HEAVY METAL INPUT TO NORTHERN LEVANTINE BASIN FROM LAND BASED SOURCES ALONG THE TURKISH COAST AND BY DARDANELLES STRAIT

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ABSTRACT

Turkey rank first in discharging fresh water in to the North Eastern Mediterranean region. The annual fresh water discharge by the main rivers in the southern coast of Turkey amounts to $3.213x10^{10}$ m^3. This amount constitutes about 8% of the total fresh water input in to the whole Mediterranean Sea. The main rivers draining in to the NE Mediterranean from Turkey is shown on Figure 1.

The annual water discharge by the industries and cities established at the southern coast of Turkey is about $1.331x10^8$ m^3.

The annual water inputs for each identified source within the frame work of this study and the annual input of the studied parameters are summarized in Table 1.

This work partly aims to give a summary and the conclusions on the work carried out in the Northern Levantine Basin and is based on:

a) A compilation of the data obtained at Northeastern Mediterranean from the so called coastal and refence (open sea) stations.

b) A compilation of the data obtained from the land based sources (rivers, industrial discharges, sewages) along the southern coast of Turkey.

The above mentioned data collection covers the period between 1983-1991 and a wide range of matrices such as waste water, river water, sea water, suspended solids, biota *etc.*

Another means of supplying materials to the Mediterranean is Dardanelles strait which connects Black Sea-Marmara Sea and the Aegean Sea. When compared with the riverine input of materials to the Mediterranean Sea, the material suply and the water flux of Dardanelles is comparable.

INTRODUCTION

The aim of this paper is to give a summary and the conclusions on the work carried out so far in the Northern Levantine Basin and in the Dardanelles Strait. The paper is based on the compilation of the data obtained from the work done:

a) in the North-Eastern Mediterranean from the so called coastal stations,

b) at land-based sources (rivers, industrial effluents, and sewage) along the southern coast of Turkey,

c) in the Marmara Sea and Dardanelles strait.

The above mentioned data collections cover the period between 1983-1991 for the Mediterranean Sea. The work includes a wide range of matrices such as waste water, river water, sea water, suspended solids, biota and sediment. The data collection for Dardanelles strait covers the period between 1986-1990 and the matrices included are; sea water, sediment and suspended matter. Here only some parts of these two works is compiled and evaluated.

METHODOLOGY

Determination of the temporal variability of the river fluxes is very difficult, for this reason the flux calculations was done by using average flux values. A simple relationship is used to calculate the material and pollutant fluxes. The average material concentrations in the source water was multiplied by annual average of water fluxes. The sampling periods include both low water stage and flood periods. But no sampling was done during the catastrophic flood events (such as exceptional floods and storms). At least two sampling was done from the rivers from both banks and care was taken to avoid contamination of the samples.

The quality assurance of the data of the work is done by checking the accuracy and precision of the methods used. To do so interlaboratory comparison of the analytical performance was done with certified reference materials (CRM`s). Among those which worth to mention are the CRM's of NBS (National Bureau of Standards, USA), BCR (Community Bureau of Reference, EEC), EPA (Environmental Protection Agency, USA). Our laboratory (Institute of Marine Sciences-Middle East Technical University), take part in the intercalibration exercises organised and/or run by IAEA

Monaco Laboratories, ICES Marine Chemistry Working Group, Intergovernmental Oceanographic Commission of UNESCO.

GENERAL KNOWLEDGE OF THE REGION

The studied area (Northeastern Mediterranean) is bordered to the north by Turkey, to the east by Syria and Lebanon and to the west by the strait of Crete. The southern border extent up to 34^{o} N.

The general water circulation in the region is from south to north along Syria and Lebanon coasts and from east to west along Turkish coast. Two main water masses are dominating the hydrographic characteristics of the region. The Levantine Intermediate Water (LIW) which is formed in the region of Rhodes gyre and sinks down to about 300 m depth (Özsoy *et al.*, 1989) and the Atlantic water coming in through the Gibraltar Strait, follows the path to the east along the African coast and on reaching Northeastern Mediterranean it split into two branches. One of them turns to the north by following an anticlockwise path and the other continues to the east ward direction and on reaching Lebanon coast turns to the north. On reaching to the Turkish coast it changes its direction once again and flows to the west following the southern coast of Turkey. The general surface water circulation in the eastern Mediterranean is given in Figure 2.

The continental shelf between Marmaris and Mersin is relatively narrow (average width 4.5 km) and deep. In the area between Mersin and İskenderun a 70 km wide continental shelf has been built by the action of several rivers draining to this region (see Figure 1 for the rivers draining in the region).

Dardanelles strait connects Marmara and Black seas to the Mediterranean Sea via Aegean Sea. There prevailing two current systems in the strait. The upper current is to the Mediterranean Sea and carries low saline water (20-22 ppt) of the Black Sea, the lower current is from Mediterranean to the Marmara Sea. The complete view of the circulation and hydrography of the Marmara sea and Turkish straits was studied by Beşiktepe et al., (1994).

SOURCES AND INPUT OF POLLUTANTS IN TO THE REGION

Turkey rank first in discharging fresh water in to the eastern Mediterranean sea. The annual fresh water discharge by the main rivers in the southern coast of Turkey amounts to 3.15×10^{10} m^3. This amount constitutes about 8% of the total fresh water input in to the whole Mediterranean Sea. The main rivers draining in to the NE Mediterranean from Turkey is shown on Figure 1.

The annual water discharge by the industries and cities established at the southern coast of Turkey is about 1.33×10^8 m^3. The main cities and industries established along southern coasts of Turkey is shown on Figure 1.

The annual water inputs for each identified source within the frame work of this study and the annual input of the studied parameters are summarised in Table 1.

TOTAL SUSPENDED SEDIMENT (TSS)

The total suspended sediment (TSS) input in to the NE Mediterranean is calculated from the data obtained at the sources under consideration (rivers, industrial discharges and sewage) between the years 1983-1991. The estimated total TSS flux to the region is about 1.99×10^6 t/y. The great portion of this load (1.84×10^6tons) that amounts to 95% of the total input is introduced by the rivers. Although some of the rivers receive domestic and industrial discharges (Ceyhan, Seyhan and Berdan Rivers) and hence values from those rivers include domestic and industrial inputs also, it is clear that TSS input from domestic and industrial sources is constitute only a small portion of the total. Table 1 and Table 2 summarises the total material fluxes from each source and measured concentrations respectively. When the TSS flux extrapolated for the other rivers (Koca, Asi, Köprü, Aksu rivers) the total TSS flux to the region is 2.27×10^6 t/y. It has been shown that about 90% of the TSS input settles down in the coastal and estuarine regions and only 10% escape to the open sea (Martin and Gordeav, 1986).

The measured average TSS load along the coastal regions of studied area (Northeastern Mediterranean) is 0.8 mg/L. This result is in agreement with the Emelyanov and Shimkus, (1972) findings. The selected TSS loads in the surface waters from the studied region is given in Figure 3.

The measured TSS load along the Dardanelles strait is ranging between 0.1-3.6 mg/L and the average load is 1.09 mg/L. The average water flux from the Marmara Sea to the Mediterranean Sea is 1218 km^3/y (Beşiktepe et al., 1994). From the average TSS load and average water flux it was calculated that annually $1.33x10^6$ tons of suspended sediment is introduced in to the Mediterranean Sea. This amount is very close to the TSS introduced into the region by the rivers.

MERCURY

Mercury itself and its compounds are very toxic to the living organisms. It is biomagnified through the food chain and it can be transformed into the more toxic methylmercury by biotic and abiotic pathways, thus it is one of the metals which receive great concern.

The total mercury input in to the NE Mediterranean from the studied sources is calculated as $5.56x10^5$ g/y. More then half of the mercury ($3.55x10^5$ about 64%) introduced in to the sea is in the particulate form. Thus, at the estuaries or coastal site a great portion of the introduced mercury is expected to settle down by precipitation of the particulate materials and incorporated in to the sediment.

It is important to note that, although, the eastern part of the region receives about 60% of the total fresh water input (including domestic and industrial discharges), the mercury contribution to this part constitute about 80% of the total input. Beside Turkey being one of the few countries having mercury ore, in the Çukurova region which is the catchment area of the rivers (Seyhan, Ceyhan and Berdan rivers) draining into the eastern part of the studied area, cotton is cultivated and mercury based fungicides are used extensively (see Figure 1). The rivers draining in this region contains more mercury than the worlds average. This is not a drastic result, since as mentioned above the catchment areas cover the regions where either mercurials are used as fungicide and natural mercury ore reservoirs or both.

The total mercury concentrations measured along NE Mediterranean coastal surface and subsurface water ranges between 2.5 to 27 ng/L with an average of 11 ng/L. Those high concentrations were measured at the coastal stations situated in the eastern part where intense industrial activities and farming take place.

The distributions of mercury at the coastal regions are shown in Figure 4. More detailed studies of mercury distribution in the region is done by several authors and can be found in Salihoglu and Yemenicioglu (1986), Salihoglu *et al.*, (1987) and Salihoglu, (1989).

The average total mercury concentration measured in surface and subsurface waters along the Dardanelles strait is 3.8 ng/L and is ranging between 3.0-4.8 ng/L. The average particulate bound mercury is 0.61 ng/L having a range of 0.51-0.90 ng/L.. Total mercury flux from Dardanelles to the Mediterranean is calculated as $4.75x10^6$ g/y.

CADMIUM

The input of the Cd from each source and the concentration in the individual source water is given in Table 1 and Table 2 respectively.

Cadmium is one of the important heavy metal in view of human health. Cadmium contamination cause the bone disease (ITAI-ITAI) which is a deadly disease to humans.

The measured Cd concentrations in particulate matter from the NE Mediterranean is ranging between 2-25.2 ng/L with an average of 4 ng/L. Since the particulate bound cadmium in the sea water forms only 20% of the total (Roth and Hornung, 1977), the total cadmium concentration in the NE Mediterranean is higher then this amount.

The estimated total cadmium input from land based sources to the NE Levantine is $6.12x10^4$ g/y and about 90% of this is carried by rivers. About 80% of the Cd introduced in to the region is in the particulate form and a great portion of this is expected to settle down with the particulate materials and incorporated into the sediment at the coastal and estuarine site.

In the Dardanelles strait upper layer (surface and subsurface water) the average total Cd concentration is 3.5 ng/L and the particulate bound Cd is 2.1 ng/L. By using the annual water input by Dardanelles strait the total Cd flux to the Mediterranean was calculated as $4.26x10^6$ g/y.

TIN

The average total tin concentration in the sea water of the region was measured as 11 ng/L. The organotin compounds was detected only in coastal waters (river deltas and estuaries). A detailed study of tin and organotin compounds has done and can be found in Yemenicioglu *et al.*, (1984), Tugrul *et al.*, (1990) and Kubilay, *et al.*, (1996).

The inorganic and methyltin concentrations measured in coastal sea water samples and in sediment samples are given in Table 3 and Table 4 respectively. As can be seen from Table 3 the trimethyltin species only detected in unpolluted regions Lamas and Göksu rivers estuaries. No organo-tin species was detected in the river water, industrial effluents and sewage. Only inorganic tin was detected.

The estimated tin flux to the NE Mediterranean is 1.09×10^6 g/y. About 70% of this is introduced by the rivers. The tin transport by the Dardanelles strait to the region was calculated as 4.0×10^6 g/y. This amount is exceeded the totals of the other sources at the coastal regions.

CONCLUSION

The rivers draining in the region contain more mercury than the worlds average. This is not a drastic result, since the catchment areas cover the regions where either mercurials are used as fungicide or natural mercury ore reservoirs or both.

Although, the eastern part of the region receives about 60% of the total fresh water input, the pollutant contribution to this part constitute more than the half of the total input (mercury about 80%, Cd 68% and TSS 41%). This is the result of intense industrialisation, cultivation and extensive use of mercury based fungicide.

If the pollutant transports are compared, the mercury and cadmium transport by Dardanelles Strait exceeds the land based sources by an order of magnitude.

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Table 1. Annual water discharges and Pollutant input of identified individual source.

Source	Discharge m^3/y	Hg-T input g/y	Hg-P input g/y	Hg-D input g/y	Cd-T input g/y	Cd-P input g/y	Cd-D input g/y	TSS input t/y	Sn input g/y
Iskenderun-S	$8.33x10^6$	133,06	115,92	17,14	26,01	10,03	15,98	832,94	$1.23x10^3$
Isdemir-I	$3.73x10^6$	0,181	0,16	0,02	0,013	0,010	0,003	1,43	1.43
Isdemir-S	$2.19x10^6$	32,61	28,39	4,22	3,24	3,24	0,000	33,67	----
Sariseki-I	$1.22x10^6$	288,00	180,90	107,10	11,18	6,38	4,80	843,36	292.8
Toros.A-I	$0.07x10^6$	2,0400	0,0015	2,039	0,0003	0,0003	0,00	6.22	$4.55 x10^{-3}$
Toros.B-I	$0.23x10^6$	9,4400	0,0092	9,4308	0,0011	0,0007	0,0004	34.47	----
Seyhan R.	$6.51x10^9$	76899	42803	34096	24103	10359	13744	124046	$4.65 x10^5$
Ceyhan-R	$8.69x10^9$	154006	114225	39781	19215	13325	5890	633878	$2.61 x10^5$
Berdan-R	$1.33x10^9$	18138	11729	6409	1071	1001	69,83	33481	$1.86 x10^3$
Mersin-S	$23.7x10^6$	1538	959,01	578,8	61,62	50,45	11,17	919,63	$1.01 x10^3$
Lamas-R	$0.22x10^9$	2861	1773	1088	371,17	262,63	108,55	7834	$1.31 x10^5$
Göksu-R	$4.31x10^9$	50901	18749	32153	10473	10236	237,05	617991	$1.33 x10^5$
Manavgat-R	$4.99x10^9$	59900	30190	69095	6986	6983	3,00	75688	$6.14 x10^2$
Antalya-S	$22.8x10^6$	573,99	234,36	339,63	16,20	6,68	9,51	184,09	----
Esen-R	$1.46x10^9$	60024	57261	2762	1351	822,47	528,03	173509	----
Marmaris-S	$2.80x10^6$	39,52	13,77	25,75	5,81	5,50	0,31	75,63	
Dalaman-R	$1.56x10^9$	$6,00x10^4$	$5,73 x10^4$	2762	1351	822,47	528,03	173509	$2.26x10^5$
TOTAL	$2,91x10^{10}$	$4,85x10^5$	$3,36 x10^5$	$1,89 x10^5$	$6,48x10^4$	$5,27 x10^4$	$1.21x10^4$	$1,93 x10^6$	$1,09 x10^6$
Dardanelles	1257**	$4.38x10^6$	$9.68x10^5$	$3.41x10^6$	$4.26x10^6$	$2.26x10^6$	$2.0x10^6$	$1.37x10^6$	$4.0x10^6$

S:Sewage; I:Industrial; R:River; Hg_T:Total mercury; Hg_{TSS}:Mercury in suspended matter; Hg_D: Dissolved mercury; Cd_T:Total cadmium Cd_{TSS}:Cadmium in suspended matter; Cd_D: Dissolved cadmium; **: Km^3/y.

Table 2. Measured concentrations of mercury, cadmium and total suspended sediment in identified individual source water.

Stat. no.	Hg_T ng/L			Hg_P ng/l			Cd_T ng/L			Cd_P ng/L			TSS mg/L		
	MAX	min	mean	max	min	mean	max	min	mean	max	min	mean	max	min	mean
ISKENDERUN-S	59	3,3	15,97	55	2,80	13,92	8,10	0,07	3,12	3,17	0,20	1,20	466	0,94	100
ISDEMIR-I	201	6,0	48,52	152	2,00	42,91	6,00	0,17	3,52	5,66	0,19	2,75	4838	1,90	382
ISDEMIR-S	59	3,2	14,89	55	3,00	12,96	5,60	0,30	1,48	5,56	0,10	1,57	38	0,60	15,3
SARISEKI-I	683	10	236	376	10,6	148	18,3	2,10	9,17	8,60	1,93	5,23	1872	140	692
TOROSA-I	94,3	1,6	29,19	88	1,90	21,42	11,7	0,12	4,01	11,0	0,10	3,78	442	1,90	88,9
TOROSB-I	188	1,4	41,07	188	1,50	39,86	11,0	0,90	4,84	5,37	0,27	3,11	507	5,12	149,9
SEYHAN-R	32,5	2,0	11,81	22	2,10	6,58	10,0	0,00	3,70	10,0	0,10	1,59	58.0	1,33	19,05
CEYHAN-R	43,5	1,5	17,72	35	1,20	13,14	4,50	0,60	2,21	4,17	0,35	1,53	216	1,50	72,94
BERDAN-R	63	0,1	13,64	30	0,35	8,82	2,34	0,10	0,81	1,93	0,10	0,75	105	8,00	25,17
MERSIN-S	446	1,7	64,89	290	1,70	40,46	11,5	0,28	2,60	7,30	0,10	2,13	432	4,10	38,88
LAMAS-R	74	2,7	13,01	33	1,70	8,06	4,00	0,33	1,69	3,20	0,30	1,19	361	1,22	35,61
GOKSU-R	36,5	3,0	11,81	9	1,70	4,35	7,24	0,00	2,43	6,14	0,10	2,38	1193	0,84	143,4
MANAVGAT-R	59	3,2	19,90	14	3,00	6,05	5,00	0,10	1,36	4,64	0,10	1,68	35	0,33	15,17
ANTALYA-S	46	10.7	25,18	33	2,40	16,40	2,10	0,30	1,13	0,90	0,25	0,47	49	0,32	12,88
ESEN-R	165	1,96	41,11	160	1,10	39,22	2,30	0,20	0,93	0,66	0,45	0,56	440	1,61	118,8
MARMARIS-S	36,5	5,5	14,11	10,3	0,90	4,92	7,24	0,10	2,07	6,14	2,79	4,11	155	0,79	27,01

Table 3. Inorganic and methyltin concentrations in coastal sea-water (ng/L).

Sampling area	Sn_I	$MeSnCl_3$	$Me_2Sn\ Cl_2$	Me_3SnCl
Lamas R. Delta	1.2-33.6	>0.30-11	>0.15-21.6	>0.25-9.7
	(13.7)	(8.47)	(7.14)	(4.93)
Göksu R. Delta	49-11.7	>0.30-9.9	>0.15-41.8	>0.25-3.2
	(30.87)	(7.0)	(13.59)	(2.53)
Seyhan R. Delta	219-11.5	>0.30-17	>0.15-25.9	>0.25
	(71.5)	(15.1)	(15.92)	>0.25
Ceyhan R. Delta	2.5-76	>0.3-13.8	>0.15-17.4	>0.25
	(32.96)	(13.8)	(10.15)	>0.25
Stat. (4)	19-98	>0.3	>0.15-8.5	>0.25
	(58.5)	(>0.3)	(8.5)	>0.25
Stat. (3)	34-782	>0.3-20.7	1.8-19.5	>0.25
	(351)	(11.25)	(11.27)	>0.25
Stat. (2)	19.6-7711	>0.3-15.4	>0.15-10.9	>0.25
	(2001)	(14.9)	(10.75)	>0.25
Stat. (1)	3.5-722	>0.3-15.4	>0.15-25.9	>0.25
	(223)	(13.8)	(16.25)	>0.25

Table 4. Inorganic and methyltin concentrations in coastal sediments (ng/g).

Sampling area	Sn_I (μg/g)	$MeSnCl_3$	$Me_2Sn\ Cl_2$	Me_3SnCl
Seyhan R. Delta	0.38-0.77	ND-0.6	ND-3.3	0.1-0.7
	(0.65)	(0.35)	(1.89)	(0.38)
Ceyhan R. Delta	0.57-0.90	ND-0.3	ND-1.9	0.1-0.5
	(0.75)	(0.30)	(0.95)	(0.28)
Sarıseki	0.56-0.58	ND-0.3	0.1-1.6	0.1
	(0.57)	(0.3)	(0.85)	(0.1)
Iskenderun	0.86-1.0	ND-0.2	ND-0.4	0.1-0.3
	(0.93)	(0.2)	(0.4)	0.2
Göksu R. Delta	0.25-0.72	ND-0.2	0.1-0.7	ND-1.0
	(0.57)	(0.20)	(0.38)	(0.55)

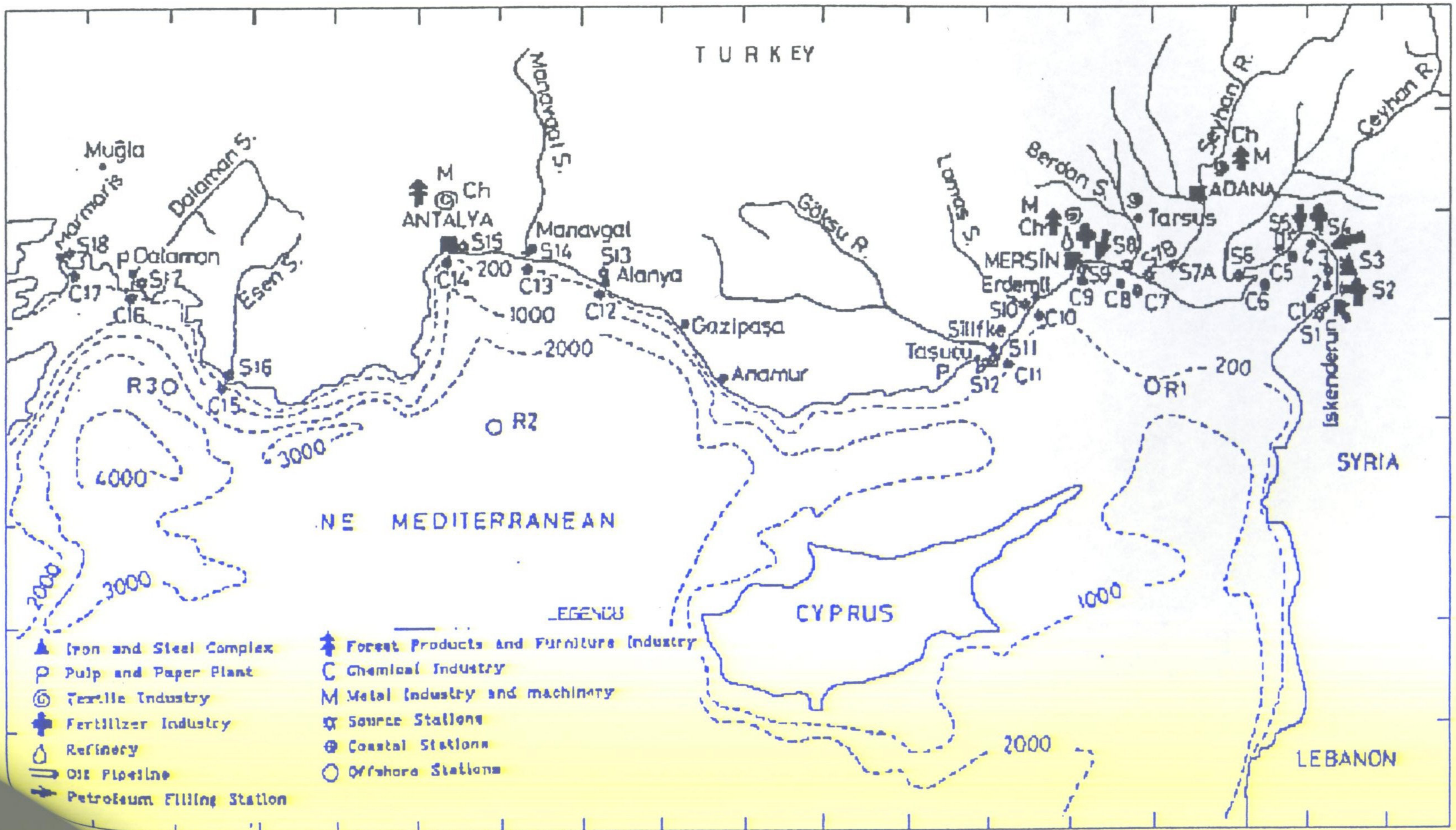

Figure :1 The studied area and sampling locations.