) in September 1997. Below TMW, concentrations decrease to 2.2 - 2.9 μM between 700 and 900 m in March, and 2.7 - 2.9 μM between 800 and 1000 m in September 1997. Deep water (CDW) concentrations vary slightly between March (3.0 - 3.4 μM) and September (3.3 - 3.6 μM). N/P values of 32.5 in March and 38.2 in September are higher than the northern Aegean, again suggesting that phosphate limitation is greatest in September.

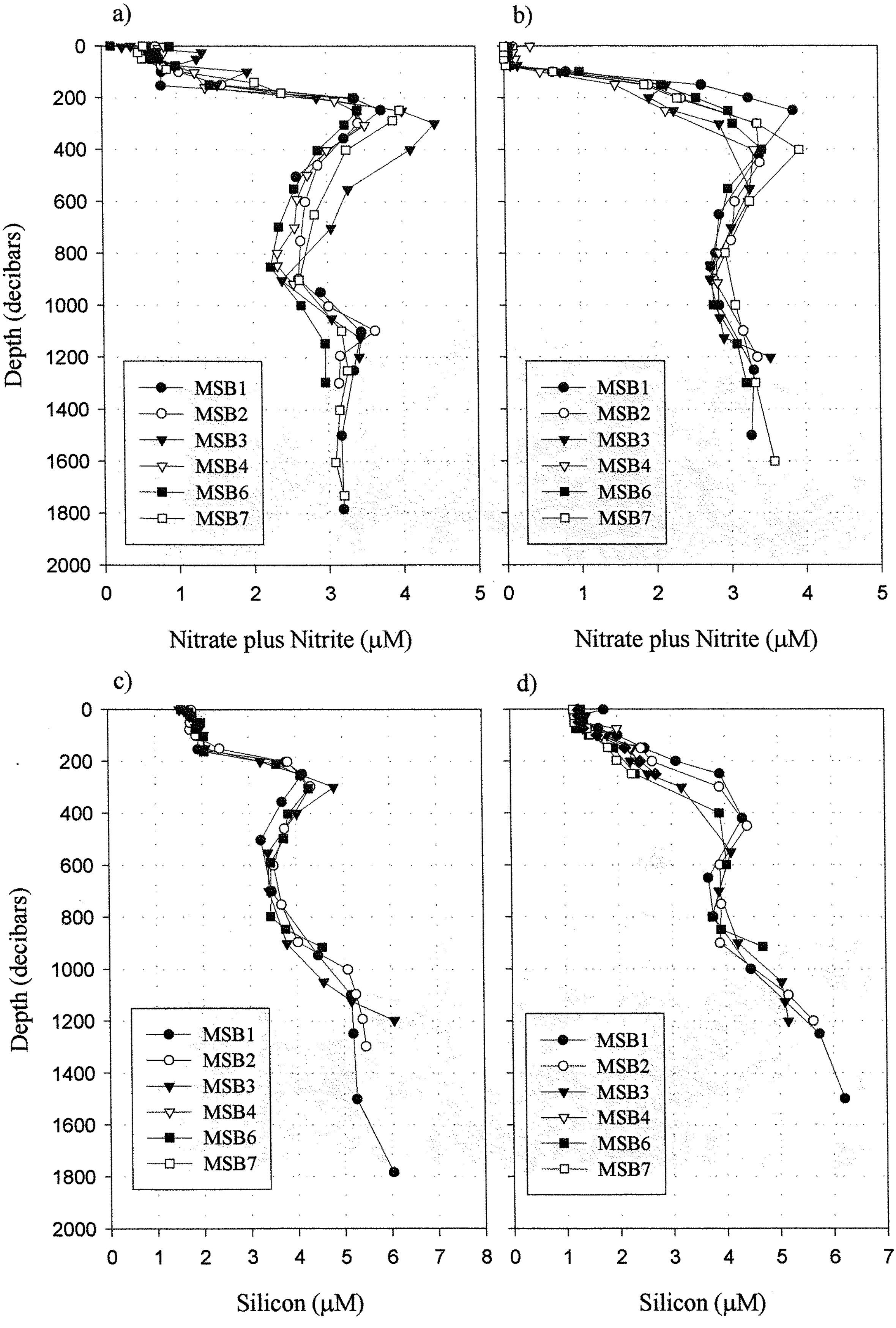

Figure 4.12. Nitrate plus nitrite and silicon depth profiles for the south Aegean in a), c) March and b), d) in September 1997. Note: Symbol size represents +/- 1 SD estimate for each maeaurement.

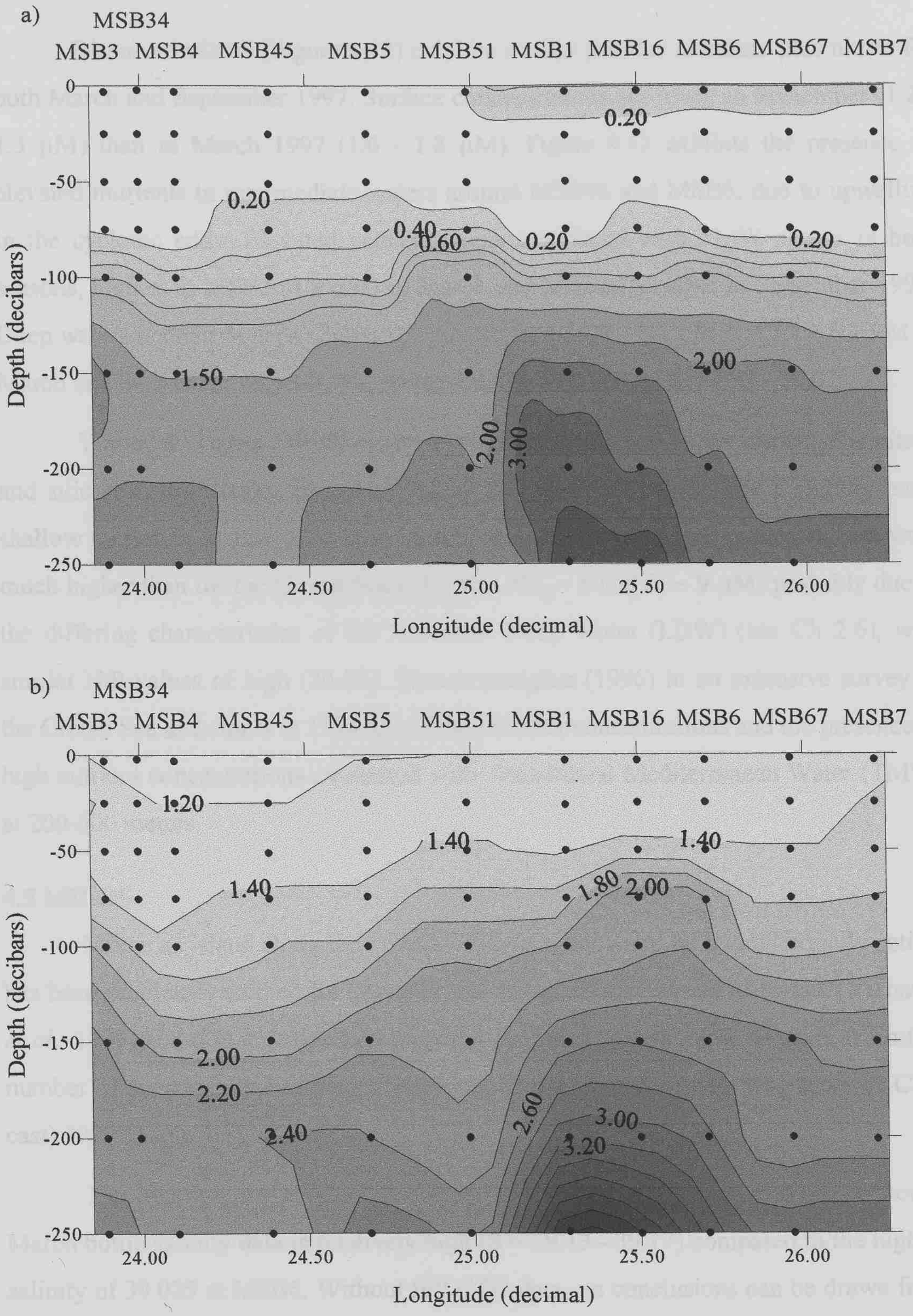

Figure 4.13. Contour plots for a) nitrate plus nitrite (micromolar) and b) silicon (micromolar) along an east-west transect across the Cretan Sea in September 1997.

Dissolved silicon (Figure 4.12) exhibits similar profiles to nitrate plus nitrite for both March and September 1997. Surface concentrations are lower in September (1.2 - 1.3 μM) than in March 1997 (1.6 - 1.8 μM). Figure 4.13 exhibits the presence of elevated nutrients in intermediate waters around MSB16 and MSB6, due to upwelling in the cyclonic eddy. Elevated concentrations associated with TMW occurs in both seasons, highest at MSB3 (4.8 μM) in March and MSB7 (5.1 μM) in September 1997. Deep waters contain highest silicon concentrations of 4.8 - 6.1 μM and 5.1 - 6.2 μM in March and September respectively, corresponding to salinities of 38.93 - 39.07.

Yimaz, & Tugrul (1998) observed similar depth profiles for nitrate plus nitrite and silicon in the Rhodes cyclonic gyre of the Levantine basin, with a slightly more shallow nutricline in July 1993 than March 1994. The deep water concentrations were much higher than for the Cretan Sea ($N0_3$ plus $N0_2$ ~ 6 and Si ~ 9 μM) probably due to the differing characteristics of the Levantine Deep Water (LDW) (see Ch 2.6), with similar N/P values of high (20-30). Souvermezoglou (1996) in an extensive survey of the Cretan Sea and straits in 1994, also found similar concentrations and the presence of high nutrient concentrations associated with Transitional Mediterranean Water (TMW) at 200-600 meters.

4.5 MILOS

Milos, an island along the cyclades Plateaux known to be hydrothermally active, has been previously studied for seawater and sediment enrichment of metals (Varnavas *et al.*, 1993) and it is regarded as a potential source of metals to the Aegean. A limited number of samples were collected in March (2 pole samples) and September (1 CTD cast) 1997 (Table 4.1).

The hydrography at Milos is similar to Cretan stations (Figure 4.14), although March bottle salinity data is relatively high (S = 39.13 - 39.17) compared to the highest salinity of 39.025 at MSB6. Without full CTD data, no conclusions can be drawn from this difference concerning different surface water masses. September 1997 data is consistent with profiles already observed in the Cretan Sea (with greatest similarity to MSB7). Nutrient data also exhibits similarities to Cretan Sea surface waters (Figure

4.14), with higher concentrations of nitrite plus nitrite in March (0.6 μM) than September (0.1-0.2 μM) and similar silicon concentrations (1.5 - 2 μM).

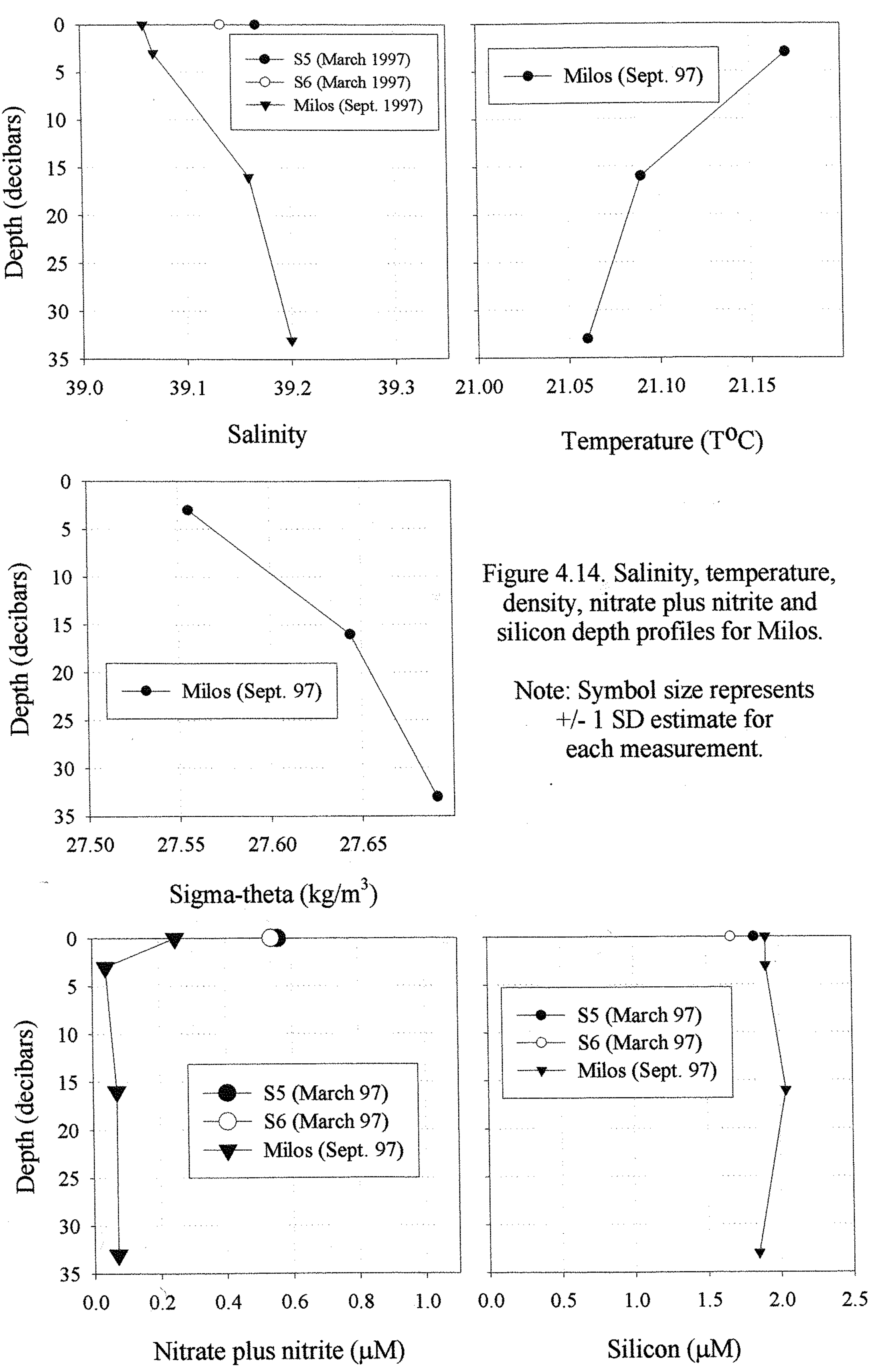

Figure 4.14. Salinity, temperature, density, nitrate plus nitrite and silicon depth profiles for Milos.

Note: Symbol size represents +/- 1 SD estimate for each measurement.

Table 4.1 Main water masses in the southern and northern Aegean Sea with their characteristics.
BSW = Black Sea Water, LSW = Levantine Surface Water, MAW = Modified Atlantic Water LIW = Levantine Intermediate Water, TMW = Transitional Mediterranean Water, EMDW = Eastern Mediterranean Deep Water, NAEGDW = North Aegean Deep Water, CDW = Cretan Deep Water.

	Northern Aegean (MNB)		Southern Aegean, Cretan Sea (MSB)	
Depth	Late Winter (3/97)	Late Summer (9/97)	Late Winter (3/97)	Late Summer (9/97)
Surface and Sub-surface	1 - 100 dbar (BSW) S = 34.25 - 38.70, T = 10.0-14.7 °C, σ_θ = 26.4 - 29.0	1 - 55 dbar (BSW) S = 32.71 - 38.70, T = 14.8 - 20.6 °C, σ_θ = 23.4 - 29.0	1 - 15 dbar S = 38.78 - 38.99, T = 15.0 - 15.5 °C,	3 - 25 dbar (LSW) S = 39.23-39.41, T = 20.2-22.3 °C,
			15 - 220 dbar (MAW) S = 38.97 - 39.00, T = 14.9 - 15.1 °C,σ_θ = 29.1	50 - 75 dbar (MAW) S = 39.06 - 39.15, T = 15.9 - 16.1 °C,σ_θ = 29.1
Intermediate		55 - 100 dbar (MAW) S = 38.60 -39.05, T = 17.5 - 18.3	15 - 220 dbar (LIW) S = 39.01 - 39.03, T = 14.9 - 15.2 °C, σ_θ = 29.1 - 29.2	75 - 100 dbar (LIW) S = 39.06 - 39.15, T = 15.9 - 16.1 °C, σ_θ = 29.1
	100 - 300 dbar (LIW) S = 38.60 - 39.05, T = 14.3 - 14.7 °C, σ_θ = 28.9 - 29.1		225-350 dbar (TMW) S = 38.93-38.97, T = 14.3-14.6 °C, σ_θ = 29.2-21.3	321-550 dbar (TMW)
Deep	400 - 1258 dbar (NAEGDW) S = 39.05 - 39.19, T = 13.1 - 13.3 °C, σ_θ = 29.5 - 29.7		420-680 dbar (EMDW) S = 38.99-39.02, T = 14.1 - 14.5 °C, σ_θ = 29.3 - 29.4	
			680-1200 dbar (western deep water) S = 39.02, T = 14.1 - 14.2 °C, σ_θ = 29.4	
			680-1790 dbar (CDW) S = 39.02 - 39.07, T = 13.9 - 14.1 °C, σ_θ = 29.4 - 29.5	

CHAPTER 5

TRACE METALS IN THE AEGEAN SEA: RESULTS

5.1 INTRODUCTION

There is very limited dissolved trace metal data in the eastern Mediterranean and Aegean Sea. The current work giving data on 415 samples for 8 metals (Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn) in the northern and southern Aegean will enable an in-depth study of the processes influencing the concentrations of trace metals with depth. This includes spatial and seasonal variations, relationship to water masses, circulation, inputs from the coast and atmosphere (plus the possible source from hydrothermal venting), biological uptake and regeneration, and sediment interactions.

In the Aegean Sea (as for the Mediterranean), the distributions of various dissolved trace metals fundamentally differ from those in the open ocean (Saager, 1994). The surrounding land masses provide a large source of trace metals via atmospheric and close to the shore by riverine/runoff, therefore resulting in higher surface concentrations. Combined with an oligotrophic environment, this results in uniform metal profiles, or with surface elevation, and no presence of the typical 'nutrient' type profile observed in the open ocean (Saager, 1994).

5.3 TRACE METAL RESULTS: THE NORTH AEGEAN

The distribution of trace metals in the northern Aegean is controlled by a number of factors: atmospheric deposition and/or elevated concentrations associated with low salinity BSW and riverine runoff, sorption onto particles and biological interactions, and the mixing of water masses. As previously discussed in Chapter 4 the north Aegean is composed of 4 main water masses, North Aegean Deep Water (NAEGDW), Levantine Intermediate Water (LIW), Modified Atlantic Water (MAW) and Black Sea Water (BSW). LIW and BSW have already been associated with elevated trace metal concentrations (Varnavas & Voutsinou-Taliadouri, 1986; Morley & Burton, 1993; Saager, 1994). Table 5.1 summarises the trace metal signature for each water mass and for each metal the relationship between salinity and nutrients will be examined to ascertain the major influences on the biogeochemistry of trace metals in the north Aegean.

Table 5.1 Summary of trace metal signature concentrations for NAEGDW, LIW and BSW for March and September 1997. *Note BSW concentrations are for the upper 10 m only

Conc. nM	North Aegean				
	March '97			September '97	
	NAEGDW	LIW	BSW*	NAEGDW	BSW*
Mn	0.3 - 0.9	2.1 - 2.5	3.6 - 10.0	0.3 - 0.9	11.0 - 16.1
Fe	0.3 - 0.7	0.8 - 3.5	1.0 - 9.1	0.2 - 0.7	2.1 - 3.9
Co	0.01 - 0.05	0.09 - 0.14	0.11 - 0.23	0.01 - 0.03	0.25 - 0.37
Pb	0.02 - 0.07	0.07	0.08 - 0.23	0.02 - 0.07	0.08 - 0.28
Cu	1.8 - 2.5	-	2.4 - 4.0	2.0 - 2.5	3.9 - 5.3
Ni	4.5 - 5.3	4.0 - 4.4	3.8 - 7.6	4.7 - 5.3	7.1 - 8.9
Cd	0.07 - 0.09	-	0.07 - 0.09	0.07 - 0.09	0.07 - 0.09
Zn	2.0 - 4.4	-	3.4 - 9.8	1.9 - 4.3	3.2 - 10.5

5.2.1 MANGANESE AND COBALT

Vertical profiles of dissolved Mn (Figure 5.1) show elevated concentrations in surface waters for both seasons, with surface concentrations 2-4 times higher in September than in March 1997 (Table 5.1). In March highest Mn concentrations are found at stations MNB5 (10.1 nM) and MNB6 (7.2 nM) and correspond to surface salinity minima of BSW and a strong thermocline. In September highest concentrations in the upper homogenous 36 m at MNB6 (16.1 nM) link to the presence of a strong thermocline, and lack of surface mixing, due to the proximity to the coast. At MNB3 there is some surface variability in Mn concentration with two maxima, at the surface and 25 m, corresponding to a temperature minima. In surface waters BSW extends over the north Aegean, and the correlation of Mn with salinity exists for most stations.

From surface concentrations Mn decreases rapidly to intermediate and deep water concentrations of 0.3 to 0.9 nM below 150 to 200 m. However in March 1997 at stations MNB3, MNB1, and MNB5, at 150 to 300 m depth, an increase in Mn is observed (to between 2.1 and 2.5 nM), corresponding to the intrusion of warm, saline and low nutrient LIW. Deep waters exhibit low concentrations, with a slight increase in bottom waters, especially at MNB6, indicating mobilisation of dissolved manganese from particulate material. Similar profiles have been observed in the eastern and western Mediterranean Sea (Saager, 1994; Morley *et al.*, 1997), but with lower surface (below 5 nM) and deep (0.1 -0.4 nM) Mn concentrations than observed in the north Aegean. Elevated Mn concentrations in surface waters from riverine sources, BSW, LIW, and atmospheric sources, contribute to higher surface concentrations and the subsequent formation of NAEGDW with a higher Mn signature than for the Mediterranean Sea.

Cobalt depth profiles (Figure 5.2) exhibit surface elevation and uniform deep-water concentrations, and Co is rapidly removed onto particles by oxidative or hydrolic scavenging (Whitfield & Turner, 1987). Surface water concentrations are highest in September 1997 (Table 5.1) at stations MNB2 (0.37 nM), MNB5 and MNB1 (0.35 nM), followed by March at MNB5 and MNB6, linked to the BSW salinity minimum. In September, MNB3 exhibits a subsurface maximum at 25 m, linked to temperature minima, also observed for Manganese. Surface BSW Co exhibits a correlation with salinity for both seasons (Figure 5.2). In March 1997 an increase in Co concentrations at MNB5, MNB1 and MNB3 at 100-300 m depth is linked to the LIW intrusion to the north Aegean. Below 300 to 400 m Co concentrations remain uniform at 0.01 to 0.05 nM.

There is a good correlation between Co and Mn, indicating their similar sources to surface waters and geochemical behaviour. Mn/Co values of 34.26 (r^2 = 0.77) in March and 49.19 (r^2 = 0.85) in September indicate a potential difference in their source material and cycling between seasons. This relationship has also been observed in the western Mediterranean Sea (Morley *et al.*, 1990) and English Channel (James *et al.*, 1993). Cobalt depth profiles indicate the presence of one or more surface sources in the Aegean. Surface Co concentrations are generally higher than observed in western Mediterranean (Zhang & Wollast, 1993; Morley *et al.*, 1997). Zhang & Wollast (1993) and Tankéré (1998) observed the strong influence of the rivers Rhone (in the NW Mediterranean) and Po (in the Adriatic Sea) on surface waters, with Co concentrations as high as 0.9 nM. Deep water concentrations in the Adriatic are similar to the north Aegean (Tankéré, 1998), whereas in the western and north-western Mediterranean Sea concentrations vary from to 0.04 nM (Morley *et al.*, 1997) to 0.08 nM (Zhang & Wollast, 1993). There is globally, very little open water Co data (i.e. Burton *et al.*, 1993; James *et al.*, 1993), in part due to analytical problems with such low concentrations.

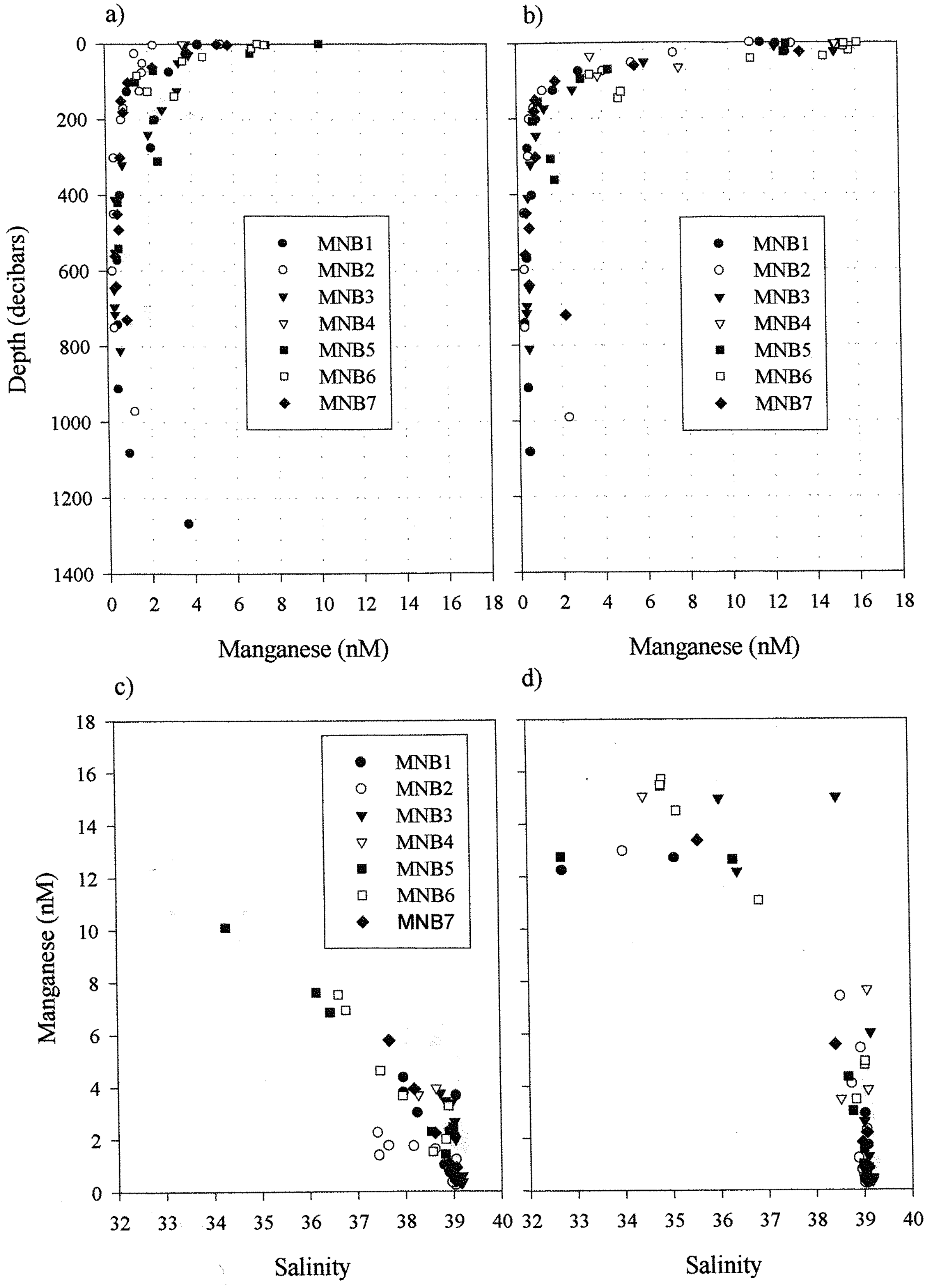

Figure 5.1. Manganese depth profiles for a) March and b) September; and Mn versus salinity for c) March and d) September 1997 in the north Aegean Sea.
Note: Symbol size represents +/- 1 SD estimate for each measurement.

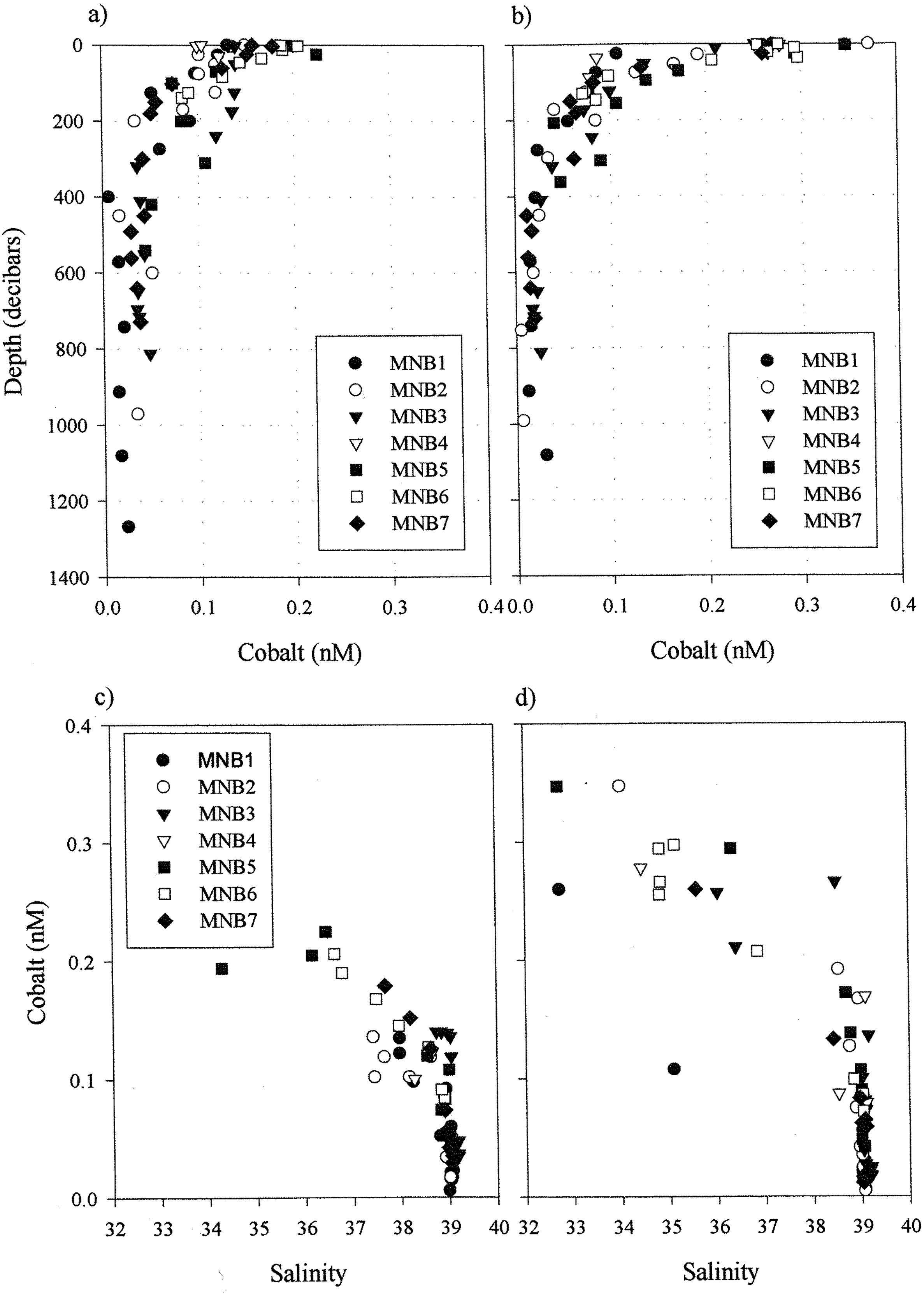

Figure 5.2. Cobalt depth profiles for a) March and b) September 1997; and Co versus salinity for c) March and d) September 1997 in the north Aegean Sea. Note: Symbol size represents +/- 1 SD estimate for each measurement.

5.2.2 IRON AND LEAD

Iron profiles for all stations exhibit elevated surface concentrations (Figure 5.3 and Table 5.1). In contrast to Mn highest surface concentrations are observed in March, at MNB5 (9.1 nM) and MNB6 (5.3 nM), associated with the surface BSW salinity minimum, and at MNB2 and MNB5 in September 1997. Within the surface BSW mass Figure 5.3 indicates a correlation of Fe with salinity for both seasons. Below the thermocline Fe decreases in concentration to a constant value of between 0.2 and 0.7 nM, but like Mn the presence of LIW in March carries a high Fe signature of between 0.8 and 3.5 nM, highest at MNB1, also observed in the eastern Mediterranean by Saager (1994). Iron is a redox sensitive element and has a behaviour similar to Mn, with a positive correlation of Mn/Fe value of 1.11 ($r^2 = 0.66$) in March and 6.27 ($r^2 = 0.73$) in September 1997. This seemingly large difference in the ratio between each season could in part reflect a difference in the composition of source material to surface waters and their differing biogeochemistry.

Lead depth profiles (Figure 5.4) exhibit surface elevation and depletion with depth, with highest surface concentrations in September 1997 (Table 5.1), decreasing below the thermocline to 0.02 to 0.07 nM. Variability in the upper 25 m in September at MNB3 corresponds to temperature difference and the presence of more than one surface water mass. The poor correlation of Pb and salinity (Figure 5.4) suggests contamination or sporadic surface sources and rapid residence times. The major source is anthropogenic vehicle gasoline (Schaule & Patterson, 1983) from the atmosphere and depositional fluxes will vary significantly depending on the distance from sites of anthropogenic emissions. Lead concentrations are typical for open Mediterranean waters (Tankéré *et al.*, 1995; Morley *et al.*, 1997), although surface concentrations are slightly higher in the north Aegean than for the Mediterranean Sea.

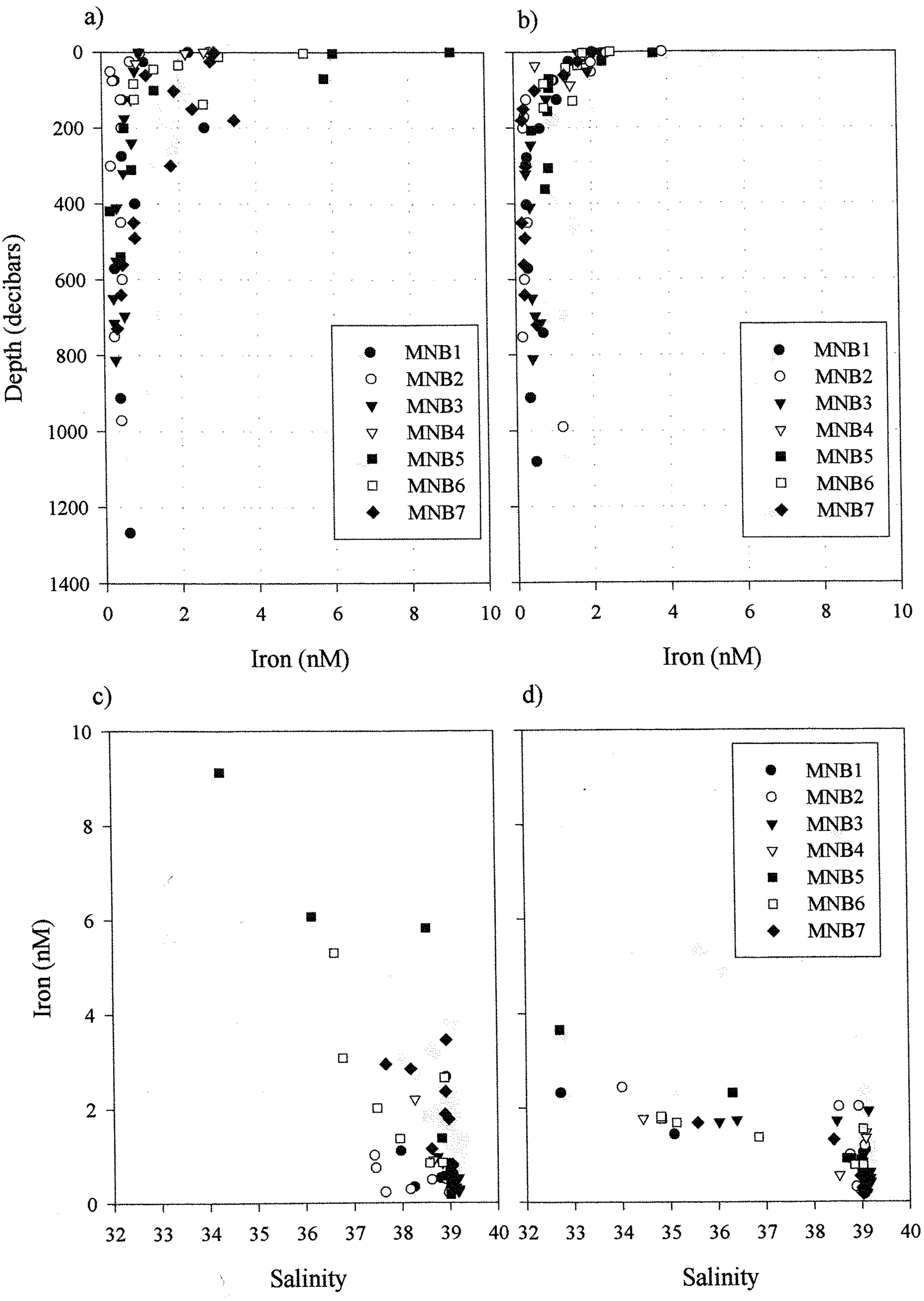

Figure 5.3. Iron depth profiles for a) March and b) September 1997; and Fe versus salinity for c) March and d) September 1997 in the North Aegean Sea. Note: Symbol size represents +/- 1 SD estimate for each measurement

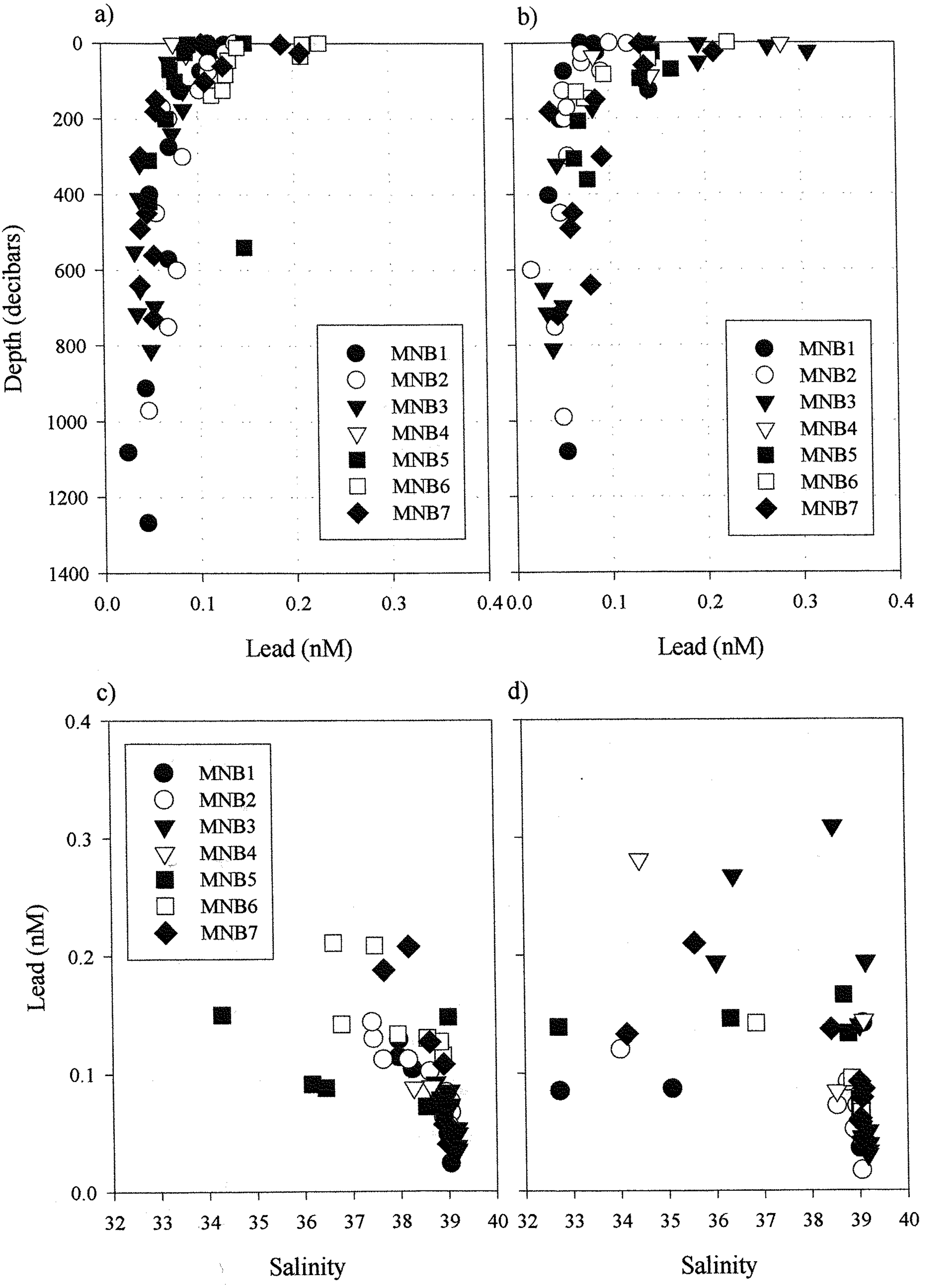

Figure 5.4. Lead depth profiles for a) March and b) September 1997; and Pb versus salinity for c) March and d) September 1997 in the North Aegean Sea. Note: Symbol size represents +/- 1 SD estimate for each measurement

5.2.3 COPPER, NICKEL AND CADMIUM

Vertical profiles of dissolved copper (Figure 5.5) exhibit elevated concentrations in surface waters, 1-2 nM higher in September than March 1997, with low Cu values below 100-200 m depth (Table 5.1). MNB5 and MNB6 exhibit highest Cu values in March, and MNB2 and MNB5 in September, both related to BSW salinity minimum and sharp thermocline at these stations. The strong correlation of Cu with salinity in BSW (Figure 5.5) indicates the potential of BSW as a source of Cu to surface waters.

Vertical depth profiles of dissolved nickel, exhibit a combination of surface elevation/depth depletion, homogenous with depth and nutrient type profiles (Figure 5.6). In March stations MNB3 and MNB5 exhibit a slight surface elevation of about 2 nM above deep-water concentrations (Table 5.1), linked to the BSW salinity minimum and thermocline. A subsurface maximum occurs at MNB4 (66 m), the shallowest station, due to enhanced biological production and chlorophyll concentrations at this station. In September 1997, surface concentrations of Ni are dominated by surface inputs (2-4 nM above deep-water values) and highest concentrations at MNB5 (Table 5.1), linked to the BSW salinity minimum. Deep-water concentrations remain relatively uniform with depth for both seasons (Table 5.1). There is a correlation between salinity and Ni for both seasons (Figure 5.6).

Cadmium concentrations (Figure 5.7) vary little with depth or season (0.07 to 0.09 nM) indicating homogenous distributions in the Aegean (Table 5.1).

5.2.4 ZINC

Zinc concentrations exhibit profiles of sub-surface elevation and relatively uniform below the thermocline (Figure 5.7), inspite of Zn proving to be the most susceptible of all the metals under study to contamination with resulting erratic depth profiles. Surface values are marginally higher in September than March 1997, at up to 3 nM above the deep-water concentrations (Table 5.1). Ruiz-Pino *et al.* (1991) reported similar Mediterranean homogenous deep water and variable surface concentrations.

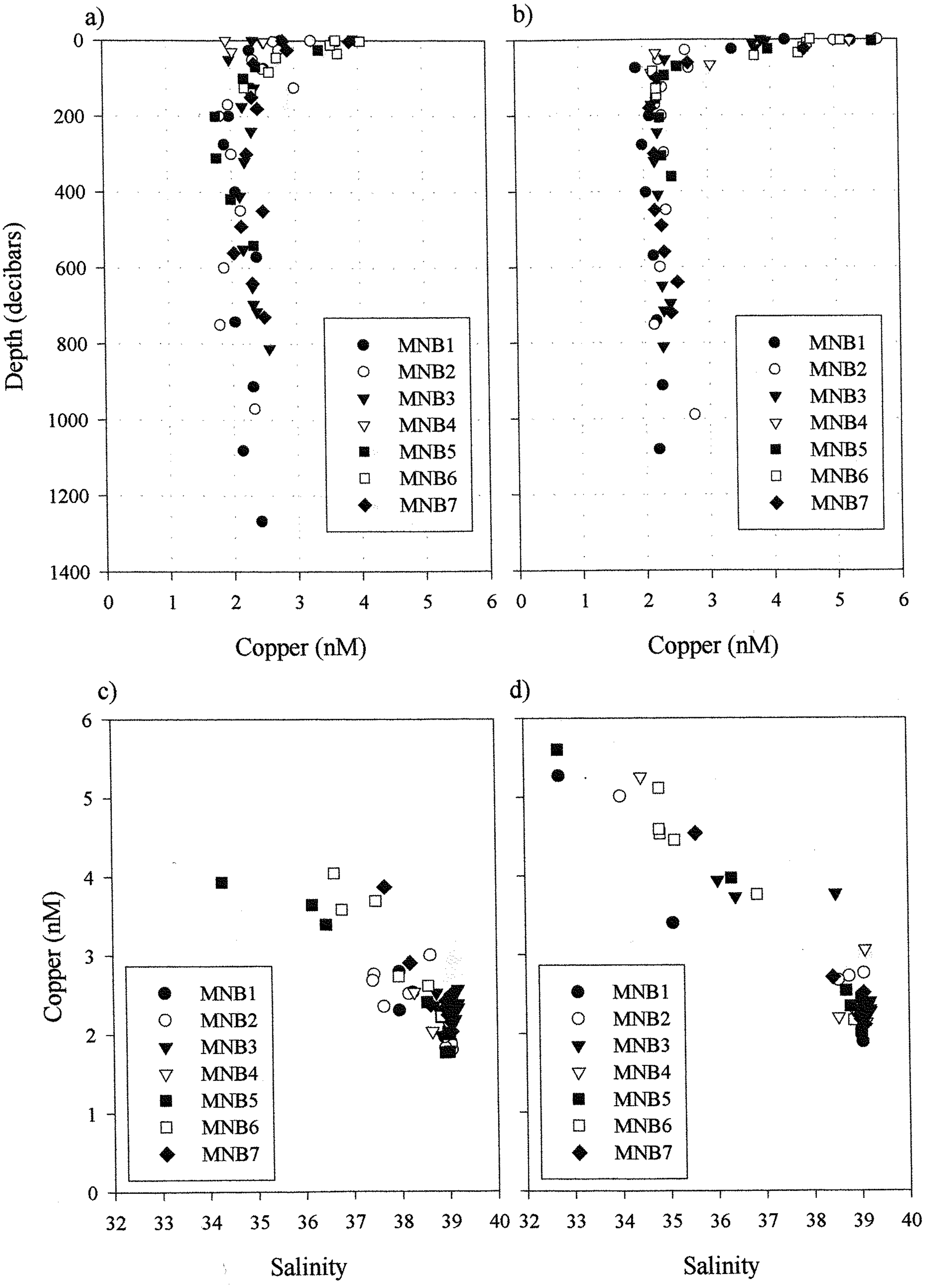

Figure 5.5. Copper depth profiles for a) March and b) September; and Cu versus salinity for c) March and d) September 1997 in the north Aegean Sea. Note: Symbol size represents +/- 1 SD estimate for each measurement.

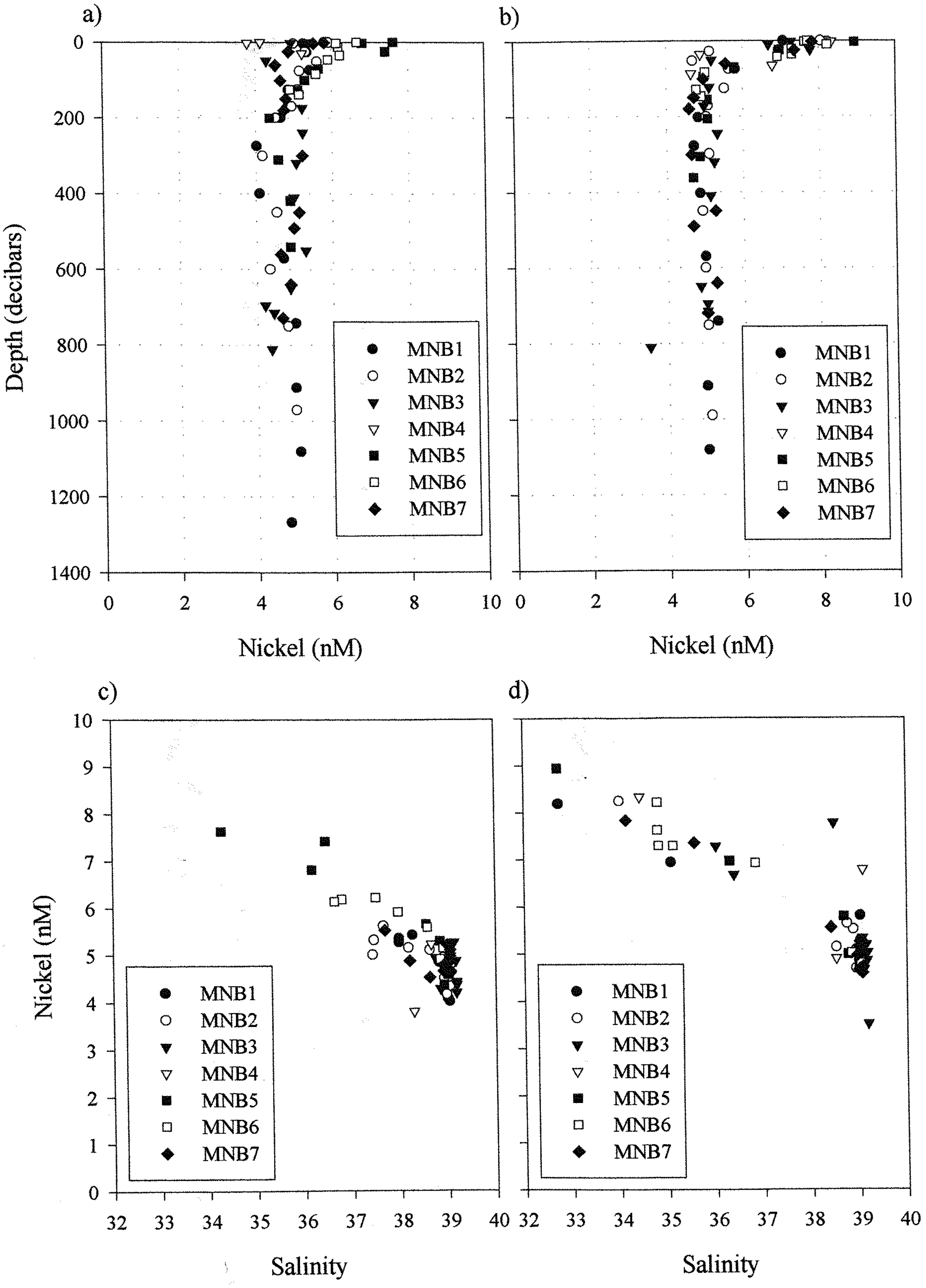

Figure 5.6. Nickel depth profiles for a) March and b) September; and Ni versus salinity for c) March and d) September 1997 in the north Aegean Sea. Note: Symbol size represents +/- 1 SD estimate for each measurement.

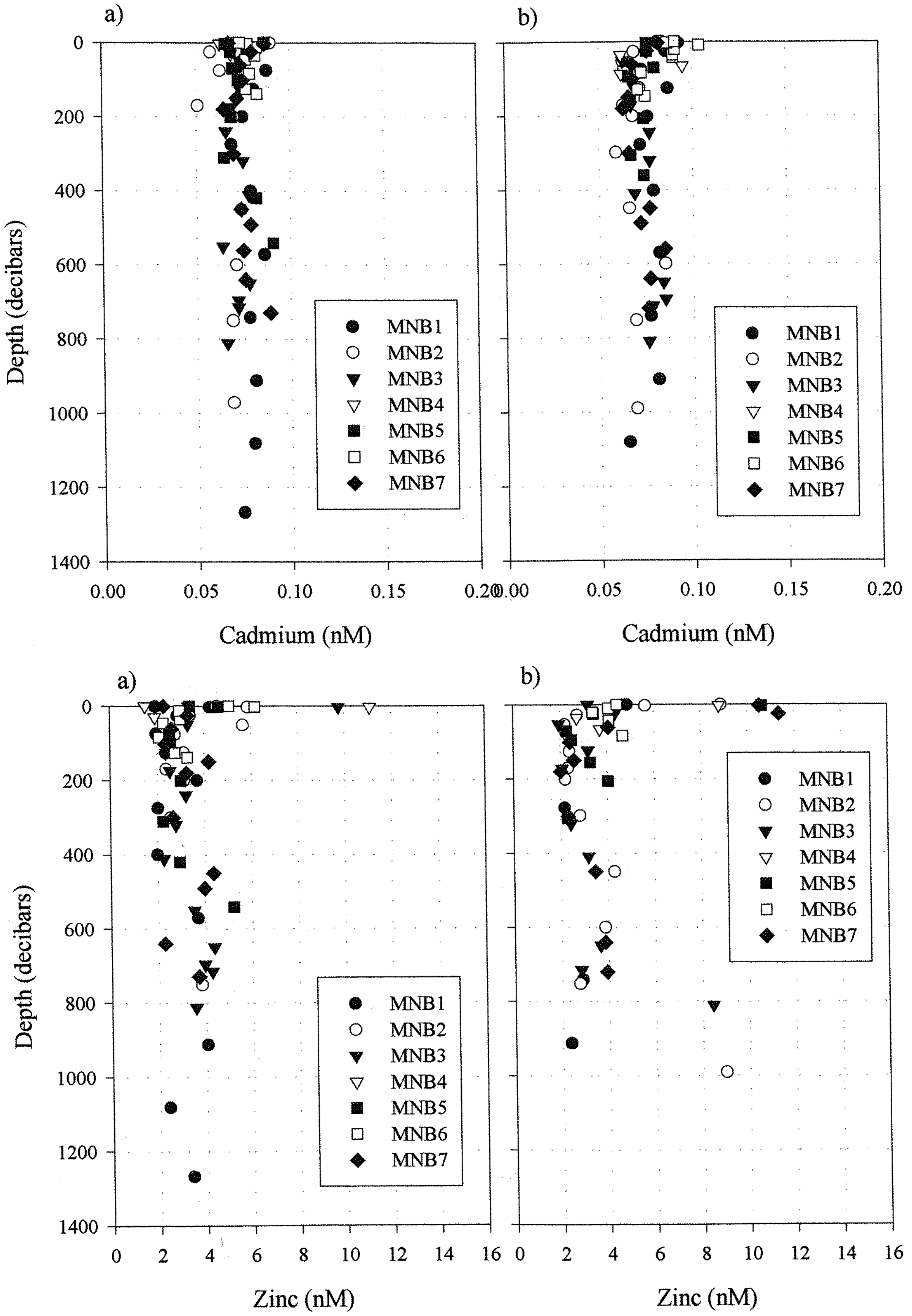

Figure 5.7. Cadmium and zinc depth profiles for a) March, and b) September 1997 in the north Aegean Sea. Note: Symbol size represents +/- 1 SD estimate for each measurement.

5.3 MIXING SERIES FOR METALS BETWEEN THE DARDANELLES AND OPEN NORTH AEGEAN

A metal salinity correlation is observed for the metals, Mn, Fe, Co, Cu and Ni in the north Aegean surface waters (Figures 5.1 to 5.6). Linear Regression analysis enables further examination of this relationship and to estimate the concentration of metals at the Straits of Dardanelles, assuming a linear conservative relationship with salinity in Black Sea Waters. Applying a linear regression to all northern stations resulted in poor correlation coefficients for all metals (with the exception of copper) due to variability in the salinity metal relationship between individual stations. Table 5.2 presents the linear regression equations and confidences (R^2) and for stations MNB5 and MNB6 in March and September 1997. These stations were selected as MNB5 is the closest to the Straits of Dardanelles and exhibits the lowest salinities observed of all stations examined. In addition MNB6, on the shelf edge closest to the northern Greek coastline and near the mouths of the rivers Nestos and Evros (see Chapter 2), exhibits a distinct upper mixed layer. Non-linear relationships were observed for some stations and indicate additional processes operating in surface waters.

There is significant variability between seasons and stations in the metal-salinity linear relationships indicated by Table 2.2. This indicates the occurrence of additional processes in the north Aegean surface waters, and therefore only an overall 'semi-conservative' relationship exists between metal and salinity in BSW of the north Aegean Sea. Manganese exhibits salinity correlations at both stations, except MNB5 (also MNB1, MNB2 and MNB3) in September where North Atlantic Water intrudes into sub-surface waters, carrying a higher Mn concentration relative to salinity at depths of 25-75 dbar. Iron exhibits a non-linear relation in March at MNB6 due to increased Fe in upper 3 m, along with cobalt at MNB5. Non linear relationships were also observed at both MNB5 and MNB6 for nickel in March 1997. Overall with the exception of Mn at MNB5, salinity metal correlations are stronger in September than March. This is in part due to the wider concentration range of surface metals, but this could also reflect a more predominant source of metals from the Marmara Sea in September, when BSW fluxes are greater than the winter season.

Table 5.2 Linear regression of salinity metal relationship for BSW at stations MNB5 and MNB6 in the north Aegean. NL = Non-linear, PR = Poor linear relationship

		March 1997	September 1997
Mn	MNB5	[Mn](nM) = -1.9491[Salinity] + 77.489 $R^2 = 0.9815$	NL
	MNB6	[Mn](nM) = -3.0227[Salinity] + 118.16 $R^2 = 0.9952$	[Mn](nM) =-2.9372[Salinity]+ 117.83 $R^2 = 0.9952$
Fe	MNB5	[Fe](nM) = -1.7073[Salinity] + 67.713 $R^2 = 0.9995$	[Fe](nM) = -0.46[Salinity] + 18.722 $R^2 = 0.9995$
	MNB6	NL	[Fe](nM) = -0.2418[Salinity] + 10.184 $R^2 = 0.9937$
Co	MNB5	NL	[Co](nM) = -0.0338[Salinity] + 1.4686 $R^2 = 0.9458$
	MNB6	[Co](nM) = -0.0487[Salinity] + 1.9907 $R^2 = 0.9699$	[Co](nM) = -0.0464[Salinity] + 1.894 $R^2 = 0.9735$
Cu	MNB5	[Cu](nM) = -0.398[Salinity] + 17.753 $R^2 = 0.9612$	[Cu](nM) = -0.5259[Salinity] + 22.8 $R^2 = 0.9958$
	MNB6	[Cu](nM) = -0.7609[Salinity] + 31.878 $R^2 = 0.9157$	[Cu](nM) = -0.5969[Salinity] + 25.47 $R^2 = 0.9783$
Ni	MNB5	PR	[Ni](nM) = -0.6008[Salinity] + 28.562 $R^2 = 0.9764$
	MNB6	PR	[Ni](nM) = -0.6591[Salinity] + 30.636 $R^2 = 0.9538$

In order to ascertain the potential influence of BSW on surface metal concentrations, the linear regressions were used to calculate the metal concentrations at the salinity of the Dardanelle Straits (Table 5.3). As previously mentioned, the outflow from the Black to the Aegean Sea varies seasonally (Ünlüata *et. al.*, 1990), and approximate salinities were taken for each season during 1995 (Stashchuk *et al.*, 1999) for the Straits of Dardanelles. The enrichment factor (above open north Aegean dissolved metal concentrations) was calculated for each metal.

Overall Table 5.3 indicates that the concentrations of Mn, Fe, Co, Cu and Ni at the Straits of Dardanelles, will be significantly higher than observed in the north Aegean surface waters. These calculated Straits of Dardanelles concentrations and enrichment factors exhibit seasonal and spatial variability. The seasonal difference can be attributed to a change in BSW flux (and corresponding metal concentrations). The variation between stations however is more complex to explain, influenced by modification of BSW as it moves across the Aegean; additional inputs such as coastal and atmospheric sources, both of which will be spatially and temporally variable; and potential differences in primary production and suspended particulate matter. An important difference between these stations is the strong thermocline and upper mixed layer present at MNB6, preventing the low salinity metal rich surface waters from mixing with the LIW and NAEGDW below. This may predominantly explain the elevated metal concentrations calculated using linear regression at MNB6 (compared to MNB5) for all the above metals with the exception of iron, although the potential influence of coastal riverine waters from the rivers Nestos and Evros can not be excluded.

Table 5.3 Linear regression calculation of metal concentration at the Straits of Dardanelles with the enrichment factor (ER). Note: Salinity at the Dardanelle Straits for both seasons is based on Stashchuk *et al.*, 1999.

	March 1997 (Salinity = 30)				September 1997 (Salinity = 27)			
	MNB5		MNB6		MNB5		MNB6	
	nM	ER	nM	ER	nM	ER	nM	ER
Mn	**19.0** ± 3.68	1.9	**27.5** ± 2.45	3.7			**38.5** ± 4.58	2.4
Fe	**16.5** ± 3.90	1.8			**6.3** ± 1.31	1.7	**3.7** ± 0.40	2.0
Co			**0.5** ± 0.05	2.6	**0.6** ± 0.10	1.6	**0.6** ± 0.09	2.3
Cu	**5.8** ± 0.77	1.5	**9.1** ± 0.72	2.2	**8.6** ± 1.22	1.5	**9.4** ± 1.21	2.0
Ni					**12.3** ± 1.56	1.4	**12.8** ± 1.35	1.7

Enrichment factors (ER) vary from 1.38 for nickel at MNB5 in September, to 3.65 for manganese at MNB6 in March 1997. For all metals ER's are greater when calculated from MNB6 metal data, although the iron concentration calculated at the Straits of Dardanelles is much lower for MNB6 in September 1997. This is due to the very low surface iron concentrations observed in late summer, unlike all other metals observed that increase from March to September. For MNB6 stations ER's are greater in March 1997, but concentrations calculated are greatest in September (for both MNB5 and MNB6) due to the higher metal concentrations in the N. Aegean (with the exception of iron) and lower salinities.

Recent research in the Black and Marmara Sea suggest higher concentrations of dissolved metals are present than in the Mediterranean Sea (Windom *et al.*, 1998; Tankéré, 1998), with a wide concentration range (Yemenicioglu & Salihoglu, 1999) and spatial variability (Tankéré, 1998). The Marmara Sea, although little researched (Yemenicioglu & Salihoglu, 1999) presents a potential additional source of metals from anthropogenic activities along the Turkish coast to the north Aegean (Ergin *et al.*, 1991; Yilmaz *et al.*, 1998). Nickel and copper concentrations calculated for the Straits of Dardanelles fall within the range of observed by Yemenicioglu & Salihoglu (1999); 7 - 92 nM for Ni and 4 - 12 nM for Cu. For the remaining metals (where Marmara Sea data is not available) calculated concentrations in the Straits of Dardanelles are similar to the Black Sea (Windom *et al.*, 1998; Tankéré, 1998).

5.4 THERMAIKOS GULF

The Thermaikos Gulf receives riverine water from the Axios, Aliakmon, Gallikos and Pinios rivers, and within a highly populated, industrialised drainage area (including the city of Thessaloniki). Samples were collected (Figure 4.2) in order to ascertain whether this Gulf is a potential anthropogenic source of metals to Aegean Waters.

Manganese and cobalt depth profiles (Figure 5.8) are similar in profile to northern Aegean stations, with elevated surface samples (greatest in September 1997), and uniform concentrations below 100 to 200 m. Compared with northern MNB stations, surface concentrations are similar to stations with higher salinities, whereas lower salinity stations closer to the source of BSW exhibit slightly higher concentrations. This suggests that BSW is a greater source of metals to the Aegean than the Thermaikos Gulf. Iron (Figure 5.8) also exhibits similar depth profiles to northern Aegean stations with some surface spatially and seasonal variability. In March 1997 highest surface concentrations were observed at S12 (2.9 nM), off the Sithoniá Peninsula, and lowest at S9 (M3) (1.4 nM). Similar concentrations were observed at MNB stations (excluding MNB5 and MNB6). In September 1997 highest surface concentrations were observed outside Thermaikos Gulf on the northern shelf edge (Figure 4.2) at T1 (4.3 nM) followed by M4 (4.0 nM) and lowest at M2 (1.57 nM). Stations T1 and MNB2, both along the eastern side of the north Aegean, exhibit highest surface concentrations in September previously linked to the easterly flow of BSW. Lead (Figure 5.8) exhibits similar concentrations to northern Aegean stations for both March and September 1997.

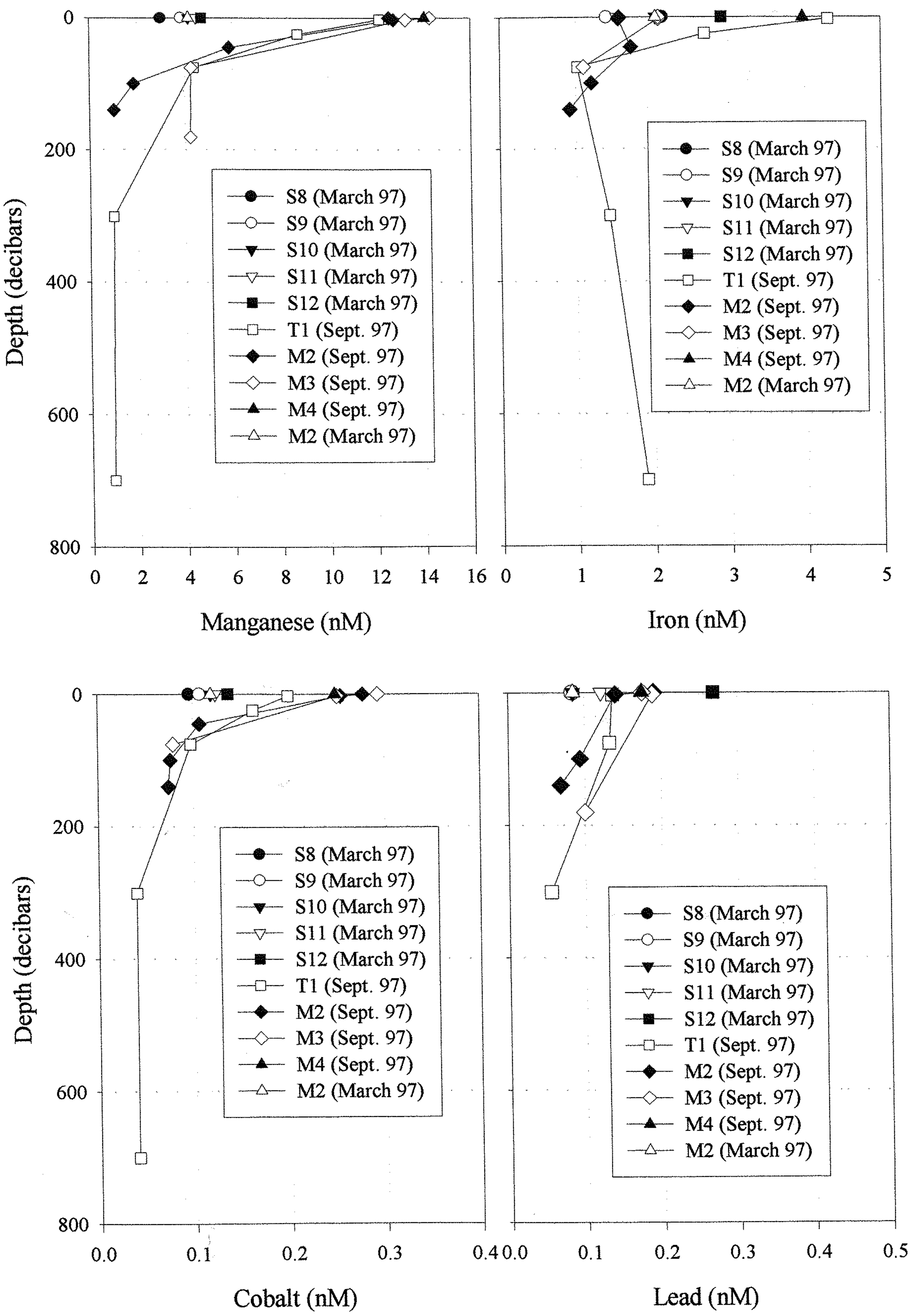

Figure 5.8. Manganese, iron, cobalt and lead depth profiles for Thermaikos Gulf.
Note: Symbol size represents +/- 1 SD estimate for each measurement.

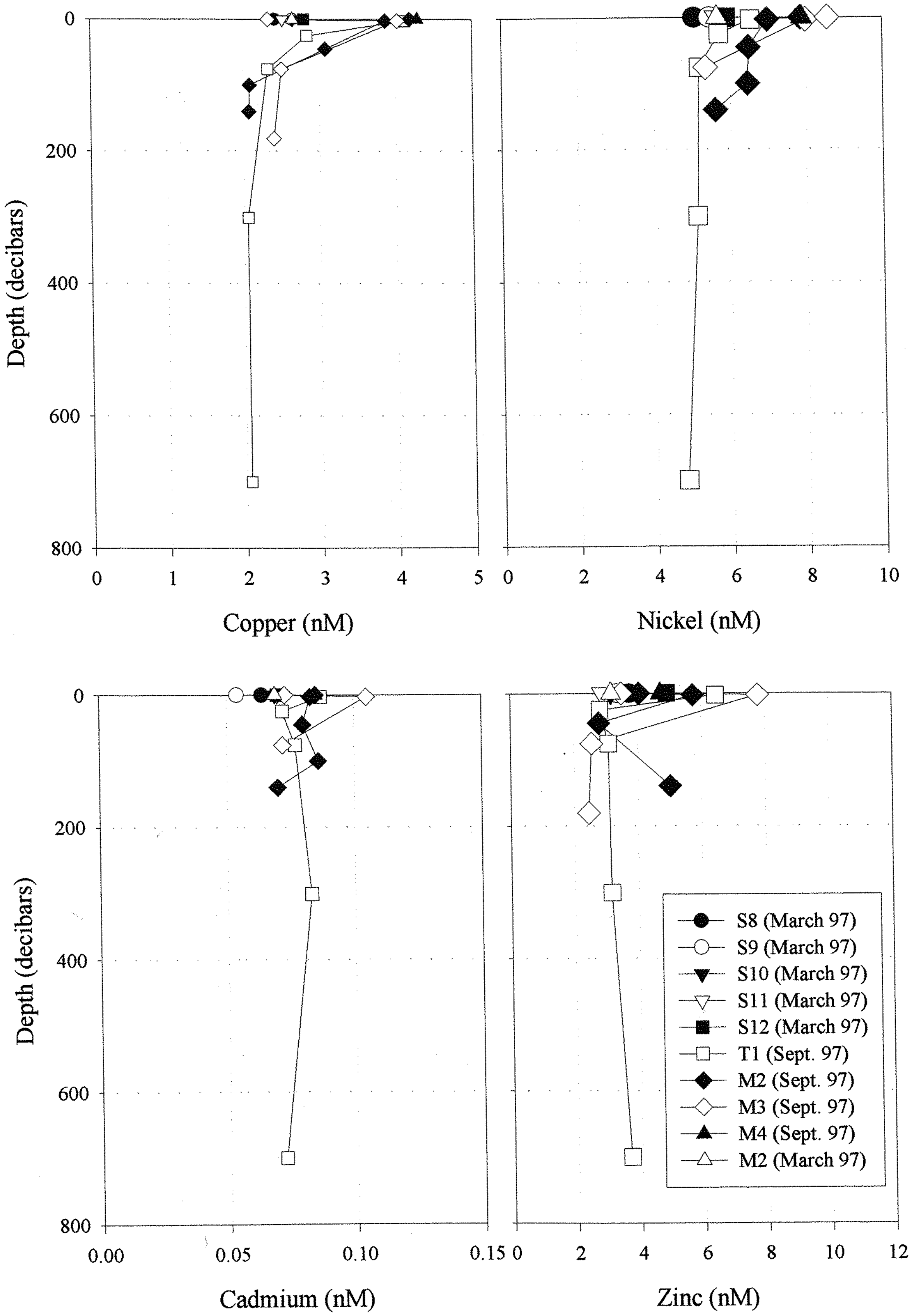

Figure 5.9. Copper, nickel, cadmium and zinc depth profiles for Thermaikos Gulf. Note: Symbol size represents +/- 1 SD estimate for each measurement.

Copper (Figure 5.9) depth profiles are similar to the northern Aegean for both seasons, although in September 1997 slightly lower surface concentrations (similar to MNB3) are observed in Thermaikos Gulf. Nickel cadmium and zinc (Figure 5.9) exhibit similar concentrations to north Aegean stations for both March and September 1997.

5.5 TRACE METAL RESULTS: THE SOUTH AEGEAN (CRETAN SEA)

The trace metal distribution in the south Aegean, like the north, is controlled by a combination of surface sources, biogeochemical removal/recycling processes and mixing of water masses. Hydrographically the south Aegean is much more complex, and more removed from coastal interactions. Metal inputs to surface waters appear to be not as significant as for the northern Aegean, with overall lower surface concentrations (Table 5.4), especially in March 1997.

Table 5.4 Summary of trace metal concentrations in deep and surface waters for March and September 1997.

Conc. nM	South Aegean			
	March '97		September '97	
	Deep waters	Surface waters	Deep waters	Surface waters
Mn	0.2 - 0.4	2.0 - 2.6	0.3 - 0.5	4.9 - 7.3
Fe	0.3 - 1.0	1.0 - 2.7	0.2 - 1.0	1.3 - 2.8
Co	0.01 - 0.05	0.08 - 0.13	0.02 - 0.09	0.13 -0.20
Pb	0.04 - 0.10	0.08 - 0.14	0.03 -0.10	0.08 - 0.24
Cu	1.0 - 2.6	1.0 - 2.6	1.8 - 2.3	2.1 - 4.1
Ni	4.6 - 5.2	4.1 - 6.4	4.5 -6.7	4.2 - 7.1
Cd	0.05 - 0.08	0.04 - 0.07	0.05 - 0.09	0.04 - 0.08
Zn	1.3 - 4.5	0.2 – 5.3	1.2 – 4.5	1.2 – 6.7

5.5.1 MANGANESE AND COBALT

Manganese profiles (Figure 5.10) exhibit elevated surface concentrations for both seasons, but with values approximately 3 times higher in September 1997 (Table 5.4). This difference reflects an increased surface source in September 1997. Surface concentrations are relatively constant down to ~ 150 dbar in March, and ~ 25 dbar in September 1997, corresponding to the depths of the upper mixed layer for each season. The shallower mixed layer in September may result in higher a surface concentration of Mn (as well as all metals) from atmospheric sources (see section 5.6).

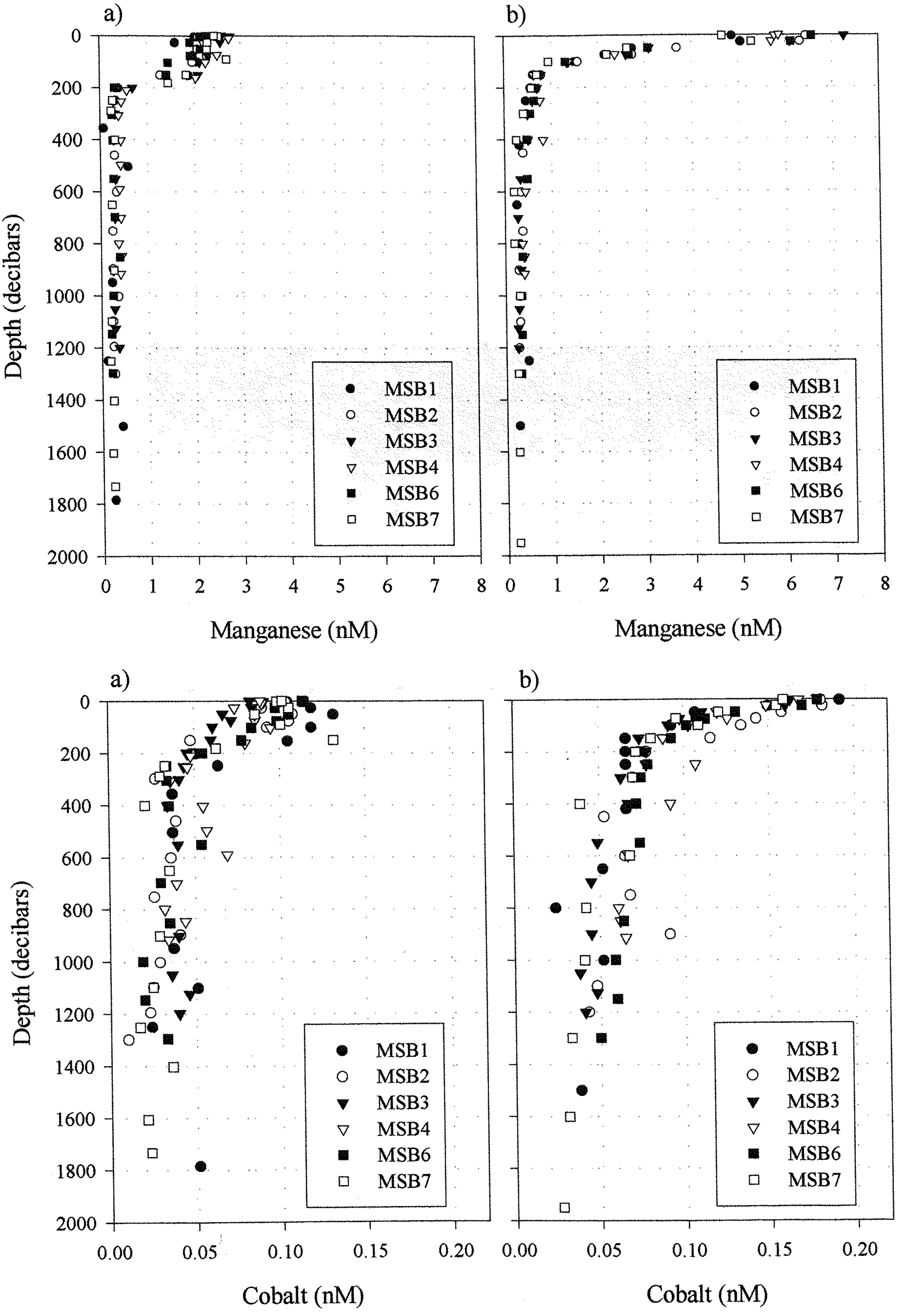

Figure 5.10. Manganese and cobalt depth profiles for a) March and b) September 1997 in the south Aegean Sea. Note: Symbol size represents +/- 1 SD estimate for each measurement.

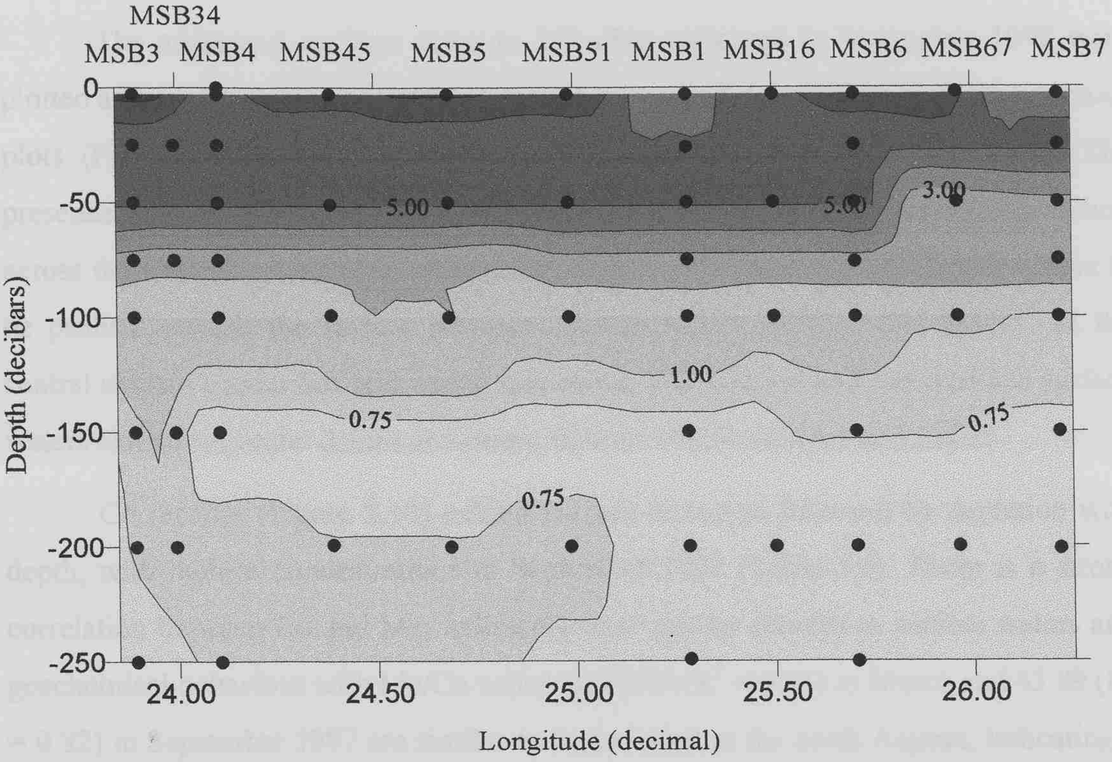

Figure 5.11 Manganese (nM) contour plot along an east-west transect across the Cretan Sea in September 1997.

In addition there is a significant difference in water mass characteristics between both seasons, suggesting a possible source from the warm, saline and low density LSW observed throughout the Cretan Sea in September 1997 only. Below the thermocline concentrations decrease to constant deep water values (Figure 5.10 and Table 5.4). Deep water Mn is slightly higher in September 1997, possibly linked to the increased surface concentrations in this season.

The additional stations down to 250 dbar collected in September 1997 were plotted as a contour plot (Figure 5.11) and when compared to CTD and nutrient contour plots (Figures 4.12 and 4.18 respectively) exhibit some marked similarities. The presence of cyclonic and anticylonic circulation result in upwelling and downwelling across the Cretan Sea, causing cool, dense, high nutrient and low Mn deeper waters to be pushed towards the surface between stations MSB1, MSB16 and MSB67 in the central eastern Cretan Sea and warm, less dense, low nutrient and elevated Mn surface waters extend to greater depths at western stations MSB4, MSB45 and MSB5.

Co profiles (Figure 5.10) exhibit surface elevation followed by depletion with depth, with highest concentrations in September 1997 (Table 5.4). There is a strong correlation between Co and Mn, indicating their similar sources to surface waters and geochemical behaviour with Mn/Co values of 24.99 ($R^2 = 0.71$) in March and 43.89 ($R^2 = 0.82$) in September 1997 are similar to those found in the north Aegean, indicating a difference in source material and cycling in surface waters between the two seasons but not between the north and south Aegean. This relationship has been observed in the western Mediterranean Sea (Morley *et al.*, 1990) and English Channel (James *et al.*, 1993). Below the upper mixed layer, Co concentrations decreases gradually with depth. Deep water values are slightly higher in September 1997 (as observed for Mn).

5.5.2 IRON AND LEAD

Iron profiles exhibit elevated surface concentrations (Figure 5.12 and Table 5.4) with similar concentrations for both seasons. Below the mixed layer Fe decreases to constant deep water concentrations. Similar profiles were observed in the north Aegean, but with higher surface concentrations (especially in March 1997). Iron is a redox sensitive element and has a behavior similar to Mn, with a positive correlation of Mn/Fe value of 1.15 ($R^2 = 0.54$) in March and 2.37 ($R^2 = 0.83$) in September 1997. This difference in the ratio between each season was also observed in the north Aegean (Mn/Fe = 1.11 in March and 6.27 in September) and reflect in part a difference in the composition of source material to surface waters. In March similar ratios suggest a similarity in source composition to both the north and south Aegean, whereas for September a higher ratio in the north due to increased Mn input to surface waters relative to Fe suggest a difference in composition of source material to the north, potentially of Black Sea origin, or a difference in removal rates due to biogenic/particulate material.

Vertical depth profiles of dissolved lead (Figure 5.12) exhibit slight surface elevation, more so in September 1997 followed by depletion with depth below the mixed layer and constant deep water concentrations (Table 5.4). Surface Pb concentrations are slightly lower than the north Aegean, but with similar deep water values (Figure 5.4 and Table 5.1). Similar profiles were observed in the western Mediterranean (Morley *et al.,* 1997), suggesting the importance of aolian inputs to surface waters.

5.5.3 COPPER, NICKEL AND CADMIUM

Copper profiles (Figure 5.13) in March 1997 are relatively uniform with depth, whereas in September 1997 profiles exhibit slight surface elevation, with uniform concentrations below the mixed thermocline (Table 5.4). Deep water concentrations are slightly higher in September 1997. Surface and deep water concentrations are lower than the north Aegean, indicating a higher Cu source to the north, with the formation of NAEGDW from LIW and/or reduced scavenging. Saager (1994) observed similar concentrations and attributed the vertical distribution of Cu in the central and eastern Mediterranean to the presence of water masses, with highest concentrations associated with LIW and low surface concentrations with low salinity MSW (Mediterranean Surface Water). Similarly in the present study highest concentrations are linked to LSW observed in September 1997 only.

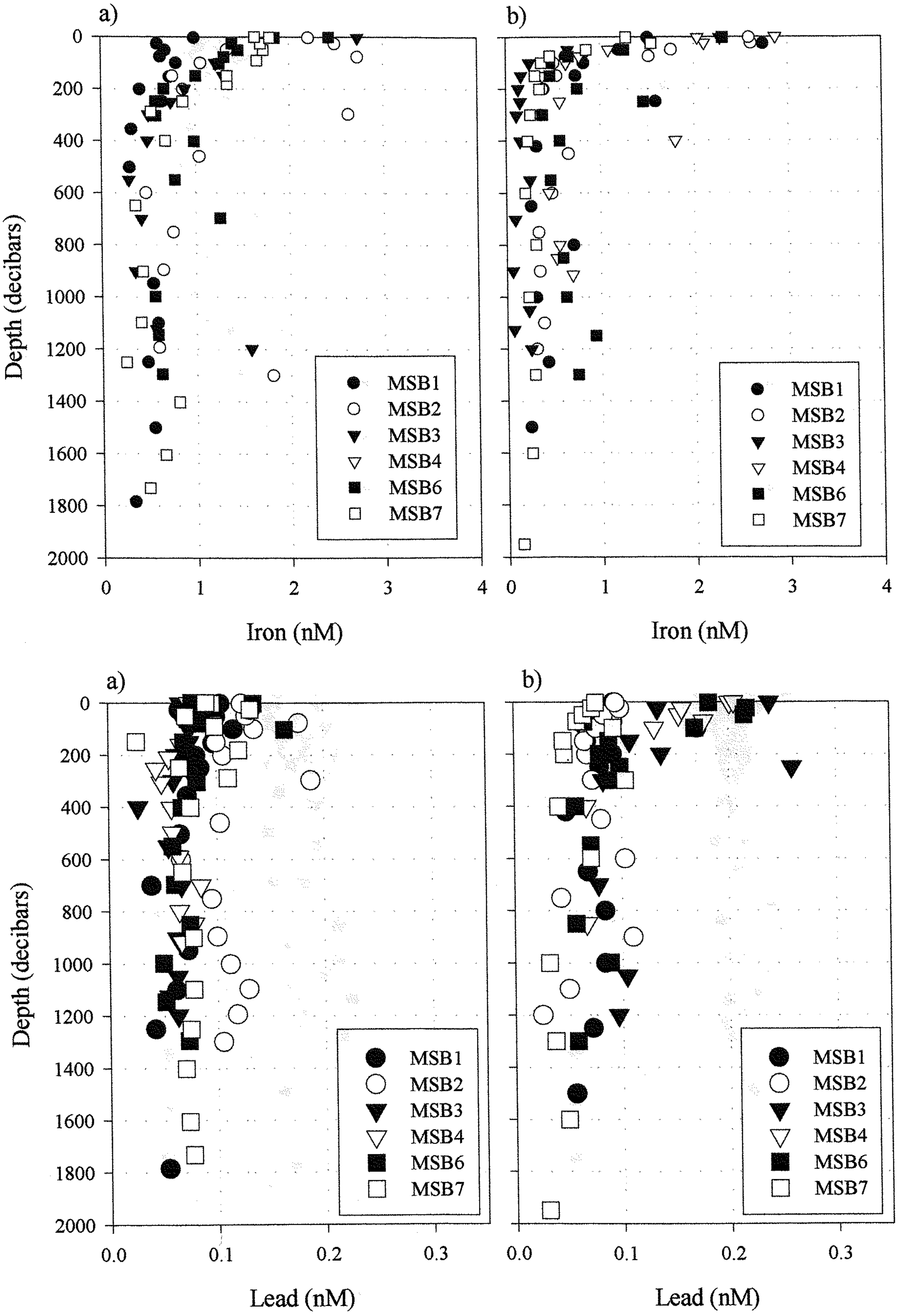

Figure 5.12. Iron and lead depth profiles for a) March and b) September 1997 in the south Aegean Sea. Note: Symbol size represents +/- 1 SD estimate for each measurement.

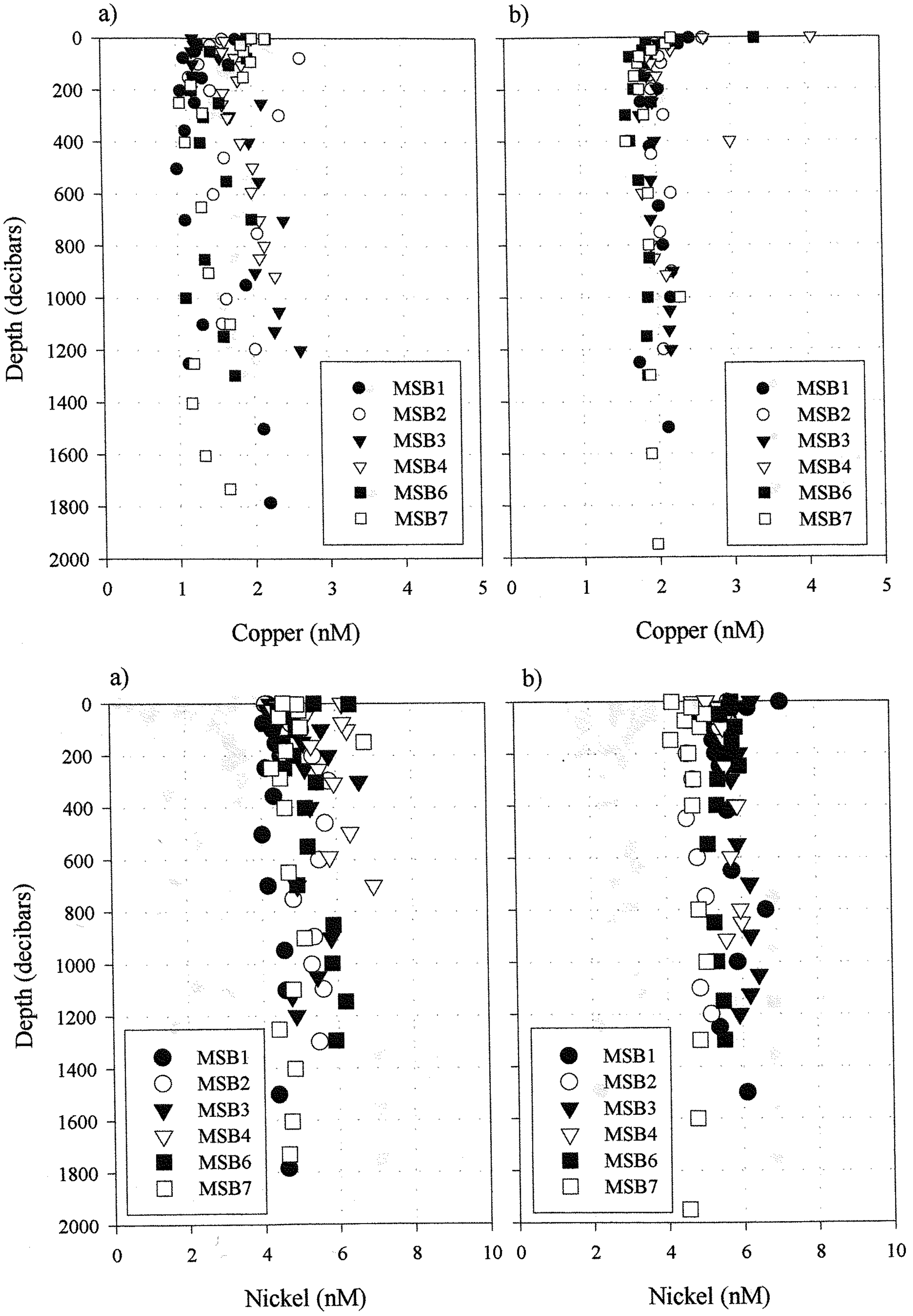

Figure 5.13. Copper and nickel depth profiles for a) March and b) September 1997 in the south Aegean Sea. Note: Symbol size represents +/- 1 SD estimate for each measurement.

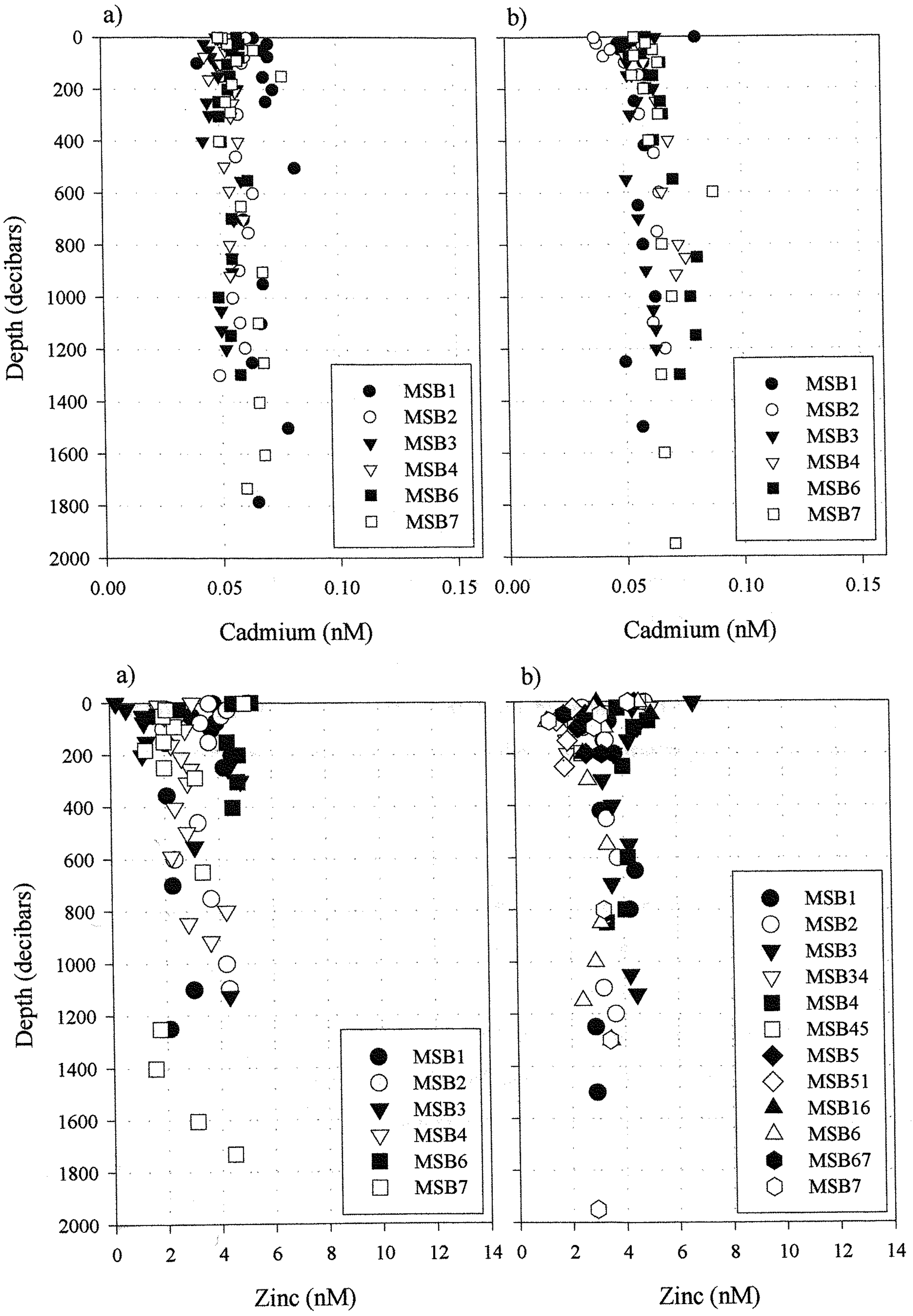

Figure 5.14. Cadmium and zinc depth profiles for a) March and b) September 1997 in the south Aegean Sea. Note: Symbol size represents +/- 1 SD estimate for each measurement.

Nickel exhibits homogenous, although variable depth profiles (Figure 5.13) with little spatial or seasonal variations. Surface concentrations are lower than for the north Aegean, but with slightly higher deep water values (Table 5.1 and 5.4). Similar profiles were observed in the eastern Mediterranean (Saager, 1994), and in the Strait of Otranto, south Adriatic Sea (Tankéré, 1998).

The vertical distribution of cadmium (like copper and nickel) exhibits homogenous depth profiles (Figure 5.14), with slightly higher concentrations in September 1997. Profiles are similar to the north Aegean but with slightly lower concentrations in the south (Table 5.4).

5.5.4 ZINC

Dissolved zinc data in the south Aegean exhibits very erratic depth profiles (Figure 5.14), with Zn being the most susceptible of all the metals under study to contamination. Deep and surface waters are not easily distinguished (Table 5.4) for both seasons, although slight surface elevation is apparent in September 1997. Some surface and sub-surface depletion in March 1997, most noticeable at station MSB3, the western most station suggests potential removal from biogenic particles. However the same station in September 1997 exhibits the highest concentration of surface Zn (Figure 5.14).

5.6 MILOS

Milos, an island along the Cyclades Plateaux, known to be hydrothermally active, has been previously studied for seawater and sediment enrichment of metals (Varnavas *et al.*, 1993) and is a potential source of dissolved metals to Aegean waters. A limited number of samples were collected in March and September 1997 (Table 5.5, Figures 5.15 and 5.16) to ascertain the influence of hydrothermal activity at Milos on the water column. Enrichment factors for each metal were calculated (above metal concentration of the Cretan Sea).

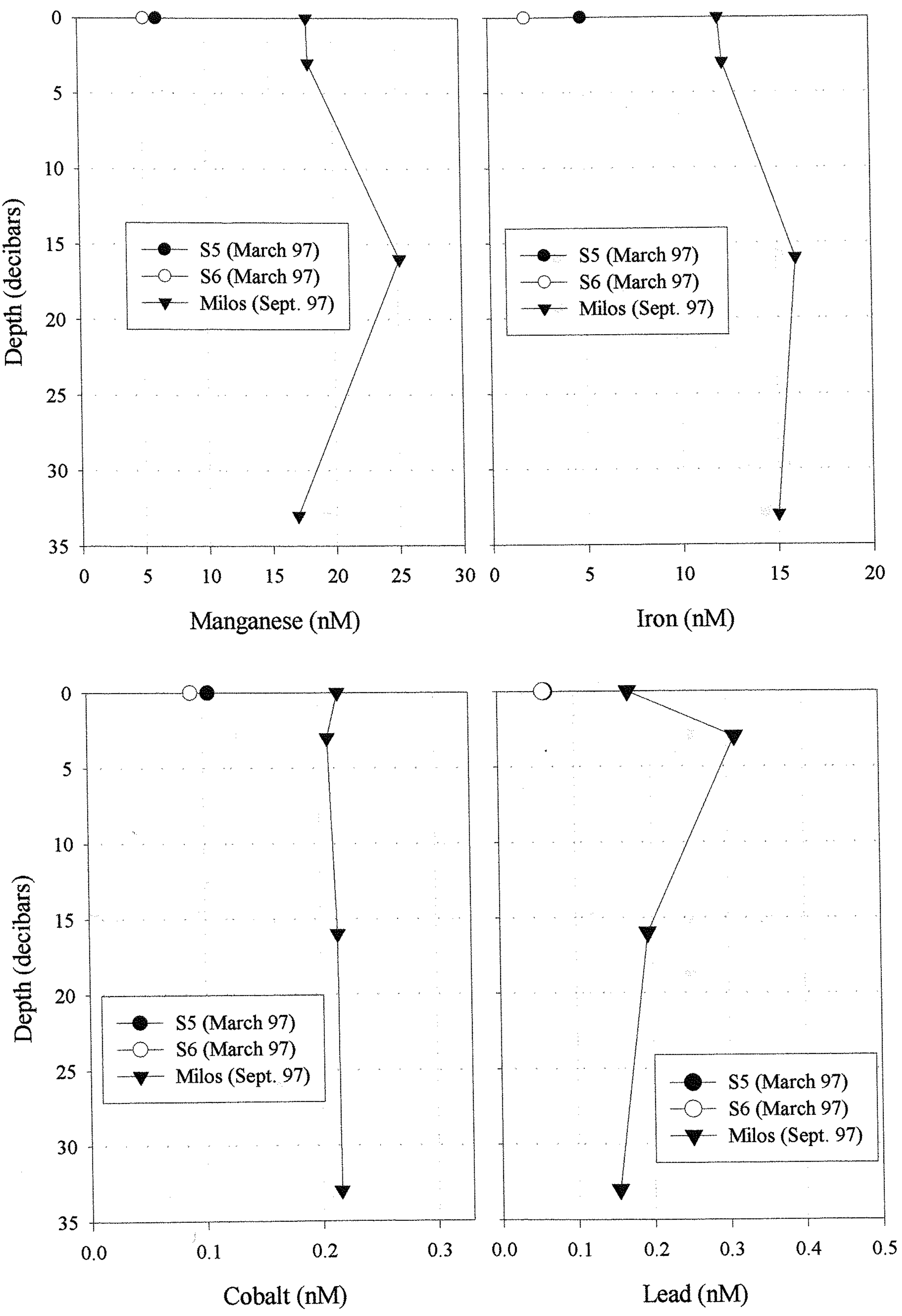

Figure 5.15. Manganese, iron, cobalt and lead depth profiles for Milos. Note: Symbol size represents +/- 1 SD estimate for each measurement.

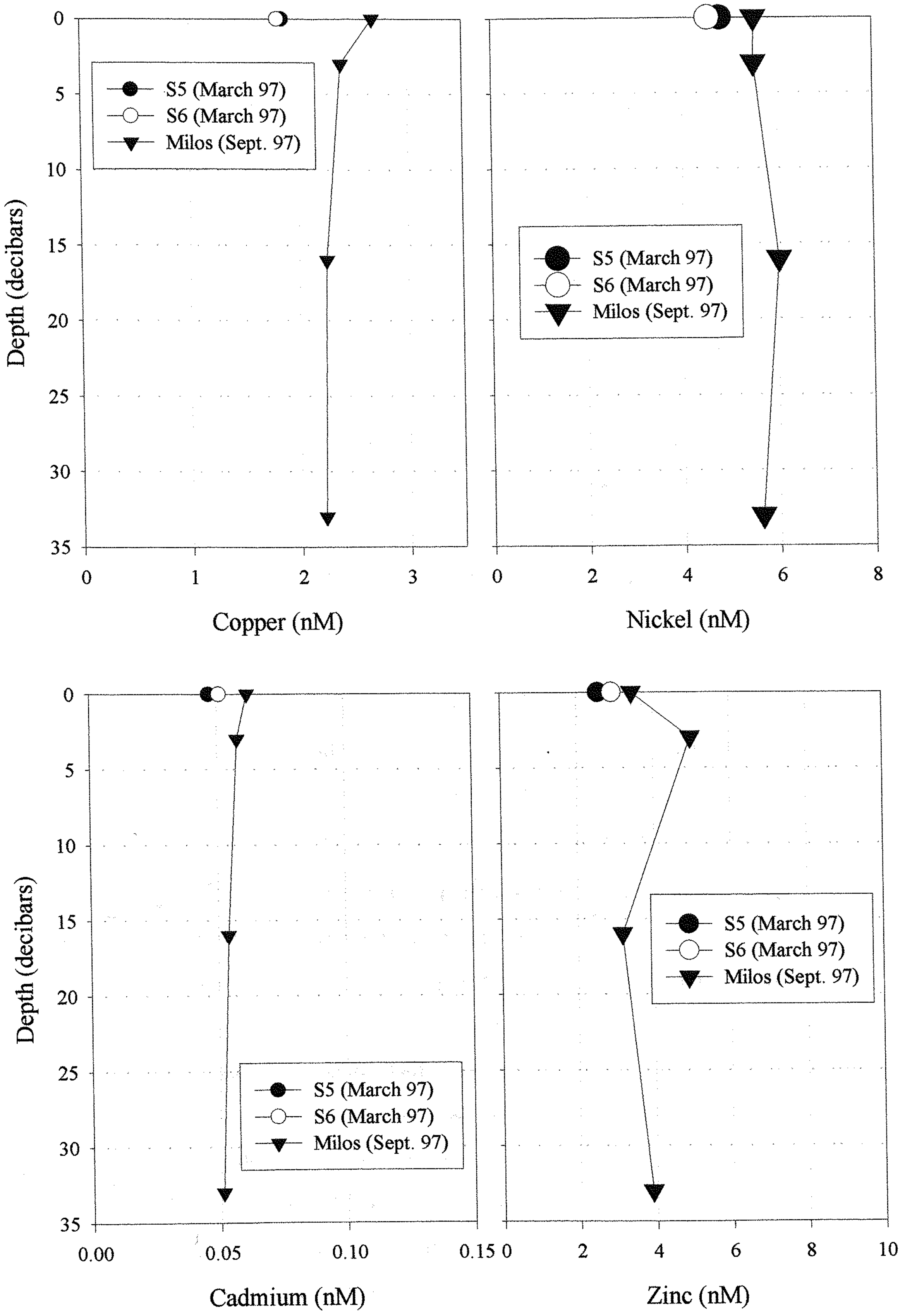

Figure 5.16. Copper, nickel, cadmium and zinc depth profiles for Milos. Note: Symbol size represents +/- 1 SD estimate for each measurement.

Table 5.5 Comparison between surface metal concentrations at Milos and the Cretan Sea (MSB) and enrichment factors (EF) for March and September 1997. NS = no significant difference

Conc. (nM)	Milos		Cretan Sea		EF	
	March '97	Sept. '97	March '97	Sept. '97	Mar. '97	Sept. '97
Mn	5.2 - 6.2	17.0 - 25.2	2.0 - 2.6	4.9 - 7.3	2.0 - 3.1	2.3 - 5.1
Fe	1.9 - 4.9	12.1 - 16.0	1.0 - 2.7	1.3 - 2.8	< 4.9	4.3 - 12.3
Co	0.09 - 0.11	0.21 - 0.22	0.08 - 0.13	0.13 -0.20	NS	1.1 - 1.7
Pb	0.06	0.15 - 0.31	0.06 - 0.14	0.06 - 0.24	NS	< 5.2
Cu	1.8	2.2 -2.7	1.0 - 2.6	2.1 - 4.1	NS	NS
Ni	4.6 - 4.8	5.5 - 6.0	4.1 - 6.4	4.2 - 7.1	NS	NS
Cd	0.05	0.05 - 0.06	0.04 - 0.07	0.04 - 0.08	NS	NS
Zn	2.6 - 2.9	3.2 - 5.0	0.2 - 5.3	1.2 – 6.7	NS	NS

There is a significant seasonal difference in the concentration of all metals under analysis at Milos, with higher concentrations in September 1997 (Figures 5.15, 5.16 and Table 5.5). This difference is greatest for Mn and Fe followed by Co and Pb. The hydrothermal activity around Milos is localised and this difference is due to a slight difference in the sample position between seasons and potential temporally variability, also observed by Varnavas *et al.* (1993). When compared to surface samples in the Cretan Sea (Table 5.5) a significant increase is observed in manganese, iron and to a lesser extent cobalt and lead at Milos. Due to the proximity of Milos to the Cretan stations (especially MSB4 and MSB5), the assumption is made that any difference in metal concentration will be due to hydrothermal activity (Table 5.5).

5.7 ATMOSPHERIC TRACE METAL FLUX CALCULATIONS AND RESIDENCE TIMES IN SURFACE WATERS

5.7.1 ATMOSPHERIC TRACE METAL FLUX CALCULATIONS

From the current data set, the importance of dissolved trace metal sources to Aegean surface waters is established. The important role of atmospheric sources of trace metals to the Mediterranean has been previously established (Guieu *et al.*, 1997; Guerzoni *et al.*, 1999). Calculations have therefore been made using atmospheric fluxes (soluble fractions) from wet and dry deposition from the central Mediterranean (Guerzoni *et al.*, 1999) and NW Mediterranean (Guieu *et al.*, 1997). This includes the soluble component of atmospheric dry deposition (Guieu *et al.*, 1997; Guerzoni *et al.*, 1999).

Table 5.6 Range of total dissolved atmospheric trace metal fluxes to surface waters, above the thermocline (calculated from wet and dry deposition) using data from the central Mediterranean (1) (Guerzoni *et al.*, 1999) and north-west Mediterranean (2) (Guieu *et al.*, 1997).Thermocline depth is given in brackets for each season.

		North Aegean nM/yr.		South Aegean nM/yr.	
	Dissolved Flux mol/km^2/yr.	March 1997 (~100 m)	Sept. 1997 (~55 m)	March 1997 (~125 m)	Sept. 1997 (~50 m)
Mn ^{2}	50 - 220 $^{(2)}$	0.5 - 2.2	0.9 - 4.0	0.4 - 1.7	1.0 - 4.4
Fe ^{1}	90 - 180 $^{(1)}$	0.9 - 1.8	1.6 - 3.3	0.7 - 1.4	1.8 - 3.6
Co ^{2}	0.3 - 2.2 $^{(2)}$	0.003 - 0.022	0.005 - 0.040	0.002 - 0.017	0.006 - 0.044
Pb ^{1}	5 - 24 $^{(1)}$	0.05 - 0.24	0.09 - 0.44	0.04 - 0.19	0.10 - 0.48
Cu ^{1}	45 - 72 $^{(1)}$	0.45 - 0.72	0.82 - 1.31	0.35 - 0.57	0.90 - 1.44
Ni ^{1}	17 - 24 $^{(1)}$	0.17 -0.24	0.31 - 0.44	0.13 - 0.19	0.34 - 0.48
Cd ^{1}	0.5 - 2.8 $^{(1)}$	0.005 - 0.028	0.009 - 0.051	0.004 - 0.022	0.01 - 0.056
Zn ^{1}	210 - 460 $^{(1)}$	2.1 - 4.6	3.8 -8.4	1.7 - 3.6	4.2 - 9.2

Thermocline depths were estimated for each station for March and September 1997, from CTD salinity and temperature data. These fluxes are used to indicate the potential input to the surface waters from the atmosphere of each trace metal. There is no data as yet for the eastern Aegean as yet, although Guerzoni *et al.* (1999) observed mean annual atmospheric mass fluxes at Crete (21 g m^{-2}) and Israel (50 g m^{-2}) were found to be highest in the Mediterranean. However the fate of an atmospherically-transported trace metal, once deposited at the sea surface, depends on its thermodynamic speciation in seawater, its speciation in the parent aerosol, and the kinetics controlling any speciation change (Guerzoni *et al.*, 1999).

Assuming a constant atmospheric flux of trace metals to surface waters, Table 5.6 gives the flux ranges for each metal. Zinc exhibits the highest flux, followed by Mn, Fe, Cu. Ni, Pb with Cd and Co the lowest fluxes. The seasonal variation is due to the change in thermocline depth between seasons, with highest fluxes corresponding with the shallowest thermocline in September for both seasons.

5.7.2 RESIDENCE TIME CALCULATIONS FOR SURFACE WATERS

The residence time is the average time spent in a reservoir by an individual molecule. To calculate the residence time of dissolved trace metals in the Aegean, information on the fluxes from the Black Sea, rivers and exchanges through the Cretan Straits would be required. Therefore for the purpose of this work the residence times of the upper water column in the north and south Aegean have been calculated. By using metal atmospheric flux calculations, the residence times of each metal can be calculated for the north and south Aegean during March and September 1997 using the equation where:

$$\tau = A/(\delta A/\delta t)$$

Where : τ = Element residence time in surface waters (years)

A = Total mass of metal in the upper mixed layer (mol/m^2)

($\delta A/\delta t$) = Rate of atmospheric input (mol/m^2/yr.)

This makes the assumptions: (1) the only source of dissolved trace metals to surface waters is from the atmospheric soluble fractions (2) the atmospheric metal fluxes to the Aegean are similar to those found in the central and western Mediterranean and remain spatially and temporally constant (3) the removal rate from surface waters will equal the atmospheric flux i.e. the Aegean Sea is in a steady state.

The residence times (RT) vary for each metal, and exhibit spatial and seasonal variation (Table 5.7). In the north Aegean the order of RT is Co > Ni > Cd > Mn > Cu > Fe > Pb > Zn, and in the south Aegean, Ni > Co > Cd > Mn > Cu > Pb > Fe > Zn. Residence times reflect the reactivity of each metal in surface waters. Shorter residence times reflect a high atmospheric source relative to observed surface water concentration and increased reactivity. As the atmospheric source decreases relative to the surface metal concentration the RT increases. In addition as shown in Table 5.6, a difference in thermocline depth, i.e. a shallow thermocline results in a higher flux of metal to surface waters, and a shorter residence time.

There is a consistent spatial and seasonal pattern of RT. In the north Aegean, significantly longer residence times are observed than the south, due to the overall greater surface metal concentrations. Black Sea Water supplies the north Aegean with an additional source of dissolved metals, therefore the assumptions made in the calculation of RT in the north is incorrect, (an additional source would increase the residence time). Seasonal variability exhibits longer residence times in March than September 1997 for both the north and south Aegean, due to the deeper thermocline throughout the Aegean in March, even though surface metal concentrations are overall greater in September.

Table 5.7 Residence times of dissolved trace metals in surface waters in the north and south Aegean for March and September 1997 and the Adriatic Sea (Tankéré, 1998).

	North Aegean (years)			South Aegean (years)		
	Mean (years)	March 1997 (~100 m)	Sept. 1997 (~55 m)	Mean (years)	March 1997 (~125 m)	Sept. 1997 (~50 m)
Mn^2	6.6	1.9 -8.5	3.0 - 13.2	3.3	1.3 - 5.6	1.2 - 5.1
Fe^1	1.8	1.7 - 3.5	0.6 - 1.2	1.2	1.0 - 2.0	0.7 - 1.3
Co^2	25.0	6.3 - 46.0	5.7 - 42.1	18.6	5.5 - 40.0	3.5 - 25.5
Pb^1	1.4	0.5 - 2.6	0.5 - 2.2	1.3	0.6 - 2.9	0.3 - 1.6
Cu^1	4.6	3.9 - 6.3	3.1 - 5.0	2.9	2.9 - 4.7	1.6 - 2.6
Ni^1	23.9	23.1 - 32.6	16.5 - 23.2	21.9	25.2 - 35.6	11.1 - 15.7
Cd^1	6.9	2.6 - 14.8	1.6 - 8.7	5.8	2.5 - 14.1	1.0 - 5.7
Zn^1	1.3	0.8 - 1.8	0.8 - 1.7	1.0	0.9 – 1.9	0.4 – 0.9

There is very little metal residence time data for the Aegean Sea. Tankéré (1998) calculated the residence times for surface waters in the Adriatic from a 3 box model and observed shorter residence times than in the present study (Table 5.7), with all metals less than 1 year. In the south Adriatic residence times for Mn, Fe, Pb, and Zn were shorter than the residence time of surface waters (0.39 years) suggesting removal from the surface waters, with Cu and Ni RT similar to that of water. During the period of investigation in the Adriatic (1994) deep water formation, in the form of EMDW, provided deep waters to the eastern Mediterranean with a resulting short residence time, which has since decreased and been replaced in dominance by CDW formation in the Cretan sea (Lascaratos *et al.*, 1999). It is therefore possible that Adriatic Sea metal residence times have significantly increased since 1994.

At present there is no residence time for water in the Aegean Sea to compare with metal RT, although Friligos (1985) calculated minimum turnover times in the Saronikos Gulf of 8.1 and 0.9 years for the surface 100 m. A residence time for the Mediterranean of about 100 years was suggested by Béthoux *et al.* (1998). The Mediterranean Sea is observed to be no longer in a steady state (per. comm. Dr. M.N. Tsimplis). If this also includes the Aegean then residence times should be re-termed turnover times. In the 1980s the residence time of the Western Mediterranean was calculated as 15.2 years, with corresponding residence times of 10-22, 5-6 and 7-11 years for Cd, Cu and Pb respectively (Martin *et al,* 1989).

5.8 PARTICULATE DATA FOR THE AEGEAN SEA

The cycling of dissolved trace metals in the marine environment is closely linked to the presence of inorganic and organic particulates, with subsequent adsorption and desorption processes, which will vary spatially and temporally. Particulate metal fluxes and data will therefore enable a more in-depth interpretation of the biogeochemistry of dissolved metals in the Aegean Sea.

5.8.1 PARTICULATE METAL FLUXES (Fe, Mn, Cu, Zn and Pb)

Particulate metal fluxes (Fe, Mn, Cu, Zn and Pb) at 500 m and 35 mab (meters above the bottom) enable a better understanding of the rate of removal of dissolved trace metals from surface and deeper waters, and will substantiate the previously calculated residence times. The comparison of water column and atmospheric fluxes can indicate the percentage contribution of atmospheric fluxes to the Aegean Sea, also investigated by Guerzoni *et al.* (1998) in the central Mediterranean. Table 5.8 compares the water column (500 m) and atmospheric fluxes for the north and south Aegean Sea during March and September 1997, assuming similar atmospheric fluxes as the central and NW Mediterranean (Guieu *et al.*, 1997 and Guerzoni *et al.*, 1999). For Cu and Zn, atmospheric flux estimates for both regions were considered due to the significant difference in fluxes between regions of the Mediterranean Sea. Although trap deployment occurred from 1/4/97 to 31/3/98, for the purpose of this work the mean flux from 1/4/97 to 31/10/97 was taken, covering the period of both cruises (Price *et al.*,1999b). Subsequent to October 1997, fluxes increased dramatically and would therefore not be representative of the period under examination. The ratio of Atmospheric/water column flux indicates the proportion of atmospheric fluxes that contribute to the water column flux at 500 m Total atmospheric fluxes have been used instead of particulate fluxes, due to the complex biogeochemistry of trace metals in the upper ocean where dissolution and absorption onto particles occurs.

Table 5.8 indicates a significant difference in water column fluxes in the north and south Aegean, along with variable Atmospheric/Water column flux values for each metal concerned. Water column fluxes are much greater in the north than the south Aegean (by a factor of 5 to 12), resulting in much lower Atmospheric/Water column flux values in the north, indicating that for Mn, Fe and a lesser extent Pb, atmospheric fluxes are not the sole source of trace metals to the north Aegean. In the south Aegean, lower water column fluxes and high ratios suggest that the atmosphere is the predominant source of all metals to the Cretan Sea. Guerzoni *et al.* (1998) observed similar Atmospheric/water column values in the south Adriatic to the north Aegean, suggesting that both areas are proportionally influenced by atmospheric sources. Fluxes to bottom sediments (in brackets) are greater for all metals in the north and south Aegean.

Table 5.8. Comparison of water column with atmospheric (Guieu *et al.*, 1997[1]; Guerzoni *et al.*, 1999) metal fluxes for the north (MNT1) and the south (MST2) Aegean Sea.

	Total	North Aegean 500 m (35mab)		South Aegean 500 m (35mab)	
	Atmos. flux kg/km^2/yr.	Water flux kg/km^2/yr.	Atm./Water	Water flux kg/km^2/yr.	Atm./Water
Total	12000 [2]	101076 (424854)	0.1	35037 (47688)	0.3 (0.3)
Al	313 - 915 [2]	6473 (27759)	< 0.1	731 (1065)	0.4 - 1.3 (0.3 - 0.9)
Mn	5.8 -22.0 [1]	211 (1297)	< 0.1	18 (31)	0.3 - 1.2 (0.2 - 0.7)
Fe	150 - 418 [2]	4222 (17371)	< 0.1	495 (718)	0.3 - 0.8 (0.2 - 0.6)
Pb	0.6 - 4.0 [2]	6.1 (18.7)	0.1 - 0.7 (< 0.2)	0.9 (1.1)	0.7 - 4.4 (0.5 - 3.6)
Cu	6.0 - 9.0 [2] 2.2 - 3.2 [1]	3.2 (14.6)	1.9-2.8 (0.4-0.6) [2] 0.7 - 1.0 (0.2) [1]	0.9 (1.4)	6.7 - 10.0 (4.2 - 6.4) [2] 2.4 - 3.5 (1.6 - 2.3) [1]
Zn	16.7 - 35.0 [2] 4 [1]	30.3 (98.8)	0.6-1.2 (0.2-0.3) [2] 0.1 (< 0.1)	6.3 (7.5)	2.6 - 5.6 (2.2 - 4.7) [2] 0.6 (0.5) [1]

Price *et al.* (1999b) summarises the Mineralogical, geochemical and isotopic composition of settling particles (MATER Work 418). In summary at MNT1, 500 m and in the bottom (35 mab) trap, mass fluxes are lower in the period of April to August 1997, followed by higher fluxes, with much higher fluxes in the bottom trap. Metal fluxes show a similar trend to mass fluxes, and that of Al is nearly identical, with higher fluxes in the bottom trap particularly in late winter/spring. C_{org}/Al ratios at 500 m infer considerable lateral supply of constituents to the northern Aegean from the resuspension of sediment caused by intense fishing activity on the northern shelf from October to May of each year. C_{org} and Si_{bio} fluxes at 500 m indicate higher biological productivity and phytodetritus fallout occurs in the winter and early spring rather than the summer.

Metal/Al ratios are generally higher in between May and October at times of low mass flux, and imply that overall the lateral sediment input is of lower metal/Al ratio than are other constituents in the traps. During this period river inputs are low, strong northerly wings occur which may carry significant aolian detritus to the basin and fishing activity is banned. The exception is Fe/Al at 500m, with high ratios throughout the period of trap collection and may be influenced by the introduction of either aolian detritus or may be biologically precipitated in the upper water column. In the winter and spring high lateral sediment input (during the fishing season) masks particulate metals derived from aolian or biological sources or abiotic precipitation in the water column. Excess Zn shows similarity with that of total mass flux, with a potential source of anthropogenic zinc from municipal and industrial waste runoff. Excess Pb, also with some similarity to mass fluxes, except with high fluxes during May to October when elemental fluxes are generally low (along with lateral inputs), implying and an anthropogenic atmospheric contribution of Pb during this period.

Within the Cretan Sea, SPM composition indicates little lateral supply of abiotic elements compared with the aolian input and biological activity is low and limited to nutrient supply within cyclonic eddies rather than from riverine sources. Mass fluxes are an order of magnitude less than the north Aegean. Al fluxes constitute a lower percentage of the mass flux than the north with generally higher fluxes in late winter and spring than in summer, following the same pattern as major biogenic constituents, particularly C_{org} fluxes, and implies that Al is effectively packaged by organic matter which follows fallout. Fe/Al ratios are higher (> 0.6) than the shelf derived sediment observed in the north Aegean and indicate the possibility of iron oxyhydroxide in the traps. Zn/Al and Cu/Al ratios are approximately twice as high in the Cretan Sea than the northern Aegean (exceeding those in surficial sediments), indicating scavenging of Zn and Cu by biogenic constituents in the water column. Zn and Cu/Al ratios of the underlying sediments are much lower due to recycling as a consequence of organic matter respiration and biogenic constitution dissolution probably at the sediment water interface. Pb/Al ratios do not differ significantly from northern traps, due to unusually high Pb loading, probably anthropogenic, and also found in the SPM of northern stations. Pb/Al ratios in the south are much higher than in the sediments, suggesting, like Cu and Zn, Pb assimilation onto falling particles.

Finally Pb and Zn fluxes were computed with respect to the composition of buried sediments ($Pb_{ex} = Pb_{tot} - Pb/Al_{buried\ sed}$) and from this fluxes are in broad agreement with C_{org} and Si_{bio} fluxes, with higher fluxes in spring 1997 and winter 1998.

5.8.2 SUMMARY OF PARTICULATE DATA

SPM, particulate Al, Ti, Si_{bio} and metals Mn , Fe, Cu, Zn, Pb in the northern (MNB) and southern (MSB) stations of the Aegean Sea were collected for March and September 1997 and the findings will be briefly summarised (Price *et al.*, 1999b).

In the north high Al (2-6 μgl^{-1}) especially in March 1997, along with a strong relationship with Fe (Fe/Al = 0.52) relate to riverine sediment resuspended on the northern shelf caused by fishing activities, with transport of this on or within a number of defined water masses, especially at 200-250 m, 300-400 m and ~ 600 m. Al concentrations are lower in the Cretan Sea (0.5 - 1.0 μgl^{-1}) than northern stations, with higher concentrations at 200 m and especially 600-800 m, suggesting pluming of resuspended sediment at the shelf edge and on pynoclines associated with the Cretan Deep Water. In the north and south Aegean Ti_{ex} and Fe_{ex} exhibit linear relationships, with higher Ti_{ex} relative to Fe_{ex} in September 1997, indicating an aolian supply of Saharan origin (characteristic of eastern Mediterranean sediments), even though the prevailing winds are northerly. The distribution of particulate Mn_{ex}, that is Mn in concentrations above that held in aluminosilicates (of Mn/Al ratio = 0.012) illustrates the direct or indirect river influence on the composition of SPM. Mn_{ex} values assume oceanic values in the Cretan Sea, with a distribution following that of Al, implying that it is likely to occur as oxyhydroxide coatings on aluminosilicates. In surface waters Mn_{ex} values are extremely low due to the photoinhibition of Mn oxidation of dissolved Mn II. In the north Aegean Mn_{ex} concentrations are higher (~ 0.1-0.2 μgl^{-1}) and like Al illustrate the influence of river runoff from northern Greece and/or injection of Dardanelles water to the area in summer.

Particulate Cu, Zn and Pb were studied with respect to their inputs into the north Aegean Sea, especially with regard to their introduction by sediment resuspension from the north Aegean shelf and their input to the basin from the Black Sea. In the Cretan Sea, particulate trace metals have been assessed in respect to biogenous constituents. For all stations in the Aegean Sea the trace metal/Al ratios are extremely high, implying a significant proportion of each element is not bound in the lattice of aluminosilicates. Particulate excess Cu, Pb and Zn concentrations were established, with in the Cretan Sea highest concentrations for Zn_{ex} and Pb_{ex} lowest. Similarity was observed with profiles of major biogenic elements, especially Si_{bio} and P_{org}, implying that these elements are likely to be bound with biogenic substances, highest concentrations occur in particulate matter in the euphotic zone. In the north Aegean, concentrations of Zn_{ex} and Pb_{ex} are higher than in the Cretan Sea, particularly in the upper 250 m in March 1997 when particulate Pb_{ex} concentrations can reach 100 - 200 ngl^{-1} in contrast to September (10 - 20 ngl^{-1}). This seasonal contrast is related to the high level of injection of metals (particularly Pb) from the northern shelf and is probably related to fishing activity in winter months (October to May). In the north Aegean, input of BSW via the Straits of Dardanelles is much more evident in late summer than winter, with associated lower salinities, although no obvious elevated excess metal concentrations occur, implying that the metal discharge via the Dardanelles is in the dissolved phase.

CHAPTER 6

DISCUSSION

6.1 INTRODUCTION

Although focusing on the distribution and biogeochemistry of dissolved trace metals in the Aegean, the aim of this work is also to examine the Aegean Sea as a dynamic system. Through the investigation of the physically and biological processes at work, along with atmospheric and particulate interactions, a more thorough understanding of the processes controlling trace metal distribution and biogeochemistry in the Aegean can be developed. In this chapter, An initial overview of each metal is given (6.2) followed by a broader examination of the major processes and sources influencing trace metals in the Aegean Sea (6.3). Finally, the interactions of the Aegean with the Mediterranean Sea are reviewed, with reference to furthering the knowledge of trace metals in the eastern Mediterranean (6.4).

6.2 TRACE METAL DISTRIBUTION AND BIOGEOCHEMISTRY IN THE AEGEAN

The biogeochemistry and distribution of each metal are discussed with respect to coastal and atmospheric sources, water masses and circulation, particulate interactions and calculated residence times for both the northern and southern Aegean Sea. The trace metal distributions in the study area are then compared to those found in the Mediterranean Sea and open ocean.

6.2.1 MANGANESE AND COBALT

In the Aegean Sea, as in the Mediterranean, Mn is one of the few elements showing a typical open ocean distribution. Elevated surface water concentrations are a result of atmospheric deposition, photochemically inhibited bacterial oxidation of Mn (II) and photoreduction of existing Mn oxides (Sunda *et al.*, 1983), with additional surface sources from the Black Sea, and potential coastal inputs to the north Aegean.

Although atmospheric fluxes of Mn to the Mediterranean are smaller than other metals, such as Fe and Zn (Guieu *et al.*, 1997), the high solubilities of Mn in seawater of 60 to 67% (Guerzoni *et al.*, 1999), result in a potentially significant soluble flux to Mediterranean surface waters (Table 5.6). In the southern Aegean, atmospheric deposition is the major source of Mn to surface waters. By comparing sediment trap fluxes at 500 m (Price *et al.*, 1999b) with total atmospheric fluxes (Guieu *et al.*, 1997; Guerzoni *et al.*, 1999) 30-120 % of the Mn particulate flux to deeper waters is from the atmosphere and 20 to 70 % to the bottom sediments (Table 5.8). In the north Aegean less than 10 % of atmospheric fluxes contribute to sediment trap fluxes, and coastal and BSW inputs play an important additional role.

In north Aegean surface waters a linear Mn/salinity relationship indicates a fresher water source predominantly of BSW origin. Calculated Mn concentrations for the Straits of Dardanelles (Table 5.3) fall within observed concentrations for the Black Sea (Tankéré, 1998; Windom *et al.*, 1998) and, thus, indicate greater Mn fluxes to the northern Aegean for September 1997. In addition, the particulate distribution of Mn_{ex} (Price *et al.*, 1999b) in the north Aegean supports the idea of a freshwater influence on the composition of SPM, whereas in the south Mn_{ex} values assume oceanic values. Slight variations in the Mn/salinity relationship between stations indicate that other processes and/or sources are present in the north Aegean, so that a one point source and a conservative relationship cannot be assumed. For example the Mn/salinity relationship is greatest at MNB6 on the Samothraki Plateau, where a strong upper mixed layer prevents mixing of surface waters rich in Mn with underlying waters. In addition MNB6 is situated close to the rivers Nestos and Evros, presenting a potential additional source of Mn. Although at present Mn data is not available for these rivers, Dassenakis *et al.* (1997) noted variable Mn concentrations in rivers and coastal areas around Greece ranging from 3 to 48 nM. The highest concentrations were found in the Elefsis Gulf (close to Athens) and Euripos Straits, thus, emphasising the importance of localised riverine Mn sources to the Aegean Sea.

The presence of numerous water masses and complex circulation, including anticyclonic and cyclonic gyres and eddies in the Aegean Sea, have been well established (Yüce, 1995; Poulos *et al.*, 1996; Georgopoulos *et al.*, 1998; Theocharis *et al.*, 1999). The inflow of Black Sea Water through the Straits of Dardanelles to surface waters of the northern and central Aegean with an elevated Mn signature has already been discussed. In addition, slightly elevated Mn concentrations were observed in Levantine Intermediate Water in the north Aegean at depths of 150 - 200 m in March

1997 only, also inferred to exist by Saager *et al.* (1993) and Morley *et al.*, (1997) in the eastern and central Mediterranean Sea respectively. The thermocline depth varies seasonally (deeper in March than in September 1997) and influences the Mn depth profiles in the northern and southern Aegean. Along an east west transect across the Cretan Sea in September 1997 (due to more intensive sampling) cyclonic and anticyclonic circulation were identified, and an Mn contour plot follows the density and temperature isolines with upwelling of Mn low concentration intermediate waters in the eastern-central Cretan Sea (Figure 5.11).

Surface Mn concentrations are generally lower in the Cretan Sea than the northern Aegean, with approximately half the surface and deep water concentrations (Tables 5.1 and 5.4). Cretan Sea Mn surface concentrations in March 1997 are in good agreement with recent data for the Mediterranean (Statham *et al.*, 1985; Saager, 1994; Morley *et al.*, 1997). However in both north and south Aegean surface waters in September 1997, concentrations are higher than previously observed in the open Mediterranean.

Deep water concentrations are slightly higher in the north Aegean (0.3 - 0.9 nM) than the Cretan Sea (0.2 - 0.5 nM) due to the increased Mn concentrations in LIW and BSW which form the NAEGDW (Theocharis & Georgopoulos, 1993; Georgopoulos *et al.*, 1998). A slight increase in dissolved Mn concentrations above the sea bed for northern stations indicate a potential release from particles, also observed in the eastern Mediterranean by Saager (1994). Similar deep water Mn concentrations to the Cretan Sea of 0.6 nM (Statham *et al.*, 1985) to 0.2 nM (Morley *et al.*, 1997) have been observed in the Western Mediterranean with concentrations of 0.1 - 0.4 nM in the eastern Mediterranean (Saager, 1994).

In the North Atlantic, surface concentrations are lower (1.2 - 2nM) than the Mediterranean (Statham *et al.*, 1985; Saager *et al.*, 1997) thus, indicating the importance of Mn surface sources to Mediterranean waters. Given the efficient removal of Mn from the water column, local sources and sinks strongly influence the distribution of Mn in the Mediterranean (Saager, 1997). North Atlantic Deep Water concentrations are similar to the Mediterranean (0.2-0.5 nM) and tend to decrease with the age of the water mass, due to continued scavenging. Therefore deep water concentrations in the Indian and Pacific Waters are lower (0.1-0.2 nM) than the North Atlantic (Landing & Bruland, 1980;1987; Morley *et al.*, 1993; Statham *et al.*, 1998).

The calculated residence time of Mn in the southern Aegean of 1 to 6 years along with high marine fluxes (18 to 31 kg/km^2/yr.) reflect the Mn particle reactivity, and the rapid concentration decrease below the mixed layer and low deep water concentrations characteristic also of open ocean waters (Landing & Bruland, 1980). The ocean Mn residence times have been calculated for surface waters, ranging from 5 to 25 years in the Pacific (Klinkhammer & Bender, 1980), 11 to 68 years in the East Atlantic (Statham & Burton, 1996) and 5 to 21 years in the Sargasso Sea (Jickells *et al.*, 1994; Jickells, 1999). However little residence time information exists for the Mediterranean Sea.

There is also little information on cobalt in the Mediterranean Sea (Morley & Burton, 1993; Zhang & Wollast, 1993; Morley *et al.*, 1997; Tankéré, 1998) or oceans (i.e. Burton *et al.*, 1993; James *et al.*, 1993; Tappin *et al.*, 1993) due to difficulties in achieving analytical detection limits, with concentrations of below 0.1 nM (Burton & Statham, 1988). The positive co-variance between dissolved manganese and cobalt has been well documented (i.e. Burton & Statham, 1988; James *et al.*, 1993; Tappin *et al.*, 1993), suggesting similar cycling pathways in the marine environment.

A good correlation between Mn and Co (correlation of 70-90%) was found at all stations in-spite of concentrations of less than 50 pM in deep waters, and this supports the view of their having a similar cycling pathway. Moffett & Ho (1996) suggested that both elements are co-oxidised via the same microbial catalytic pathway and this is an important mechanism for the incorporation of Co into marine Mn oxides. The uptake mechanism of dissolved Co onto suspended particles is governed by the abundance and activity of Mn oxidising bacteria and the biological demand of Co as a micronutrient (Moffett & Ho, 1996).

In the Aegean Sea Mn/Co values differed significantly between seasons, with overall higher values in the North. Values of 34 and 49 in the northern Aegean for March and September 1997 respectively, and 25 and 44 in the southern Aegean Sea were calculated. Longer residence times than Mn, of 4 to 40 years (due to large range in atmospheric deposition) in the south Aegean suggest a similar but slower particle reactivity, possibly adsorbed onto freshly formed ferro-manganese oxides in the upper water column. The Mn/Co ratio may reflect the composition of the source material (atmospheric and BSW), i.e. relatively richer in Mn in September 1997 at all stations, and overall richer in Mn in the northern Aegean. However a longer Co residence time (4-40 years) indicates that the Mn/Co value will decrease with the age of the water mass, which could imply that southern waters are older than northern Aegean waters.

In the north Aegean Sea elevated Co signatures are associated with LIW and BSW. For BSW the Co/salinity ratio suggests concentrations of 0.6 nM in the Straits of Dardanelles, which falls within the range of previously observed concentrations in the Black Sea (Tankéré, 1998; Windom *et al.*, 1998). The importance of freshwater sources of Co to the Mediterranean has previously been established with Co concentrations of 0.9 nM near the rivers Po (Tankéré, 1998) and Rhone (Zhang & Wollast, 1993). Northern Aegean surface Co concentrations are elevated, with respect to the Cretan Sea and open Mediterranean (Morley *et al.*, 1990, 1997), with similar surface concentrations in the Cretan Sea to the southern Adriatic (Tankéré, 1998). Deep water concentrations (0.01 - 0.05 nM) are comparable to the EMDW's of the southern Adriatic (Tankéré, 1998) and to west Mediterranean Deep Waters (Morley *et al.*, 1997).

Like Mn, surface concentrations of Co in the North Atlantic are lower (0.03-0.06 nM) than the Mediterranean (Morley *et al.*, 1997), with similar deep water concentrations, and there is a decrease in deep water concentrations from younger Atlantic to older Pacific waters (Burton & Statham, 1988).

6.2.2 IRON

The distribution of dissolved iron in the Aegean Sea is controlled by sources to surface waters followed by rapid removal onto particles with depth. Elevated Fe concentrations were observed at all stations in both March and September 1997. The total atmospheric input of iron to surface waters is the greatest for all metals under study (Table 5.6). Although the solubility of Fe in atmospheric particles in seawater is low, ranging from 3-11 % (Guerzoni *et al.*, 1999), the soluble fraction of Fe fluxes (along with Mn and Zn) releases considerable quantities of dissolved Fe to seawater in the dissolved form. Atmospheric and marine fluxes (at 500 m) in the south Aegean, show that 30 - 80 % of particulate fluxes originate from the atmosphere, compared to of less than 10 % in the North Aegean (Table 5.8), thus, implying additional sources of Fe to this region (from BSW and the coast). Price *et al.* (1999b) suggest that an enhanced aolian supply of Saharan origin in September 1997, although prevailing winds are northerly, emphasising the potential variation in atmospheric metal fluxes and composition between seasons.

Surface concentrations are higher in the North Aegean for both seasons (Tables 5.1 and 5.4), where coastal and BSW provide an additional source of Fe. A linear Fe/salinity relationship in Black Sea surface waters and a calculated Fe concentration for the Straits of Dardanelles of 4 - 17 nM (Table 5.3), fall within observed Fe concentrations for the Black Sea (Windom *et al.*, 1998; Tankéré, 1998). There is a significant difference in Fe/salinity between stations and seasons, with greater Fe/salinity values in March than in September 1997. This indicates that although freshwater fluxes through the Straits of Dardanelles are greater in late summer, the Fe contribution to the North Aegean is greater in March. Such finding is in contrast to all other metals under study, which exhibit elevated concentrations in September 1997.

Iron is a redox sensitive element and has a behaviour similar to Mn in the Aegean Sea, with positive correlation between Mn and Fe, which varies spatially and seasonally. A similar relationship was also suggested by Tankéré (1998) in the Adriatic. In the north Aegean Mn/Fe values of 1.11 and 6.27 for March and September 1997 respectively, compared to values of 1.15 and 2.37 in the Cretan Sea, imply a seasonal difference in the composition of source material, combined with a shorter residence time for Fe in surface waters. In March 1997 Mn/Fe values indicate a comparable composition of source material (i.e. atmospheric) to both the north and south Aegean. On the other hand, higher values in September suggest a more Mn-rich atmospheric source to both the northern and southern Aegean, but may also be a reflection of a past atmospheric event, followed by the more rapid removal of Fe from surface waters. This is further confirmed by the short residence times of 0.7 - 2 years for Fe compared to 1 - 6 years for Mn. Stumm & Sulzberger, (1992) observed a quicker oxidation and precipitation of soluble iron species in the presence of oxygen relative to Mn. The highest Mn/Fe value in the northern Aegean in September reflects the additional source of Mn to surface waters from BSW.

There is a limited amount of reliable Fe data in the Mediterranean Sea due to the sensitivity of Fe to contamination (i.e. Saager *et al.*, 1993; Saager, 1994; Morley *et al.*, 1997; Tankéré, 1998; Yoon *et al.*, 1999). Surface concentrations of iron are greater in the north Aegean (1 - 9 nM) than in the Cretan Sea (1 - 3 nM). Similar surface concentrations to those in the north Aegean were observed in the central and northern Adriatic (Tankéré, 1998) where the coastal and riverine sources provide additional iron to surface waters. Cretan Sea surface Fe concentrations are comparable to Mediterranean surface waters (Saager, 1994; Morley *et al.*, 1997; Yoon *et al.*, 1999). However, Yoon *et al.* (1999) observed an increase in Fe from the Alboran Sea to the Sicily Strait due to atmospheric and coastal enrichments. Saager (1994) attributed the distribution of Fe in the Mediterranean to the presence of local sources and sinks which were related to the presence of water masses. Deep water Fe concentrations given here for the Cretan Sea are lower (0.2 – 0.7 nM) than previously observed in the Mediterranean (Saager, 1994; Morley *et al.*, 1997; Tankéré, 1998; Yoon *et al.*, 1999), but whether this is due to reduced contamination and more accurate analytical techniques, or a real difference between deep waters of the Mediterranean remains uncertain.

The short Fe residence times calculated in the Cretan Sea (0.7 - 2 yrs.) indicate the rapid removal in surface waters by scavenging. In the open ocean longer residence times of 1 to 20 years have been estimated in the upper 500 m of the Pacific (Landing and Bruland, 1987), 0.8 years in the upper 100 m of the Sargasso Sea and 2 years from modelling by Johnson *et al.* (1997). Unlike the open ocean nutrient type profiles, Fe profiles in the Mediterranean are dominated by significant sources to surface waters (atmospheric and coastal) and reflect, mainly, inorganic processes (hydrolysis, colloid formation and precipitation) rather than organic complexation (Luther III & Wu, 1997).

Surface Fe concentrations are higher in the Mediterranean than in the open ocean, where Fe exhibits nutrient type profiles with surface concentrations ranging from 0.05 nM in remote Pacific waters (de Baar *et al.*, 1999) to ~ 1 nM in North Atlantic waters (Morley *et al.*, 1997; Yoon *et al.*, 1999). Mediterranean deep water iron concentrations are within a similar range to the open ocean. Concentrations of dissolved iron are comparable in the deep Atlantic and 'older' waters of the deep Pacific (in sharp contrast to N and P) and accumulates in deep ocean waters, a behaviour uncharacteristic for a highly reactive metal (Sunda, 1997). Johnson *et al.* (1997) proposed that dissolved concentrations of Fe in sub-surface waters are maintained by the strong chelation of Fe by one, or more, organic ligands. The kinetics of this reaction are relatively rapid, allowing a fast equilibrium where a homogenously distributed ligand maintains constant dissolved concentrations of the ligand (0.4 - 0.6 nM) or just above (Johnson *et al.*,1997; Sunda *et al.*,1997). This suggests that according to Johnson *et al.* (1997), Fe may be in a steady state in Aegean deep waters, and in contrast to observations in the western Mediterranean by Yoon *et al.* (1999).

6.2.3 LEAD

Lead (as manganese) in the Aegean Sea exhibits typical open ocean distributions, with elevated surface concentrations derived from atmospheric and coastal sources, and low concentrations due to particle scavenging with depth. The atmospheric flux of Pb in the Mediterranean (Table 5.6) is a significant source to surface waters (Guieu *et al.*, 1997; Guerzoni *et al.*,1999), despite the phasing out of leaded gasoline since the 1980's. Milliman & Martin (1997) computed the mass balance for Pb in the western Mediterranean and indicated an accumulation of Pb in water of 440 tons yr^{-1} for the period 1970–1985, related to the consumption of leaded gasoline during that period. However, more recently Mignon & Nicholas (1998) observed a reduction (over the period 1987-1995) of atmospheric fluxes of dissolved Pb from 3.5 to 1.5 mg m^{-2} yr^{-1}, and of surface water concentrations in the western Mediterranean from 300 to 120 pM.

In the present study Pb atmospheric fluxes of 0.6-4.0 mg m^{-2} yr^{-1} (soluble fraction) were used (Guerzoni *et al.*, 1999) to calculate a residence time of 0.6 to 2.9 years for the southern Aegean Sea. Milliman & Martin (1997) calculated a Pb residence time of 5.2 years for the western Mediterranean (for the whole basin) and with a water residence time of ~ 15 years. This is similar to a Pb residence time of 7-11 years and 15.2 years for water observed by Martin *et al.* (1989). These studies indicate that the residence times of Pb is only 23-35 % of the total water residence times. These short residence times reflect, like Fe, the high particle reactivity of Pb. In addition high particulate Pb fluxes are observed at 500 m in the Aegean (Table 5.8), consisting of between 70 - 440 % of the total atmospheric fluxes to the south Aegean (Guieu *et al.*, 1997; Guerzoni *et al.*, 1999; Price *et al.*, 1999b). Even in the north Aegean (where coastal inputs can play an additional role in the sources of surface Pb), marine fluxes are 10-70% of atmospheric fluxes. Price *et al.* (1999b) imply that Pb_{ex} to be bound with biogenic substances, with highest concentrations in particulate matter in the euphotic zone. Surface concentrations of Pb are only slightly higher in the North Aegean (0.08-0.28 pM) than the Cretan Sea (0.08-0.24 nM) and exhibit a poor relationship with salinity, which suggests that the coastal and BSW contribution of Pb to the Aegean is not significant. Guerzoni *et al.*, (1999) suggest a figure of around 7% of dissolved inputs (compared to atmospheric) to the Adriatic are from riverine sources, and 3% for the north-western Mediterranean; such percentage values are the lowest for all metals considered.

Surface concentrations of Pb in the Aegean Sea vary between 0.08 and 0.28 nM (Tables 5.1 and 5.4) and fall within the range of Pb surface concentrations found in the Mediterranean Sea (Copin-Montegut *et al.*, 1986; Morley *et al.*, 1997; Yoon *et al.*, 1999). Maximum concentrations of 0.3 nM were observed in the Sicilian Straits (Morley *et al.*, 1997; Yoon *et al.*, 1999) suggesting a progressive increase from the Alboran Sea to the Sicily Straits. Deep water concentrations (0.02-0.10 nM) are lower than observed in the WMDW (0.12-0.13nM) byYoon *et al.* (1999), implying that the inputs of Pb exceeds the removal capacity of the Western Mediterranean and may accumulate in the water column.

Open ocean Pb concentrations are variable and reflect the influence of atmospheric sources from industrialised regions, and a general decrease over time in leaded gasoline emissions. In the early 1980's surface concentrations ranged from 0.06-0.07 nM in the Pacific to 0.13-160 nM in the Atlantic (Nolting *et al.*, 1999), with a decrease in 1996 to ~ 0.05 nM in the Sargasso Sea. The phasing out of leaded gasoline in Europe has lagged behind North America, with higher surface Pb in the northeast Atlantic (1989/1990) at 0.2 nM, compared to 0.08 nM at the equator. Nolting *et al.* (1999) observed Pb concentrations of 0.03-0.20 nM in the North Sea in 1993, compared to 0.3 nM in 1981. Mediterranean surface waters are therefore elevated in Pb relative to Atlantic and other open oceans, considering Pb data for the 1990s (i.e. Morley *et al.*, 1997; Nolting *et al.*, 1999; *Yoon et al.*,1999).

Deep water concentrations vary from ~ 0.005 nM in older Pacific waters to 0.02 nM in younger Atlantic waters (Bruland & Franks, 1983; Burton & Statham, 1990; Nolting *et al.*, 1999), reflecting, like Mn, the scavenging of Pb over time. Dissolved Pb concentrations in Aegean deep waters are comparable with Atlantic waters, but lower than western Mediterranean waters.

6.2.4 NICKEL, COPPER AND CADMIUM

The vertical distributions of dissolved nickel, copper and cadmium profiles in the Aegean do not resemble that of nutrients, in contrast with the typical situation for open waters. Elevated surface concentrations for Ni and Cu in the north Aegean and to a lesser extent in the south, suggest the importance of surface sources (atmospheric and coastal) over vertical downward transport with biological particles. Cadmium profiles are uniform with depth and are left to be discussed last.

Elevated surface concentrations of Ni and Cu are due to atmospheric deposition in the south and additional coastal influences in the north Aegean. Dissolved atmospheric fluxes of Ni in the central Mediterranean of 17-24 mol/km^2/yr (Guerzoni *et al.*, 1999) result in relatively long residence times (along with Co) of 11 to 36 years in the south Aegean. This reflects the limited down-column transfer of Ni in association with particulate material sinking from the euphotic zone (Morley *et al.*, 1993), with Ni being associated with the hard parts of phytoplankton, and a slow regeneration cycle (Le Gall *et al.*, 1999). Dissolved atmospheric fluxes of Cu are greater than for Ni (45-72 mol/km^2/yr) resulting in very short calculated residence times of 2 to 5 years in surface waters. Martin *et al.*, (1989) observed similar short Cu residence times in the western Mediterranean of 5-6 yr. (with a residence time of water at 15.2 yr.).

Compared to a low marine flux 0.9 kg/km^2/yr at 500 m (Price *et al.*, 1999b), it is possible that the Cu atmospheric fluxes may have been overestimated and, if fluxes of 12-20 mol/km^2/yr are taken from the northwestern Mediterranean (Guerzoni *et al.*, 1999), than the corresponding residence time calculations for south Aegean surface waters would increase to between 6 and 18 years. However, as well as the downward flux, Tankéré (1998) observed a high proportion of upwelling and remobilization of Cu in surface waters of the southern Adriatic, indicating the importance for Cu fluxes to upper layers from deeper waters.

The solubility of atmospheric Cu exhibits more variability (49-82%) than Ni (54-58%) in Mediterranean seawater due to higher solubilities from anthropogenic-rich than crust-rich end-member (Guerzoni *et al.*, 1999). Therefore, in calculating residence times in the Mediterranean it is essential that realistic atmospheric fluxes are used. In the open ocean deep waters of the North and Equatorial Pacific Noriki *et al.* (1998) also observed shorter Cu residence times of 500 years compared to 638 years for Ni. These shorter residence times of Cu can be attributed to particle reactivity and high removal rates from surface waters. In the Aegean, Price *et al.* (1999b) noted high Cu/Al values in the south Aegean and suggested the scavenging of Cu by biogenic constituents in the water column.

Ni and Cu surface concentrations are greater in the North Aegean and both exhibit metal/salinity relationships in September 1997 only (Tables 5.2 and 5.3). This is due to a greater range in salinity and metal concentration in BSW, and the presence of an additional water mass, MAW (Zervakis & Georgopoulos, 1998) at depths of 50-100 m in March 1997. The calculated concentrations for the Straits of Dardanelles are estimated at 12 and 9 nM for Ni and Cu, respectively, and are in good agreement with recent data for the Marmara Sea (Yemenicioglu & Salihoglo, 1999). The metal to salinity ratio at MNB6 is slightly higher than MNB5, due to its proximity to the northern coastline and potential influence of the rivers Nestos and Evros. At present, metal data for these rivers is not available. However Dassenakis *et al.* (1997) observed elevated Ni and Cu concentrations in a number of Greek rivers and coastal areas ranging from 6 – 71 nM for Cu and 3 - 48 nM for Ni, which confirm the potential importance of coastal sources to the North Aegean.

In the Aegean Sea surface elevation dominates with higher concentrations in the northern (4-9nM for Ni and 2-5 nM for Cu) than the southern Aegean (4-7 nM for Ni and 1-4 nM for Cu). Overall, concentrations are higher in September 1997 and in both the north and south Aegean. Ni and Cu profiles exhibit much variability in the Mediterranean, from nutrient type to homogenous or maximum concentrations at the surface and/or the sea bed (van Geen *et al.*, 1988; Martin, *et al.*, 1993; Saager *et al.*, 1993; Saager, 1994; Varnavas & Voutsinou-Talidouri, 1996; Tankéré & Statham, 1996; Morley, *et al.*, 1997; Yoon *et al.*, 1999). Burton & Statham (1988) suggest that the range of factors influencing the Cu distribution is greater than for the other metals considered. There is some variation in profiles from the west to east Mediterranean, with an overall increase in surface concentrations in this direction (Saager, 1994; Morley *et al.*, 1997 Yoon *et al.*, 1999). Nutrient type profiles for Ni (and Zn) were observed in the western Mediterranean (Yoon *et al.*, 1999), along with uniform profiles in the western and central Mediterranean (Saager, 1994; Morley *et al.*, 1997; Tankéré, 1998; Yoon *et al.*, 1999) and surface and sub-surface elevation in the central and eastern Mediterranean (Saager *et al.*, 1993) associated with surface and LIW waters. Surface Ni and Cu concentrations in the Aegean Sea are elevated (~ 3 nM for Ni and ~ 2 nM for Cu) in comparison to surface waters of the Straits of Sicily (Morley *et al.*, 1997 Yoon *et al.*, 1999). Similar concentrations to the southern Aegean in March 1997 were observed in eastern Aegean, south of Crete (~ 5 nM and ~ 2 nM for Ni and Cu respectively) by Saager (1994), and in the southern Adriatic Sea (Tankéré, 1998). Deep water Ni and Cu concentrations also appear to increase from the western (Morley *et al.*, 1997 Yoon *et al.*, 1999) to the eastern Mediterranean (Saager, 1994), with similar deep water concentrations in the Aegean and eastern Mediterranean (Saager, 1994).

Cadmium (like Ni and Cu) has no resemblance to open ocean nutrient profiles, and profiles are homogenous with depth (Tables 5.1 and 5.4). As found for Ni and Cu, reported Cd profiles for the Mediterranean Sea exhibit some variability, with surface elevation in the eastern Mediterranean (Saager, 1994) and uniform and nutrient type profiles in the western Mediterranean (Morley *et al.*, 1997; Tankéré, 1998; Yoon *et al.*, 1999). Concentrations are a fraction higher in the north (0.07 - 0.09 nM) than in the south Aegean (0.05 - 0.08 nM), indicating the potential influence of additional sources in the northern Aegean. It is difficult to assess the variations in deep water cadmium in the Mediterranean due to low concentrations and analytical precision and accuracy. Cd (unlike Ni and Cu) does not appear to increase from the western to eastern Mediterranean, which was also confirmed by Saager (1994). The elevated surface concentrations observed in the eastern Mediterranean by Saager (1994) are associated with Mediterranean Surface Water (MSW) and LIW and they indicate a significant source to these waters in 1987, though not apparent in Aegean surface waters in 1997. Tankéré (1998) found similar Cd profiles and concentrations in the southern Adriatic Sea in 1994. The residence time for Cd is between 1-14 years in the southern Aegean surface waters (Table5.7). Martin *et al.* (1989) found a Cd residence time of 10-22 years in the western Mediterranean, similar to the residence time for water (15.2 years) and suggested that Cd distributions are governed by water dynamics. This result is in good agreement with the biogeochemical properties of Cd, occurring basically as dissolved complexes, eliminated along with water renewal.

In the open ocean Cu, Ni and Cd exhibit nutrient types profiles with overall lower surface concentrations than the Aegean and the Mediterranean Sea. Surface concentrations of Ni varies from 1.7 - 3.0 nM, Cu from 0.7 - 1.3 nM and Cd from 0.01 - 0.05 nM in the North-east Atlantic (Saager *et al.*, 1997). Deep water concentrations are also lower in North-eastern Atlantic waters for Ni (4.6-6.7 nM), Cu (1.0-2.6nM) and Cd (0.02-0.03 nM) than the Aegean and the Mediterranean Sea (van Geen *et al.*, 1988; Morley *et al.*, 1997; Saager, *et al.*, 1997; Yoon *et al.*, 1999). In contrast to scavenged metals (i.e. Mn and Pb), the regeneration with depth of nutrient type metals results in an increase in deep water metals, as one moves from the younger Atlantic to older Pacific waters; with an increase of 6 to 10 nM for Ni, 2 to 3 nM for Cu and 0.3 to 1 nM for Cd. The increase in copper is less substantial than Ni and Cd, as copper exhibits deep water scavenging and occasional regeneration at the sediment water interface (Bruland & Franks, 1983).

ZINC

Zn profiles for the north and south Aegean Sea are erratic, due to problems of contamination during sampling, and the presence of a zinc sacrificial electrode within the CTD set-up. Profiles (using selected data only) exhibit surface elevation in the north Aegean (3.2 – 10.5 nM) and, to a lesser degree, in the south Aegean (1.2-6.7nM) in September 1997. Deep water concentrations are similar for both the north and south Aegean (1.2-4.5 nM). Ruiz-Pino *et al.* (1991) in the Eastern Mediterranean and Tankéré (1998) in the south Adriatic observed similar profiles and concentrations, whereas Yoon *et al.* (1999) and Sherrell and Boyle (1988) found nutrient type profiles in the central and western Mediterranean. The present dataset further supports two conclusions for Zn in the Mediterranean: i) deep water concentrations (in contrast to Ni and Cu) decrease from west to east and ii) that the Mediterranean Sea is not in a steady state with regards to Zn (Béthoux, *et al.*, 1990; Ruiz-Pino *et al.*, 1991; Saager, 1994).

There appears to be many factors controlling the distribution of Zn, including atmospheric and coastal sources, biological uptake and regeneration, and mixing and benthic inputs. Considerably short residence times of 0.5-2.4 years, compared to the open ocean (50,000 years), were calculated for the south Aegean based on atmospheric fluxes in the Central Mediterranean given by Guerzoni *et al.* (1999). Data from the northwestern Mediterranean are more variable (15-1150 mol/km^2/yr) which, if applicable to the Aegean Sea, could result in erratic profiles, and would alter the residence times to between 0.2 and 26.8 years. The solubility of atmospheric Zn in surface waters is between 68-76% (Guerzoni *et al.*, 1999), with higher solubilities from anthropogenic-rich than from the crust-rich end-member, because of their different speciation signatures in these two aerosol types. Price *et al.* (1999b) noted that particulate Zn is scavenged by biogenic constituents in the Aegean Sea, with higher concentrations of Zn_{ex} in the North Aegean, especially in March 1997, due to the resuspension of sediment caused by intense fishing activity on the northern shelf from October to May of each year. In the North Aegean, where surface dissolved Zn is elevated, Price *et al.* (1999b) suggests anthropogenic sources of particulate zinc from municipal and industrial waste. Dassenakis *et al.*, (1997) reported concentrations of dissolved Zn of 5 to over 300 nM in various rivers and coastal areas of Greece, indicating the significance of anthropogenic and/or natural coastal sources of Zn to the Aegean Sea. Trace metal concentrations of over 200 nM were measured in the Marmara Sea (Yemenicioglu & Salihoglu, 1999), presenting a potentially huge zinc source to the North Aegean, although the relationship between Zn and salinity in surface waters of the North Aegean suggest a non-conservative behaviour. In contrast, Guieu *et al.*, (1998) found Zn concentrations of only 6 nM in the Danube river in the Black Sea. These findings show the potentially huge variability in Zn sources, like atmospheric fluxes, unless the higher values can be attributed to contamination during sampling and analysis procedures.

Dissolved zinc in the open ocean exhibits lower surface (<0.5 nM) and deep water concentrations in the North Atlantic than in the Aegean and Mediterranean (Bruland & Franks, 1983). Van Geen *et al.* (1988) and Yoon *et al.* (1999) observed slightly higher concentrations in NASW close to the Straits of Gibraltar, where coastal and atmospheric sources are likely to be more significant than in the open ocean. Zn deep water concentrations increase from 1.7 nM in the North Atlantic to 8.5 nM in older North Pacific waters, due to regeneration from biogenic particles (like Ni, Cu, and Cd) and may present a source of deep water dissolved Zn to North Atlantic waters (Bruland & Franks, 1983; Van Geen *et al.,* 1988; Yoon *et al.,*1999).

6.3 MAJOR PROCESSES AND SOURCES INFLUENCING THE DISTRIBUTION OF TRACE METALS IN THE AEGEAN SEA

The major processes and sources that influence the distribution and biogeochemistry of dissolved trace metals in the Aegean Sea are discussed with particular reference to i) atmospheric and coastal/BSW sources, ii) hydrothermal activity, iii) biological production and iv) hydrography.

6.3.1 ATMOSPHERIC AND COASTAL/BSW SOURCES TO SURFACE WATERS

Metal depth profiles in the Aegean Sea exhibit surface elevation for Mn, Co, Fe, Pb, Cu, Ni and Zn in the north, and for Mn, Co, Fe, Pb and to a lesser extent Cu and Ni, in September 1997 in the south Aegean due to the influence of atmospheric deposition and coastal/BSW sources. In the south the predominant source appears to be atmospheric, whereas in the north Aegean a combination of atmospheric and coastal/BSW is responsible for surface concentrations. This is further supported by additional information on i) atmospheric (Guieu *et al.*, 1997; Guerzoni *et al.*, 1999), ii) riverine and coastal (Dassenakis, *et al.*, 1996;1997) and iii) BSW sources (Guieu, 1998; Windom *et al.*, 1998; Yemenicioglu & Salihoglu, 1999); iv) calculated surface metal residence times, v) comparison of reported atmospheric (Guerzoni *et al.*, 1999) with water column metal fluxes (Price *et al.*, 1999b), and vi) particulate metal data (Price *et al.*, 1999b).

Although at present no atmospheric metal fluxes have been calculated for the Aegean Sea, recent work in the Mediterranean (Martin, *et al.*,1989; Guieu *et al.*, 1997;

Chester *et al.,* 1999; Guerzoni *et al.,* 1999) and the Black Sea, (Hacisalihoglu *et al.,* 1991; Kubilay *et al.,* 1995), allow comparability in the present study. The dust input to the nutrient limited Mediterranean is considered as one of the greatest in the contemporary ocean and the mass flux deposition over the eastern Mediterranean (~21 g/m^2) is greater than over the central or western Mediterranean (Guerzoni *et al.,* 1999). It is, therefore, possible that overall metal fluxes have been underestimated for the Aegean Sea, thus, resulting in overestimated calculated residence times.

Surface metal concentrations exhibit spatial and temporal variation, with highest concentrations in the north Aegean, and overall in September 1997 for the northern and southern Aegean Sea. Most metals in the troposphere have very short residence times (ranging between days and weeks), are not well mixed and, therefore, aerosols and rainwater exhibit strong spatial and temporal metal variability (Hacisalihoglu *et al.,* 1991; Kubilay *et al.,* 1995; Guerzoni *et al.,* 1999). The trace metal composition of aerosols varies depending on their origin. Aerosols transported to the Mediterranean and the Black Sea may be considered to consist of anthropogenic-rich 'background' materials supplied continuously from Europe, upon which sporadic pulses of Saharan crust-rich dust are superimposed (Kubilay *et al.,* 1995; Guerzoni *et al.,* 1999). These two end-member aerosols have a different trace metal composition, with higher enrichment factors relative to Al (EF_{crust}) in European aerosols, and higher solubilties for Cu, Zn and Pb in anthropogenic-rich than in the crust-rich end-member. This is due to their different speciation signatures in these two aerosol types (Guerzoni *et al.,* 1999). As a result, interpretation of the dissolved metal fluxes to Aegean surface waters is difficult without actual atmospheric data during the period of sampling. However, overall higher dissolved concentrations in September 1997 suggest a potential event of atmospheric deposition, also observed by Price *et al.,* (1999b), with high particulate Ti_{ex}/Fe_{ex} values suggesting a Saharan origin, although during this period northern Etesian winds dominate. Elevated dissolved Mn/Fe and Mn/Co values in surface waters in September compared to March 1997, reflect a seasonal difference in surface sources, relatively richer in Mn in September 1997. The fact that manganese is known to be enriched in emissions from ferromanganese industries indicates that in the Black Sea high Mn concentrations associated with trajectories from Europe may be due to more abundant ferromanganese industry in western European countries (Hacisalihoglu *et al.*, 1991).

Assuming a constant source of dissolved atmospheric metals in the north and south Aegean Sea, where the south Aegean surface waters are governed by atmospheric deposition alone, it is then possible to calculate the proportion of coastal/BSW and atmospheric inputs to the North Aegean as given in Table 6.1.

Table 6.1. Percentage contribution of BSW and coastal input (compared with atmospheric) to the North Aegean.

	March 1997	September 1997
Mn	44 - 74 %	54 – 55 %
Fe	0 – 70%	28 – 38 %
Co	27 – 43 %	46 – 48 %
Pb	0 – 39 %	0 – 14 %
Cu	35 – 58 %	23 – 46 %
Ni	0 – 16 %	20 – 41 %
Cd	22 – 43 %	11 – 43 %
Zn	46 – 70 %	36 –63 %

The above percentage analysis also assumes similar removal rates of metals from surface waters, whereas Price *et al.*, (1999b) found variations in particulate (biogenic and inorganic) concentrations, indicating differences in removal rates onto particles. In addition, the spatial and temporal variations of atmospheric deposition observed in the Mediterranean and the Black Sea (Kubilay *et al.*, 1995; Guerzoni *et al.*, 1999), with elevated atmospheric metal deposition close to Istanbul (Kubilay *et al.*, 1995), indicate the potential for elevated atmospheric metal deposition in the North Aegean due to the proximity of industrialised regions around northern Greece and Turkey.

By comparing the total inputs between atmospheric and riverine origin for the Adriatic and NW Mediterranean (Guieu *et al.*, 1997; Guerzoni *et al.*, 1997), dissolved atmospheric fluxes represent a significant proportion of the total input. More than 50% of the dissolved Ni input followed by Cu, Co, Zn, Mn, Fe, Cd and a maximum of over 90% of dissolved Pb input to the marine system originates from the atmosphere (Guieu *et al.*, 1997). This is in agreement with Table 6.1, inspite of the previously made assumptions, particularly for Pb. Notice that the elevated dissolved metal concentrations in rivers and BSW have already been discussed for each metal.

Dissolved trace metals were also determined within Thermaikos Gulf and exhibit similar profiles and concentrations to stations in the northern Aegean. In contrast, Dassenakis *et al.* (1997) reported elevated concentrations of Cu (~20nM), Pb (~ 5 nM), Ni (~52 nM) and Mn (~18 nM) between 1986-1993, although whether from the same area is not specified . The hydrography at the Thermaikos stations in the present study do not exhibit a clear, low salinity, riverine source which is distinguishable from the BSW, observed throughout the northern Aegean. Therefore it is possible that samples were collected too far seaward in order to observe the freshwater signal, and may not be comparable with previous studies. However, work on sedimentary metal concentrations would provide a clearer indication of metal loading to the Thermaikos Gulf.

6.3.2 HYDROGRAPHY AND MIXING OF WATER MASSES

Within the Mediterranean, the numerous water masses, complex circulation and shorter water turnover times than in the open ocean play a dominant role in the distribution of dissolved trace metals. The presence of dissolved trace metal signatures associated with water masses in the Mediterranean has been previously reported (Statham *et al.*, 1985; Sherrel & Boyle, 1988; Ruiz-Pino *et al.*, 1991; Saager 1993;1994; Morley *et al.*, 1997; Yoon *et al.*, 1999). Within the Aegean Sea, elevated surface water concentrations have been discussed above. In addition, distinct metal signatures were found to be associated with LIW and deep waters of the north (NAEGDW) and south (CDW) Aegean Sea.

In the Aegean Sea, LIW is transported from the Levantine Basin through the eastern Cretan Straits and propagates northwards along the eastern boundary to the Limnos Plateau, where it encounters BSW (Poulos *et al.*, 1993). Trace metal concentrations above that of the deep waters are distinguished for Mn (~2-3 nM), Fe (~1-4 nM), Co (~0.1 nM) and Pb (~0.1 nM), associated with LIW in the north Aegean. Saager (1993;1994) and Morley *et al.*, (1997) reported elevated metals concentrations in the Straits of Sicily, and suggested that benthic and off-shelf inputs of trace metals to the LIW occur during its passage through the Straits. Saager (1994) also observed elevated Fe, Cu Ni and Cd in LIW within the eastern Aegean. Concluding that surface concentrations of Cu and Cd increase from the west to east Mediterranean, Saager (1994) attributed these elevated metal signatures to the formation site of LIW in the eastern basin. In the north Aegean in March 1997, Price *et al.* (1999b) reported that intense fishing activity occurs on the northern shelf (from October to May) thus causing the resuspension of sediments especially at 200-250 m; such phenomena could lead to desorption of particulate Mn into solution (supported by lower Mn_{ex} concentrations found at stations MNB1 and MNB5 and low Mn/Al ratios). Elevated metal concentrations in LIW are, therefore either due to the release from particulate phases during resuspension or from elevated concentrations in Levantine Surface Waters, which under certain conditions sinks to form LIW (Lascaratos, 1993b; Klein *et al.*, 1997). Although at present there is no dissolved metal data for the Levantine Basin, the formation of LIW from surface waters of potentially elevated dissolved metal concentrations presents an interesting topic for future work. The spatial and temporal variability in the source of metals to the Levantine basin, (predominantly atmospheric) would result in LIW of variable metal concentrations over time.

Deep water formation occurs separately in the north (NAEGDW) and south (CDW) Aegean Sea, from surface waters. Deep waters will, therefore, reflect the dissolved metal concentrations in the surface waters from which they were formed. Pb, Cu, Cd and Zn concentrations are fractionally higher in the NAEGDW than in the CDW (Tables 5.1 and 5.4). Considering that NAEGDW is formed from LIW and BSW (both elevated in dissolved metals), it is likely that the metal concentrations of North Aegean Deep Waters will be higher than CDW, especially for metals controlled by mixing, i.e. Cd. Finally, traces of MAW at 45-100 m in the north Aegean in September 1997, result in some slight variability in metal concentrations and poor metal/salinity correlations for Mn, Co and Pb. However, the limited data prevents further interpretation.

The influence of circulation and hydrography in the Mediterranean on the distribution of dissolved trace metals has been mentioned by several authors (Statham *et al.*, 1985; Sherrel & Boyle, 1988; van *Geen et al.*, 1988; Ruiz-Pino *et al.*, 1991; Saager 1993;1994; Morley *et al.*, 1997; Yoon *et al.*, 1999). However, the relationships between dissolved trace metals and physical parameters (temperature, salinity and density) is rarely clear enough to examine these relationships closely in open waters. A contour plot of manganese across the Cretan Sea in September 1997 (Figure 5.11) indicates the influence of upwelling and downwelling associated with cyclonic and anticylonic eddies, with a similarity to density, temperature, nitrate plus nitrite and silicate (Figures 4.12 and 4.14). Upwelling is associated with a cyclonic gyre in the central Cretan Sea, previously examined by Theocharis *et al.*, (1993). Mn data exhibits small errors and the greatest concentrations range of all the metals considered. Therefore, it is likely that other metals follow a similar distribution, but due to the errors associated with metal analysis of low concentrations and the unreliability of contour plot programmes, any further comparison is not possible.

6.3.3 HYDROTHERMAL ACTIVITY

The hydrothermal activity within the Hellenic Volcanic Arc, including Milos, has been investigated (Varnavas & Cronan, 1991; Varnavas *et al.*, 1993; Dando *et al.*, 1995; Fitzsimons *et al.*, 1997; Karageorgis *et al.*, 1998; Dando *et al.*, 1999). Samples at Milos were enriched (relative to south Aegean samples of similar hydrography) in Mn and Fe for both March and September 1997, along with Co and Pb for September 1997 only. Overall concentrations are greater in September 1997, due to the localised nature of hydrothermal activity, a slight difference in the sample position between seasons and potential temporally variability, also observed by Varnavas *et al.* (1993). In Milos hydrothermal waters, Varnavas *et al.* (1993) observed much higher manganese (50 to 20,000 nM) and iron (17 to 15,000 nM) concentrations than in the present study where samples were collected at only approximate positions of reported hydrothermal vents. Dando *et al.* (1999) also reported enriched Fe (4400-fold), Mn (800-fold), Cd, Cu and Zn in Santorini hydrothermal waters, within the Hellenic Volcanic Arc. Including the spatial and temporal variability previously reported, it is therefore difficult to assess the potential release of these metals to overlying waters in this study. Due to the shallow depths and lower temperatures of the Hellenic Volcanic Arc hydrothermal system, no widespread hydrothermal influence in the surficial sediments has been recognised (Dando *et al.*, 1999).

6.3.4 NUTRIENTS AND THE OLIGOTROPHIC STATUS OF THE AEGEAN SEA

Recent research on dissolved nutrients in the Mediterranean (i.e. Béthoux & Copin-Montegut, 1988; Béthoux *et al.*, 1998b; Crise *et al.*, 1998; Denis-Karafistan *et al.*, 1998; Yilmaz & Tugrul, 1998; Kress & Herut, 1999) and Aegean Sea (Kucuksezgin *et al.*, 1995; Civitarese *et al.*, 1998; Balopoulos, *et al.*, 1999; Tugrul *et al.*, 1999; Yilmaz *et al.*, 1999) have examined the oligotrophic nature of the Mediterranean. The eastern Mediterranean is one of the well known regions of low productivity in the world due to limited nutrient supply to its surface layer from external and internal sources (Yilmaz *et al.*, 1999).

Within the Aegean Sea low surface nitrate plus nitrite (< 0.8 μM) and silicon (1-2 μM) are typical of eastern Mediterranean oligotrophic waters, with similar concentrations reported in the Aegean (Kucuksezgin *et al.*, 1995) and eastern Mediterranean (Yilmaz & Tugrul, 1998; Kress & Herut, 1999). Surface nitrate plus nitrite concentrations are slightly higher in the northern Aegean (~ 0.5 μM) than the Cretan Sea (~ 0.1 μM) for September 1997. This difference may be linked to the outflow of BSW, where similar nitrate plus nitrite concentrations have been measured in the Bosphorus Strait (Polat & Tugrul, 1995), with concentrations in the Black Sea of approximately 10 times greater than the Aegean (Moncheva *et al.*, 1999). Within the Marmara Sea a potential additional source from domestic/industrial waste from the city of Istanbul (Polat *et al.*, 1999) may enhance nutrient concentrations in BSW to the northern Aegean.

As well as spatial variability in nutrient concentrations surface nitrate plus nitrite and silicon concentrations are slightly lower in September than in March 1997 for both the north and south Aegean. This difference is likely to be related to the overall lower primary production in September 1997 (Ignatiades *et al.*, 1999). Price *et al.* (1999b) found higher particulate concentrations of biogenous elements, P, Si_{bio} and Si_{org} in September 1997 and suggested that in September, deep water biogenous elements are considered to be a remnant of the fallout of the spring bloom, while in March there is limited biogenous fallout during and after the period of low water production.

The nutricline depth varies spatially and seasonally, with depths in the Cretan Sea of ~ 150 m in March and ~75 m in September, and a similar depth of ~75 m in September 1997 for north Aegean stations. Kucuksezgin *et al.* (1995) observed a similar seasonal difference in nutricline depth in the northern Aegean. The nutricline was not clearly discernible in March 1997 in the north Aegean due to the presence of low concentrations of dissolved nitrate plus nitrite (0.7-1.0 μM) and silicon (1.1-1.9 μM) associated with an intrusion of LIW at depths of 200-300 m. LIW is formed from surface waters in the Levantine basin and south Aegean (Klein *et al.*, 1999) and are therefore expected to have low dissolved nutrient concentrations characteristic of surface waters.

The presence of upwelling and downwelling in the Aegean Sea is of importance to the distribution of nutrients and primary production. Within the Cretan Sea, upwelling within a cyclonic gyre (between stations MSB1 and MSB6) result in elevated nutrients concentrations in surface waters in September 1997. Price *et al.* (1999b) associated upwelling in the Cretan Sea in March 1997 with a high standing crop of diatoms at 150m, coincident with the chlorophyll-*a* maximum. An enhanced chlorophyll-*a* standing crop is also associated with upwelling within a cyclonic eddy in the Cretan Sea during February and September 1994 (Price *et al.*, 1999a; Price *et al.*, 2000). This highlights the importance of upwelling for primary production and dissolved nutrient concentrations within the Aegean.

Dissolved nutrient concentrations increase with depth below the nutricline. In addition to this general trend, in the south Aegean, a layer of nutrient rich dissolved nitrate plus nitrate (4.0-5.0 μM) and silicon (3.5-4.5 μM) corresponds to an intrusion of TMW. Balopoulos *et al.* (1999) observed a similar increase in dissolved nitrate plus nitrite, silicon and phosphate with low oxygen, associated with TMW in 1994. TMW enters the Cretan Sea through the eastern and western Cretan Straits, at depths between 225-350 m in March and 321-550 m in September 1997. Deep water concentrations exhibit some spatial variability, linked to the presence of different deep water masses. North Aegean deep waters exhibit slightly higher nitrate plus nitrite (2.8-3.8 μM) and silicon (5.0-7.5 μM) concentrations than CDW, especially at MNB3, situated in the Chios basin, representing a likely formations site for NAEGDW. Interestingly deep water nitrate plus nitrite and silicon concentrations in the North Aegean are approximately 0.5-1.0 μM higher in September 1997 and correspond to elevated S_{org} relative to P_{org} (Price *et al.*, 1999b). This is related to elevated concentrations of DMS produced during the senescence phases of phytoplankton and grazing by zooplankton (Bardouki *et al.*, 1998). Deep water nutrients in the Aegean Sea are at lower concentrations than those found in the eastern Mediterranean, with concentrations of 4-6 μM for $N0_2$ plus $N0_3$ and 8-10 μM for silicon (Yilmaz & Tugrul, 1998; Yilmaz *et al.*, 1999). These higher concentrations outside the Aegean, explain the elevated nutrient concentrations in TMW, formed in the eastern Mediterranean from a mixture of EMDW and LIW (Theocharis *et al.*, 1993; Balopoulos *et al.*, 1996).

Chlorophyll-*a* data was available for only the north Aegean in September 1997. Maximum concentrations are found between 50-125 m, varying for each station. Highest chlorophyll-*a* values at MNB4 (0.75 μg/l) correspond to elevated nutrient concentrations. The shallow depth of MNB4 (96 m), combined with northwards flowing circulation along the eastern boundary of the Aegean (Poulos *et al.*, 1997) suggests that there is upwelling of nutrient rich deep waters into the euphotic zone. Ignatiades *et al.* (1999) also observed elevated chlorophyll-*a* concentrations at MNB4 for both March and September 1997 in comparison with other northern stations. A well-developed chlorophyll maximum near the base of the euphotic zone is a characteristic feature of the north-eastern Mediterranean throughout the whole year while this peak is broadened and observed at shallower depths during bloom periods (Yilmaz *et al.*, 1999).

Although phosphate data was limited due to the limits of detection, where available N/P values of ~21 and ~26 in the north Aegean and ~33 and ~38 for the south Aegean were calculated for March and September 1997 respectively, and are significantly higher than the overall oceanic Redfield ratio of 16:1 (Redfield, 1963). This suggests that the south Aegean is more phosphate limited than the north Aegean, and overall lower N/P values in March 1997 are related to primary production. N/P values of 21 were observed in the Aegean Sea in 1992 (Kucuksezgin *et al.*, 1995). Yilmaz & Tugrul (1998) observed an average N/P value of 27-29 in deep waters of the Levantine basin, with values of up to 120 at the top of the nutricline, and attributed this to the preferential uptake of reactive phosphate by plankton species. Overall N/P values are greatest for the Cretan Sea, followed by the Levantine Basin (Yilmaz & Tugrul, 1998), western Mediterranean (19.1) and north Atlantic deep waters (15.2). This suggests that the Cretan Sea may be area of greatest phosphate limited primary production in the Mediterranean Sea.

6.4. IMPLICATIONS OF THE AEGEAN SEA DATA FOR THE MEDITERRANEAN SEA TRACE METAL BIOGEOCHEMISTRY

From dissolved metal data over the last 15 years the knowledge of biogeochemistry of trace metals in the Mediterranean has been greatly advanced (Statham *et al.*, 1985; van Geen *et al.*,1988; Martin *et al.*, 1989; Béthoux *et al.*, 1990; Ruiz-Pino *et al.*, 1991; Saager *et al.*,1993; Zhang & Wollast, 1993; Saager, 1994; Tankéré & Statham, 1996; Morley *et al.*,1997; Yoon *et al.*,1999). However, there has been limited data for the eastern Mediterranean and the Aegean (i.e. Saager *et al.*,1993; Saager, 1994; Balopoulos *et al.*, 1999). The present work in the Aegean Sea has enabled a further understanding of the trace metal biogeochemistry of the eastern Mediterranean, and supports previously made conclusions regarding the distribution of metals across the Mediterranean.

Within the Mediterranean, spatial variability of dissolved trace metals is reported from the western to the eastern basin. NASW enters the Mediterranean through the Straits of Gibraltar in the upper 60-80 m and flows towards the eastern basin, increasing in salinity to become MSW or MAW. In the eastern basin, LIW is formed and spreads westwards across the entire Mediterranean in intermediate waters, forming the well-known salty water tongue of the Mediterranean Outflow Water of the northern Atlantic (Lascaratos, 1993b; Klein *et al.*, 1999). Deep water formation occurs separately in the western (WMDW) and eastern basin (CDW and EMDW).

The depth profiles of the scavenged metals, Mn, Co, Pb and Fe are characterised by elevated surface concentrations followed by rapid removal with depth, and distributions in the Mediterranean depends on surface sources of each metal, removal rates and hydrography. For Mn and Co surface concentrations are greater in September 1997 in the Cretan Sea than previously measured in the open Mediterranean. These observations may reflect the importance of spatial and temporal variablity of the atmospheric inputs and the effect of a shallow thermocline in 'converging' surface metal concentrations rather than being a real difference between the eastern and western Mediterranean basins. Fe and Pb surface concentrations have been reported to increase eastwards, from the Alboran Sea to the Straits of Sicily (Morley *et al.*, 1997; Yoon *et al.*, 1999), which may further influence surface concentrations in the eastern basin.

Mn and Co deep water concentrations are similar throughout the Mediterranean (Statham *et al.*, 1985; Morley *et al.*, 19997); however, Fe and Pb concentrations are lower in CDW than WMDW. Saager (1994) observed similar Fe values in eastern basin to the WMDW, but concluded these to be upper estimates due to low precision. The difficulties in accurate analysis of Fe due to potential contamination leads to uncertainty over this apparent difference between western and eastern basins. Lead concentrations in deep waters reflect their surface sources, which have changed since the 1960's due to the consumption of leaded gasoline (Schaule & Patterson, 1983; Mignon & Nicholas, 1998). Therefore any variations in Pb concentrations may reflect temporal, as well as spatial, differences. Yoon *et al.* (1999) concluded that the external inputs for Pb and Fe exceed the removal capacity of the Western Mediterranean and thus, they may accumulate in the water column. However, deep water concentrations of Pb and Fe in the Cretan Sea are similar to Atlantic waters and suggest a greater removal capacity than the western Mediterranean. A longer deep water residence time of 85-125 years in the eastern than the western Mediterranean of 15-50 years would result in greater removal of Pb and Fe in the eastern basin.

The 'nutrient type' metals Ni, Cu, Cd and Zn do not exhibit nutrient profiles due to the importance of surface sources and low primary production in the eastern Mediterranean. Zinc will not be discussed in detail due variability from potential contamination during sampling. Residence times of these metals in surface waters are overall longer than for scavenged metals (Table 5.7). The concentrations of Ni, Cu and Cd in Atlantic surface waters entering the Mediterranean are lower than MSW. During the transit from west to east, a continuous input to surface waters (from atmospheric and coastal sources) results in an increase eastwards in the surface concentration of Ni and Cu, as previously observed by Saager (1994) and Morley *et al.* (1997) and also confirmed in the present study. This phenomena may be further enhanced by the increase in oligotrophy towards the eastern basin. In this work in the Cretan Sea Cd concentrations fall within the range of those observed (including standard deviations) for the Mediterranean Sea (Morley *et al.*,1997; Yoon *et al.*, 1999). Martin *et al.* (1989) estimated longer residence times for Cd (10-22 years) than for Cu in the western Mediterranean, with a similar residence time for water (15.2 years), and they suggested that Cd distributions are governed by water dynamics. Due to the increase in the surface waters of the eastern Mediterranean, deep waters will also reflect this increase, with higher Ni and Cu concentrations in CDW (as seen in this study) than in western basin WMDW (Morley *et al.*,1997; Yoon *et al.*, 1999). Therefore it appears that the Mediterranean is not in a steady state with regards to Ni, Cu and Cd.

By understanding the processes that control the biogeochemistry and distribution of trace metals in the Mediterranean Sea, potential changes in trace metal concentrations over time can be better understood, especially when related to anthropogenic sources. The temporal variability of trace metal concentrations in the Aegean Sea between March and September 1997 has already been discussed. In addition, changes over longer time scales may be the result of variability in atmospheric and coastal sources, biological production and mixing of water masses within the Mediterranean; such changes may be a combination of natural and anthropogenic processes.

The increase in Pb concentrations since the 1960's in Mediterranean surface waters has been attributed to the consumption of leaded gasoline in Europe (Schaule & Patterson, 1983; Milliman & Martin 1997). The subsequent reduction of leaded gasoline has been reflected in a decrease of dissolved Pb since the late 1980's (Mignon & Nicholas, 1998). For other metals changes over time are less certain due to the limited availability of reliable atmospheric, riverine and seawater data. Bethoux *et al.* (1990; 1996; 1999) suggest an increase of 6% a year for Zn and Pb and 2% a year for Cu and Zn between 1960-1983. These inputs were connected to an increase in atmospheric and terrestrial inputs of predominantly anthropogenic origin.

Mediterranean nutrient levels are low and the open Mediterranean is regarded as oligotrophic, with even lower (of about 3 times) primary production in the eastern basin (Yilmaz & Tugrul, 1998; Turley, 1999; Yilmaz *et al.*, 1999). However, over the last three decades there has been a steady 0.5% per year increase in deep water nitrate and phosphate (Bethoux *et al.*, 1999) from atmospheric (Herut *et al.*, 1999; Guerzoni *et al.*, 1999) and terrestrial inputs (Turley, 1999; Guerzoni *et al.*, 1999), potentially of anthropogenic origin. High loadings of nutrients from excess fertilizers and atmospheric inputs have resulted in eutrophication and toxic algal blooms in some coastal regions of the Mediterranean (Turley, 1999; Guerzoni *et al.*, 1999). In the open ocean, sporadic atmospheric events can lead to patches of enhanced primary production (Guerzoni *et al.*, 1999). This potential for localised nutrient increases, combined with upwelling as already discussed, may lead to increased primary production, which in turn may manifest in the surface concentrations of the nutrient type metals, Ni, Cu, Cd and Zn.

Finally, recent changes in the formation of deep water in the eastern Mediterranean, with dense water formation having moved from the Adriatic (EMDW) to the Aegean (CDW and NAEGDW) has caused an overflow of CDW (or CSOW) from the Aegean to the Ionian and Levantine Basins (Theocharis, *et al.*, 1993; Klein *et al.*, 1999; Lascaratos *et al.*, 1999; Tsimplis *et. al.*, 1999). The phenomena may be the result of climatic changes in the eastern Mediterranean, which leads to a deep water increase in salinity and temperature (Klein *et al.*, 1999; Tsimplis *et al.*,1999), combined with wind stress and the reduction of BSW outflow (Tsimplis & Baker 2000). The fluxes of dissolved trace metals were calculated in 1994 through the Antikithira and Kassos Straits of the Cretan Sea with overall net fluxes for all metals to the Ionian and Levantine basins (Balopoulos *et al.*,1999). Therefore, the trace metal concentrations observed in the Cretan Sea in 1997 will influence the deep waters of the entire eastern basin.

In addition the changes in deep water circulation have caused the shallowing of the thermocline (personal communication Dr. M. Tsimplis). As a result, elevated surface metal concentrations have been observed above the thermocline, as seen in September 1997 in both the northern and the southern Aegean Sea. However, since 1998, the changes in deep water production appear to have presently stopped (Tsimplis & Baker, 2000). Although the long-term changes of trace metal concentrations in the deep waters of the Mediterranean are currently unknown, climatic changes in the Mediterranean may influence the distribution of metal signatures associated with water masses in the eastern Mediterranean and also affect the metal concentrations at the surface, when related to thermocline depth.

CHAPTER 7

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The distributions of dissolved trace metals in the Aegean Sea are dependant on the biogeochemistry of each metal, atmospheric and fresh water sources and the hydrography and circulation of the Aegean and Mediterranean water masses.

Dissolved metal depth profiles in the Aegean Sea exhibited surface elevation for Mn, Co, Fe, Pb, Cu and Zn with relatively uniform deep water concentrations. Spatial variability exists with greater surface concentrations in the northern Aegean. This was attributed to the influence of BSW entering the north Aegean through the Straits of Dardanelles and potential additional coastal sources from the rivers in northern Greece and Turkey. A positive correlation of Mn, Co, Fe, Cu and Ni with salinity was observed and the extrapolated concentrations of these metals to the salinity of the Straits of Dardanelles were calculated, in order to assess the potential influence of BSW in the northern Aegean. The estimated metal concentrations fell within a similar range to those observed in surface waters of the Marmara and Black Sea. However, slight variations in metal/salinity values, with higher values for Mn, Co, Cu and Ni on the northern shelf edge close to the rivers Nestos and Evros, suggest that additional sources and/or processes control the surface concentrations of dissolved metals in the north Aegean.

The atmospheric fluxes of soluble metals to surface waters represent a major source of metals to the Aegean Sea. Atmospheric metal flux calculations for the central and north-western Mediterranean (Guieu *et al.*, 1997; Guerzoni *et al.*, 1999) were used to calculate residence times and soluble metal fluxes to the Aegean surface waters. In comparison with sediment trap metal fluxes and metal particulate data in the Aegean Sea, atmospheric deposition was assessed to be the predominant source of metals in the south Aegean and a major contribution, in addition to BSW and coastal sources, in the northern Aegean.

Temporal variability in Aegean surface waters is observed between March and September 1997, with greatest surface concentrations for Mn, Co, Fe, Pb, Cu, Ni and Zn in September 1997. Although Price *et al.* (1999b) suggested an enhanced aolian input of

Saharan origin in September, atmospheric flux calculations to surface waters and residence times suggest that the shallowing of the thermocline, from approximately 100 to 50 m between March to September 1997 results in elevated concentration of dissolved metals in the upper mixed layer.

Trace metal signatures have been associated with several water masses of the Aegean Sea. In addition to BSW, elevated dissolved Mn, Co, Fe and Pb are attributed to an intrusion of LIW in the north Aegean in March 1997. LIW formation occurs in the Levantine basin from surface waters that sink under certain wind and temperature conditions and retain their elevated surface metal signatures. Due to the bathymetry of the Aegean Sea, there is little communication between northern (NAEGDW) and southern (CDW) deep waters masses. Dissolved Pb, Cu and Cd concentrations are slightly higher in NAEGDW, formed from BSW and LIW which are associated with elevated metal concentrations. The presence of cyclonic circulation in the Cretan Sea has been linked to upwelling of dissolved nitrate plus nitrite, silicon and manganese, following density isolines in an east to west transect across the south Aegean in September 1997, as also observed in March 1997 by Price *et al.* (1999a).

The scavenged metals Mn, Co, Fe and Pb exhibit elevated surface concentrations from atmospheric, freshwater and coastal sources, followed by rapid removal by particulate scavenging below the thermocline and homogenous deep water concentrations. The short calculated residence times in the southern Aegean of 0.3 to 6.0 years in surface waters reflect their particle reactivity, with the exception of Co, which exhibits a similar cycling pathway to Mn but with a longer surface residence time of 4 to 40 years.

The vertical distributions of Ni, Cu, Cd and Zn do not resemble those of the dissolved macro-nutrients. Ni, Cu, and Zn show surface elevation in the northern Aegean, and to a lesser extent in the southern Aegean, whereas Cd depth profiles are homogenous. These profiles are a result of surface metals sources combined with the oligothrophic nature of the Aegean Sea. Therefore it has been suggested that the Aegean Sea (as well as the Mediterranean) is not in a steady state with respect to Ni, Cu, Zn and Cd.

Due to its small size and short deep-water residence times (estimated at 85-125 years) the Mediterranean is particularly sensitive to inputs from the continent. The importance of dissolved trace metal surface sources to the Aegean Sea has been conclusively established. However, there is still limited information on atmospheric and riverine/estuarine fluxes to the Mediterranean, and even less for the eastern Mediterranean. Therefore, time series of atmospheric fluxes over the Aegean are considered essential in order to establish the contribution and temporal variability of trace metals to the Aegean Sea.

Although extensive work on dissolved and particulate metals in the Black Sea has been carried out in recent years, there is little information on the Marmara Sea. The temporal variability of BSW fluxes through the Straits of Dardanelles, with reference to metal fluxes, needs to beinvestigated. Recent trace metal fluxes have been derived for the Straits of Dardanelles (Yemenicioglu & Salihoglu, 1999) for Ni and Cu and can be used to calculated more realistic residence time for surface waters of the north Aegean, and the relative contributions of BSW and atmospheric fluxes.

Of interest in the north Aegean is the extensive fishing activities between October and May each year, resulting in huge particulate resuspension on the northern shelf. Although no clear influence on the concentrations and distributions of dissolved metals, particulate metals and sediment trap fluxes were affected, along with benthic biology. The effects of this phenomena on SPM, biogeochemistry and biology, presents a important subject for future work.

Finally, lateral water fluxes are being currently calculated in the northern Aegean, for the period of September 1997 and these fluxes can be used to calculate dissolved metal and nutrient fluxes in the north Aegean and across Thermaikos Gulf.

A full analysis of the relationship between particulate and dissolved trace metal data is intended to be developed for future publications.

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APPENDIX I

RESULTS OF ^{54}MN ADDITIONS TO SEAWATER TO CALCULATE EFFICIENCY OF CHLOROFORM EXTRACTION METHOD

Method	Sample	Mean Counts	Mean - blank	SD	% SD	Effeciency (%)
Method 1	Secondary standard	14790.25	**14756.25**	69.31	0.47	
Experiment 1	Blank	34.00		0.00		
	(A) chloroform 1 (3ml)	11686	11652.00			
"	(B) chloroform 1 (3ml)	11964.50	11930.50	181.73	1.52	
"	A chlor 2	2996.00	2962.00	12.73	0.42	**(A) 99.04**
"	B chlor 2	2562.50	2528.50	28.99	1.13	**(B) 97.99**
"	Secondary standard	14902.17	**14868.17**	144.13	0.97	
"	A chlor 3	9480.33	9446.33	56.71	0.60	
"	B chlor 3	9835.33	9801.33	136.14	1.38	
"	A chlor 4	3656.50	3622.50	36.48	1.00	**(A) 88.56**
"	B chlor 4	3283.00	3249.00	22.86	0.70	**(B) 88.44**
Experiment 2	Seconday standard	14801.50	**14767.50**	157.08	1.06	
	A chloroform 1 (3ml)	12783.17	12749.17	155.65	1.22	
"	B chloroform 1 (3ml)	12083.67	12049.67	159.49	1.32	
"	A chlor 2	1671.67	1637.67	23.24	1.39	**(A) 97.42**
"	B chlor 2	2567.00	2533.00	43.60	1.70	**(B) 98.75**
"	Secondary standard	14838.20	**14804.20**	15.07	0.10	
"	A chlor 3	9403.50	9369.50	62.66	0.67	
"	B chlor 3	10239.33	10205.33	96.93	0.95	
"	A chlor 4	2877.67	2843.67	57.00	1.98	**(A) 82.70**
"	B chlor 4	2487.17	2453.17	23.93	0.96	**(B) 85.72**
Mehod 2	Secondary standard	14218.17	**14182.00**	137.34	0.97	
Experiment 4	Blank	36.17		3.43		
	A evaporation	14020.83	13984.66	90.15	0.64	**(A) 98.61**
	B evaporation	13564.67	13528.50	62.74	0.46	**(B) 95.40**
Experiment 5	Secondary standard	13914.00	**13876.17**	169.32	1.22	
	Blank	37.83		5.19	13.73	
	A evaporation	14070.00	14032.17	96.36	0.68	**(A) 101.12**
	B evaporation	14144.50	14106.67	41.15	0.29	**(B) 101.66**
Experiment 6	A evaporation	13462.83	13425.00	115.23	0.86	**(A) 96.75**
	B evaporation	10450.50	10412.67	103.02	0.99	**(B) 75.04**
Experiment 7	Secondary standard	13941.50	**13903.67**	106.03	0.76	
	Blank	37.17		9.56	25.72	
	A evaporation	13163.00	13125.17	123.75	0.94	**(A) 94.40**
	B evaporation	13643.83	13606.00	167.48	1.23	**(B) 97.86**

APPENDIX II

TABLE OF DATA (ON DISKETTE)

Includes the following:

Station number
Sample period (March and September 1997)
Depth (CTD pressure in decibars)
Bottle salinity
CTD salinity
Dissolved iron (nM)
Dissolved zinc (nM)
Dissolved cadmium (nM)
Dissolved manganese
Dissolved copper (nM)
Dissolved cobalt (nM)
Dissolved nickel (nM)
Dissolved lead (nM)
Dissolved inorganic nitrate plus nitrite (μM)
Dissolved inorganic silicon (μM)
Dissolved inorganic phosphorus (μM)

Note: where data is not available it is due to the following reasons:

i) Bottle sample not collected or analysed, due to the go-flo not firing at the correct depth (as seen in variations between bottle and CTD salinity)

ii) Contamination of sample during collection or analysis.

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