DETERMINATION OF ENVIRONMENTAL DISTRIBUTION OF SOME TOXIC AND NON-TOXIC SUBSTANCES IN SELECTED BASIN

"STUDIES ON QUALITY OF ENVIRONMENTAL DATA"

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by

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ABSTRACT

DETERMINATION OF ENVIRONMENTAL DISTRIBUTION OF SOME TOXIC AND NON-TOXIC SUBSTANCES IN SELECTED BASIN "STUDIES ON QUALITY OF ENVIRONMENTAL DATA"

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In this study three selected analytical methods, AA, ICP and INAA were used for analyzing the trace metal distributions of the "Göksu" river sediments.

During the study, the problems related to the homogeneity of the samples and the contamination control were also studied.

Results of ICP, AA and INAA were compared statistically. Comparison of ICP and AA showed a correlation greater than 80 % for most elements.

ICP results were used to determine the pollution finger prints of river "Göksu" sediments to open sea sediments. For this purpose eight selected elements,

Sr, Ca, Cr, Mn, Pb, Ni, V and Mg out of twenty one were considered.

Results of the study showed that "Göksu" river is not a pollution source only for lead in sea sediments. The lead accumulation in the "Taşucu" sediments may be due to the traffic or atmospheric transport of the element from the main land.

Vanadium level in the "Silifke" sediment is very high and it may concluded that there was an "anthropogenic" source of this pollution.

KEY WORDS : Data quality, Atomic Absorption, Inductively Coupled Plasma, Neutron Activation Analysis, Trace Metals, Sediment.

ÖZET

BAZI TOKSİK VEYA TOKSİK OLMAYAN MADDELERİN SEÇİLMİŞ BİR HAVZADA ÇEVRESEL DAĞILIMININ BELİRLENMESİ "ÇEVRESEL VERİ KALİTESİ ÜZERİDE ÇALIŞMALAR"

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Bu çalışmada üç seçilmiş analiz metodu, atomik absorpsiyon (AA), inductively coupled plasma (ICP) ve nötron aktivasyon analizi (NAA), "Göksu" nehri sedimanlarındaki eser element dağılımını incelemek üzere kullanılmıştır.

Çalışma sırasında, örneklerin homojenitesi ve kontaminasyon kontrolleri ile ilgili problemlerde çalışılmıştır.

ICP AA ve INAA sonuçları istatistiksel olarak karşılaştırılmıştır. ICP ve AA sonuçlarının karşılaştırılması elementlerin çoğunda % 80' nin

üzerinde uyum göstermiştir.

ICP sonuçları "Göksu" nehri sedimanlarının açık deniz sedimanlarına olan kirlilik etkisini belirlemekte kullanılmıştır. Bu amaçla yirmi bir elementten sekiz seçilmiş element olan Sr, Ca, Cr, Mn, Pb, Ni, V ve Mg göz önüne alınmıştır.

Sonuçlar "Göksu" nehrinin deniz sedimanlarındaki kurşun için bir kirlilik kaynağı olmadığını göstermiştir. "Taşucu" sedimanlarındaki kurşun birikimi trafiğe, veya bu elementin ana karadan atmosferik taşımına bağlı olabilir.

"Silifke" sedimanlarındaki vanadyum seviyesi çok yüksektir, dolayısı ile burada antropojenik bir kirlilik kaynağı olduğu sonucuna varılmıştır.

Anahtar kelimeler: Veri kalitesi, AA, ICP, INAA, eser elementler, sediman.

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CHAPTER 1

INTRODUCTION

Environmental analytical measurements were developed for a variety of purposes, such as the determination of the environmental fate (transformation and transport) of chemicals and determination of the environmental concentration of a chemical, for use in environmental risk assessments or in some cases for regulatory purposes.

The pollution of the environment is nowadays a potentially important problem and many environmentalists are investigating this matter within different frameworks such as the Mediterranean Action Plan, IOC Marine pollution monitoring system etc.

Among the various possible forms of pollution, that caused by heavy metals is perhaps the most important one as these substances are accumulated in the food-web, especially in the marine food-web, and are not destroyed with time.

River, lake and sea sediments, and filter-feeding animals are often considered as contamination indicators of the environment. Mussels react quickly to the

pollution of the surrounding water body, while mechanisms of transfer and fixation of heavy metals into sediments often reflect long term processes.

SCOPE AND OBJECTIVE

In this study the present situation of the quality of the environmental data in national and international studies are considered, the importance of trace metals in environment and available techniques for determination of trace metals are briefly discussed.

Three important analytical technique were selected and previously collected sediment samples were analyzed. In the selection of the analytical techniques their world wide usage was also considered.

As the homogeneity and the contamination of the sample used will affect the results some precautions were taken against contamination and the homogeneity of the sediment samples were checked.

Each sample was analyzed by the use of atomic absorption, inductively coupled plasma and neutron activation analysis techniques and their results compared statistically.

The purpose was to show the sensitive, economic, fast, easy to use, precise and accurate method(s) for a specific element.

Also by the use of one of the analytical

techniques, selected sampling site sediments were considered from an environmental point of view.

"Göksu" river is selected for sampling since it is considered as "non-polluted" with respect to other rivers. The river is surrounded with fields so there can only be "non-point" metal pollutants which can only be due to irrigation as some of the metals are used in herbicides, insecticides and fertilizers.

The methods used to analyze environmental samples in this study; atomic absorption, inductively coupled plasma and neutron activation analysis are compared for the first time for environmental samples in Turkey.

CHAPTER 2

LITERATURE SURVEY

2.1. Trace Elements As Toxic Substances

Man's activities contribute substantially to the fluxes of certain elements in the environment. For substances such as carbon dioxide, cadmium, arsenic, lead and mercury, fluxes of anthropogenic material approach or exceed the natural fluxes (GESAMP,1982).

Wood and Goldberg, (1977) divided metals of biological concern into three groups :

(i) light metals normally transported as mobile cations in aqueous solutions such as Na and K;

(ii) transition elements such as Fe, Cu, Co and Mg, which may be toxic at high concentrations and essential at low concentrations;

(iii) heavy metals or metalloid, that may be required for metabolic activity at low concentration, but which at slightly higher levels are toxic to the cell such as Hg, Se, Pb, Sn and As.

Several factors must be considered in relation to the movement of metals in biogeochemical cycles: chemical form (solution, colloidal, particulate) and speciation; reactions with inorganic and organic matter

(including biota); the magnitude of sources and sinks; and their location or distribution (Wood and Goldberg,1977).

Metals may be classified in terms of their relative toxicity and availability. Toxic metals forming organo-metallic compounds, like metalalklys, are of special concern. These include mercury, tin, arsenic, selenium, cadmium and lead.

Man's activities play a major role in the environment. The release of metals by man is most evident in coastal waters, shallow sea areas, rivers and lakes.

The terms "heavy metals" and "trace metals" are used very loosely. They include a wide range of elements which are not "heavy" metals or even metals. The concept of toxicity is usually associated with these terms and the following elements are included: Hg, Cd, Cu, Zn, Co, Mn, Mo, Ni, Pb, Fe, As, Al, Cr, Sn, Ti, V, Ag, Bi, Be, Se, Te.

As mentioned above , trace metals enter the environment, especially to the oceans, as a result of natural processes and human activities via rivers, land run-off, dumping, the atmosphere and the sea bed. Major natural sources are rock weathering, degassing, releases from terrestrial and submarine volcanoes and dissolution from sediments. The dominant inputs for most trace metals are through river and land run-off, but for a few elements, such as Hg and Pb, the atmospheric route is

important, particularly in the open ocean, although even for these elements local discharges and rivers can dominate the coastal input because deliverly is from a point source. The mere presence of trace metals does not indicate a potential to produce damage. Several metals such as Fe, Cu, Zn, Co, Mn, Cr, Mo, V, Se, Ni and Sn, are known to be essential nutrients. An insufficient supply of an essential element will cause deficiency disease. Whether a metal is essential or not, exposure above a certain level may cause adverse effects. For some essential elements the body has a wide tolerance, whereas for others the safety margin between adequate supply and toxic exposure is relatively narrow.

In Minamata Bay, Japan, methylmercury from a chemical plant was discharged to the bay for at least 30 years up to 1968. Severe mercury intoxication affected human consumers of fish and there were a number of deaths. After the Minamata incident, particular attention has been paid to the concentrations of some metals in edible fish and shellfish (GESAMP,1982).

Trace metals in the environment have become a significant topic of concern for scientists and engineers in various fields associated with environmental quality, as well as a concern of the general public. Direct toxicity to man and aquatic life and indirect toxicity through accumulations of metals in the aquatic food chain are the focus of this concern. Mercury, cadmium and lead are but a few dramatic

examples on which attention has been focused.

The presence of trace metals in the environment originates from the natural interactions between water, sediments, soil and atmosphere with which the water is in contact. The concentrations fluctuate as a result of natural hydrodynamic, chemical and biological forces. Man, through industrialization and technology, has developed the capacity, perhaps unknowingly, to alter these natural interactions to the extent that his very use of these waters and aquatic life therein is threatened.

The role that trace metals play in natural biological life cycles is certainly of importance in defining the behavior and well-being of individual biological systems directly and, therefore, in defining the overall character of a water ecosystem. Understanding of this role is intimately connected to the exact forms and mechanisms of transformation of the trace metals in the system. These considerations relate both to those metals that are essential to biological function and those that may be inhibitory to organisms in the aquatic system. Regarding the latter point, biological transformations may convert inorganic metal forms to organic compounds of much greater toxicities (McBrride,1971).

Also we may assess the real impact of man-made alterations in natural environments. In fact, the natural cycle of a few elements is altered in smaller

environments but given enough time, they are incorporated back into the whole terrestrial cycle. As the result of this alteration, anomalous metallic concentrations are discovered near cities, freeways, smelters, powerplants and industrial sites.

Evaldo, (1973) mentioned geochemistry as a comparatively young and growing science which studies the chemical composition of earth. It was pioneered by F.W.Clarke, V.M.Goldschmidt and V.I.Vernadskii in the late 1920's. Increase growth began with the use of geochemistry as an applied science. Tracing the route and determining the concentration of substances or elements is a most important aspect of applied geochemistry. The first application was in economic geology and in tracing the origin, age, stability and transformation of certain biogenic and anthropogenic substances.

In the last two decades, anthropogenic emissions of increased amounts of metal pollutants have generated world-wide concern. Emissions enter all three phases: atmosphere, water and land. They admix and transfer within the phases and during meteorological phenomena such as dust storms, rain and oceanic breezes.

Of biological importance are some elements such as boron, copper, zinc, molybdenum, cobalt, selenium which in low concentration foster life. At higher concentrations, these elements may be toxic. Therefore, it is important to know their concentration in the

natural environment and how these concentrations affect the healthy deployment of life on earth. Thus, soil chemistry, water chemistry, some areas of oceanography and air chemistry are interrelated.

The environment constitutes a seamless web that may be studied from many viewpoints. It has been examined in detail by the methods of numerous scientific disciplines.

2.2. Determination Of Inorganic Pollutants

2.2.1 The use of General Techniques

Braun, (1987) While evaluating the recorded knowledge in nuclear and instrumental analytical techniques, mentions that, there are basically two ways of assessing or evaluating the progress, trends, advances, growth, etc., of a given field or sub field of science;

- Peer evaluation
- Statistical evaluation of recorded knowledge (subject literature).

Most of the first type of assessment papers, written by well recognized individuals, are based on commonly shared insights, casual impressions and estimations, but they seem in general to lack a solid empirical base.

Braun, (1987) prefers second way "it is using statistical evaluation of the literature of analytical chemistry". The goal of the effort has been to chart comparatively what was studied in the field of nuclear

and other instrumental techniques.

Data on the distribution of uses of different instrumental techniques in analytical research papers published during the 1981-1984 period is given in Table 2.1. Braun, (1987) selected 15 elements and for each element the individual use of instrumental analytical techniques has been encountered in the subject index of each volume of the **Analytical abstracts**. The list of selected elements is given in Table 2.2.

Geographical distribution of the uses of different instrumental techniques given in Table 2.3. A selection of "hot spots" in his study is given in Table 2.4.

Table 2.1. Frequency Distribution of The Uses of Instrumental Techniques In 1981-1984 Research Papers.

Technique	no. of uses	%
Atomic absorbtion spectrophotometer	1648	24.1
Spectrophotometry	1271	18.5
Emission spectrometry	1005	14.7
Neutron activation analysis	585	8.5
X-ray fluorescence	452	6.6
Thin layer chromatography	149	2.2
High performance liquid chromatography	117	1.7
Atomic emission spectrometry	116	1.7
Polarography	94	1.4
Ion chromatography	81	1.2
Differential pulse polarography	61	0.9
Ion selective electrode	59	0.9
Flow injection analysis	57	0.8
Kinetic methods	56	0.8
Fluorimetry	52	0.8
Anodic stripping voltammetry	49	0.7
Voltammetry	47	0.7
Inductively coupled plasma	46	0.7
Proton induced X-ray emission	45	0.7
Atomic fluorescence spectrometry	42	0.6
Mass spectrometry	32	0.5
Amperometry	29	0.4
Stripping potentiometry	26	0.4
Gas Chromatography	25	0.4
Oscillopolarography	23	0.3
Chemiluminescence	17	0.2
Isotope dilution	17	0.2
Auger electron spectrometry	14	0.2
Electron microprobe	12	0.2
Liquid chromatography	12	0.2
Conductometry	11	0.2
A.c. polarography	9	0.1
Mol.emission cavity spectrometry	9	0.1
Paper chromatography	9	0.1
Photoacoustic spectrometry	8	0.1
Proton activation	8	0.1
Stripping voltammetry	8	0.1
Electron spin resonance	7	0.1
F.a.n.e.s.	7	0.1
Inverse voltammetry	7	0.1
Pulse polarography	7	0.1
Miscellaneous	420	6.1
TOTAL	6852	100.0

Table 2.2. Percentage Distribution of The Uses of Merged Instrumental Analytical Techniques In 1981-1984 Research Papers

Element	Technique				
	OPT	NUCL	ELEC	CHROM	MISC
Ag	59.1	14.1	15.7	3.5	7.7
As	70.4	15.1	7.8	4.2	2.5
Au	59.1	25.9	10.0	2.7	2.3
Bi	67.9	3.3	15.9	9.3	3.7
Co	62.9	13.6	9.5	10.3	4.1
Cr	70.2	14.0	7.4	5.8	2.6
Cu	66.3	8.2	14.6	6.8	4.1
Fe	70.8	13.5	5.6	5.2	4.9
Ga	71.6	11.9	12.8	1.8	1.8
Hg	65.9	12.9	9.8	9.1	2.3
Mn	73.2	16.2	3.9	4.1	2.6
Mo	70.1	12.6	9.6	4.8	3.0
Sb	59.5	21.6	11.4	3.4	4.2
U	47.2	29.1	13.9	6.8	2.9
V	74.7	11.1	7.2	3.6	3.4

Table 2.3. Geological Distribution of The Uses of Instrumental Techniques in 1983-1984 Research Papers

Location	AAS	ICP	INAA
USA&Canada	14	18	73
United Kingdom	47	9	1
Fed. Rep. of Germany	65	1	12
France	8	1	2
USSR	73	1	38
Japan	95	2	10
Asia	63	9	15
Latin America	10	-	2
Eastern Europe	87	1	26
North Africa&Near East	4	-	2
Rest of Devel. Count.	150	4	35

Table 2.4. Selected Emerging Specialty "hot spot" Clusters

- Pollution of aquatic environments
- Sulfur compounds in the atmosphere
- Atmospheric Chemistry: Air pollution

2.2.2 Selection of the analytical method

The choice of an analytical method is quite complex. Several factors must be taken into account:

1) The nature and composition of the sample which affect the sample treatment prior to measurement;
2) The approximate concentration of the analyte present in the measured sample and the limit of detection by the analytical procedure to be used;
3) The precision and accuracy required in the final analysis;
4) The speed required for obtaining a result;
5) The amount of sample available;
6) The number of samples to be measured ;
7) The variability of the sample matrix from sample to sample;
8) The cost per analysis;
9) The instrumentation and methodology available.

As mentioned by Tölg, (1987) and most researchers on analytical chemistry "one method is no method". Slavin, (1986) stated that " there is no best technique; the choice depends on your skill and on the analytical situation". Therefor only a multi-method concept can avoid the danger of developing a new method that does not meet the requirements of the actual problem. It must not be forgeten that, not only the instrumentation for the determination of the elements, but also sample

pre-treatment and chemical aspects play important roles in achieving progress.

2.2.3. Spectroscopic Techniques

1- Flame Atomic Absorption Spectroscopy

Flame Atomic absorption is very well established. It has few interferences, and these are well identified and often easily controlled. Standardization is usually simple. The equipment is relatively inexpensive and easy to use. From among the compared techniques it requires the least operator experience. Slavin, (1986) mentions the disadvantages of the flame Atomic absorption as; the more refractory elements such as B, V, Ta and W are only partially dissociated in the flame and are not readily accessible by flame Atomic absorption, samples containing metals such as Mo and the alkaline earths are not fully dissociated in the flame . Although the technique in rapid Atomic absorption instruments are rarely automated to permit simultaneous determinations of several elements.

Tölg, (1986) mentioned the power of Atomic absorption in his paper and said that "AAS became the most sensitive technique for direct and indirect determination of many elements , except the carbide forming elements and several non metals such as C, N, O, P, S and the halogens."

The detection limits of the flame atomic absorption spectrometry are given in Fig 2.1 and a summary of the best detection limits are given in Fig 2.2.

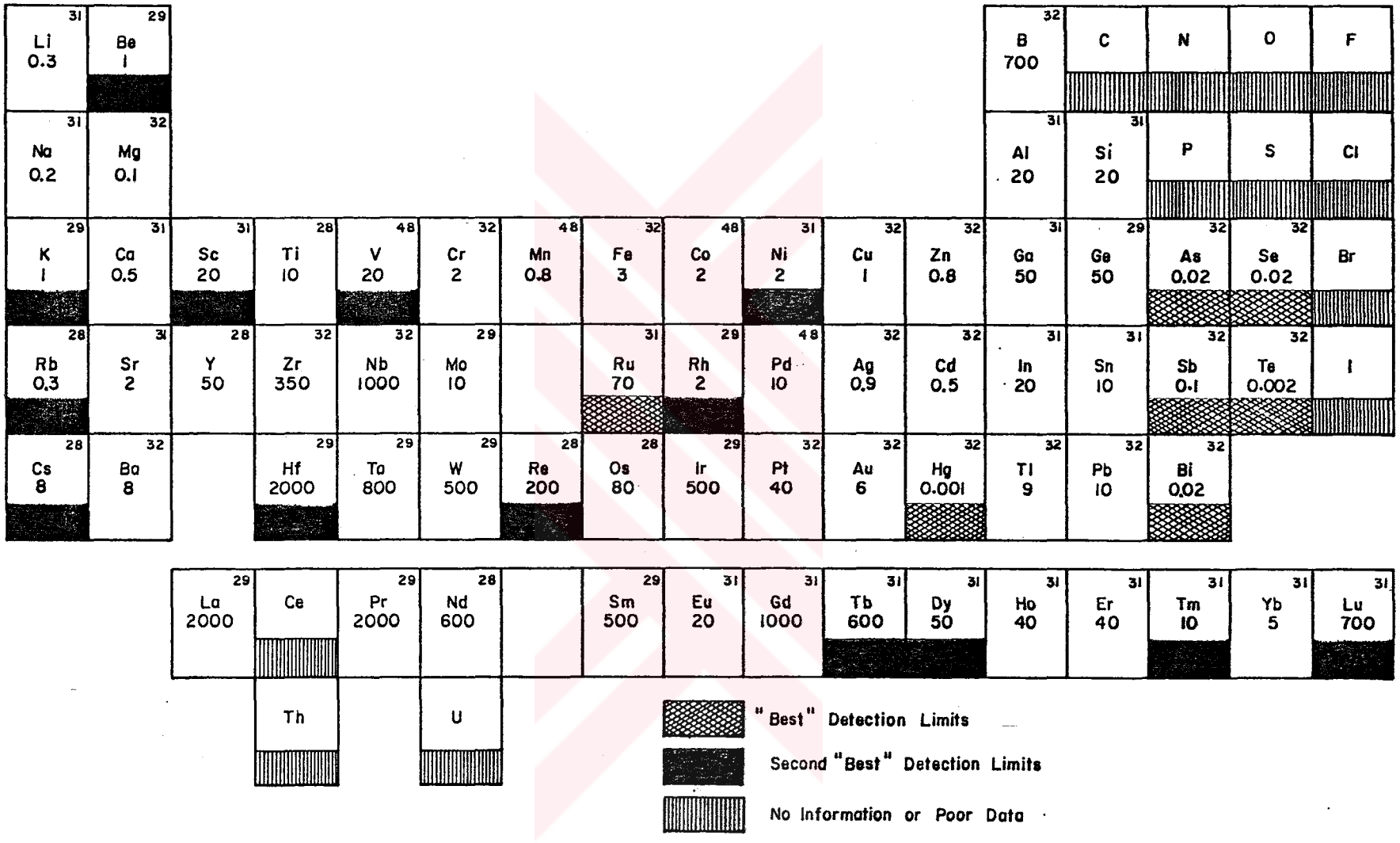

Figure 2.1. Flame atomic absorption spectroscopy limits of detection (nanograms per milliliter).

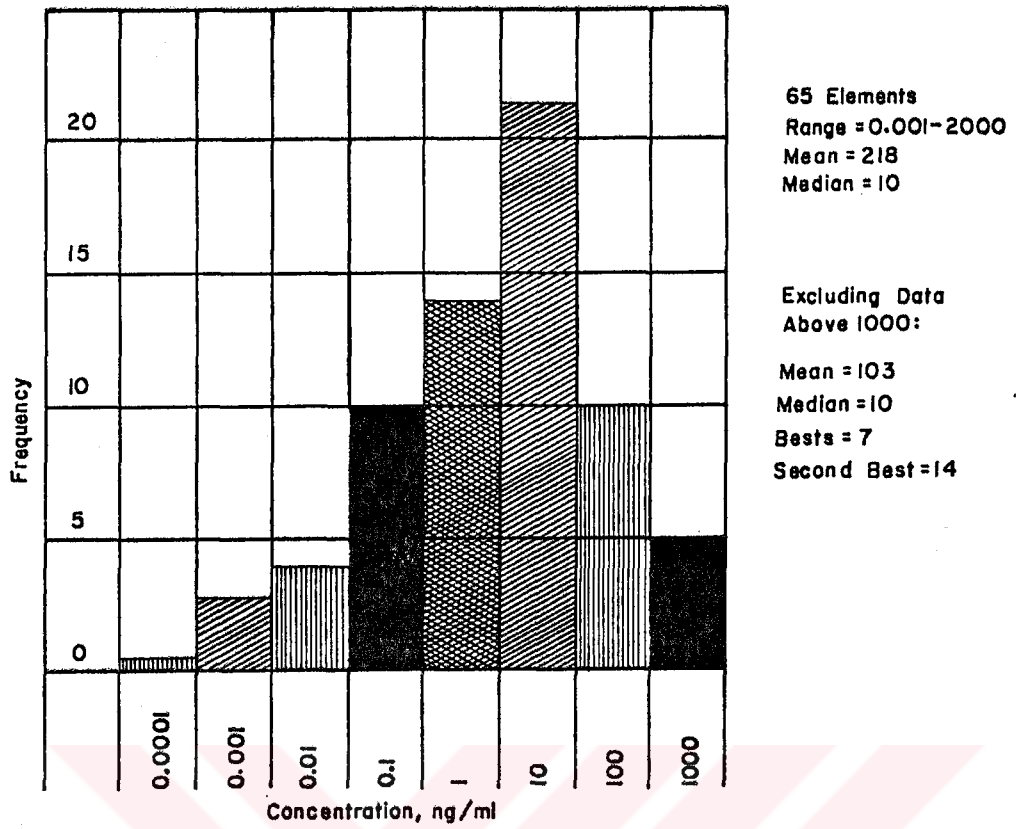

Figure 2.2. Summary data, FAAS (nanograms per milliliter).

2- Furnace Atomic Absorption Spectroscopy

Furnace atomic absorption has the lowest detection limits that can be obtained with spectroscopic techniques. On a relative or concentration basis, furnace detection limits are 10 to 100 times better than flame AA and ICP. On an absolute mass basis, furnace detection limits are often 1000 times more sensitive because only a very small sample volume is required for the furnace. Most of the reported interferences for furnace AA is eliminated by, high-quality graphite material, modern , fast photometric instrumentation and

zeeman background correction. "The level of interferences is now no greater than flame Atomic absorption and Inductively coupled plasma". Although this is stated by Slavin, there is still opposing ideas for this concept. On the one hand determinations are slow, (several minutes per sample) and are usually single element. Furnace Atomic absorption is preferable if the technique provides an inadequate detection limit.

3- Flame Atomic Emission Spectroscopy

As the oldest multi element atomic spectroscopic method, flame emission spectroscopy has earned its well established position. As the power of detection for numerous elements is relatively good, it was the classical spectroscopic method of choice until AAS became available. Even today it is still preferred, particularly for fast, roughly qualitative overview analyses in the micro gram per gram levels.

4- Inductively Coupled Plasma Spectroscopy

The Inductively coupled plasma provides detection limits for most elements that are within a factor of two or three times those of flame Atomic absorption, (for some metals a little better, for some a little poorer). The elements which are dissociated partially in flame are usually completely dissociated by the high temperatures achieved by the Inductively coupled plasma. So it seems that Inductively coupled plasma is freer of chemical interferences than flame Atomic absorption. However, interferences of other type are present in the

Inductively coupled plasma e.g. high concentrations of inorganic matrix can shift the location of the hot portion of the plasma and therefore alter the signal of specific signal a for the sample. Spectral interferences are important consideration for the Inductively coupled plasma and different lines are preferred for a specific element in different matrices. Inductively coupled plasma is a fast multi element technique. Most of the scientists are interested in Inductively coupled plasma for its automation and for those metals that cannot be determined by flame Atomic absorption. Another important advantage of Inductively coupled plasma is that no special sources are necessary. It is most useful for the elements which are determined once a year.

5- Neutron Activation Analysis

Neutron activation analysis has been used for a long time for trace metal determinations. Neutron activation can be accomplished by a pile or by instrumental techniques. Particular interest is given to the instrumental technique. Instrumental neuton activation is a "non destructive" method. Gordon, (1980) stated the use of instrumental neutron activation analysis in environmental studies as follows; to reduce the labor involved in dealing with large numbers of samples and to avoid contamination or loss of species during chemical manipulations, it is desirable to use multi element methods that are completely instrumental.

Although methods such as atomic absorption spectroscopy, spark source mass spectrometry, emission spectrometry, etc., can provide accurate data when performed carefully, the completely instrumental methods of X-ray fluorescence, and instrumental neutron activation analysis are better suited to the analysis of large numbers of samples for many elements.

Instrumental neutron activation analysis can be used for many of the elements, the major exceptions being Si, P, Ni, and Pb. On the other hand, Instrumental neuton activation measures many trace species with great sensitivity such as Se, As, Sb, In, I and many rare earths. A major disadvantage of Instrumental neuton activation is the long tun-around time for complete analysis. Samples are usually irradiated for a few minutes to analyze species with half lives up to a few hours, allowed to decay, and then re-irradiated for several hours to build up large activities of long-lived species. One must wait about three weeks after long irradiations for short lived activities to decay before some of the longest-lived species can be observed.

2.3. Importance Of High Quality Analytical Data And Present Status.

The quality of data obtained in environmental studies is related to three principle factors:

-The design and conduct of a representative sampling programme,

-The selection and use of suitable storage procedures for samples to minimize changes in the analyte concentration and form prior to analysis,

-The adoption of analytical procedures which enable measurements of appropriate accuracy and precision to be made in relation to the aims of investigation.

Unless these factors are given adequate consideration before and during the study the aims will not be achieved and valuable time, effort and facilities will be wasted.

In 1976 Hamilton mentioned the quality of data, in spite of advanced technology and availability of adequate basic analytical instruments there is a need to improve the quality of data obtained in many programmes of environmental monitoring (Hamilton, 1976). Although this concern was expressed in relation to the growing number of relatively inexperienced scientists engaged in these studies, it was clear from Hamiltons remark then, and subsequently Hamilton, (1981), Hamilton, (1983), Hamilton, (1984) that he was and is, addressing the bulk of scientists involved in environmental studies.

In the environmental sciences and especially those concerned with pollution vast amounts of data are now being produced, much of which finds its way into various types of data bases which can be interrogated by anyone with a working knowledge of computers. It is not

essential that they should have a full understanding of the extent to which the data are amenable to scientific interpretations.

In analytical chemistry, through very significant technological advances, various types of push-button, black-box instruments are now available, for some purposes that are ideal for repetitive types of analysis. Once they are primed and fed they are capable of churning out vast amounts of direct and indirect data, and because they are not man-power intensive they are attractive in terms of cost and efficiency. As a consequences of numerous studies which have been carried out over the last decade we know how difficult it can be to obtain quantitative data for many elements and organic compounds which are common to the environment.

In recent years Goldberg and Taylor (1985) questioned the quality of data currently being submitted to, and stored in, data banks, suggesting that little progress has been made in the intervening period on the improvement of data quality by the main body of environmentalists involved in monitoring programmes.

Environmental data are stored in computers on both national and international scales such as the US Environmental Protection Agency through its STORET programme, National Oceanic Data centers in Moscow and Washington, D.C.. In Turkey, the Electrical Power Resources Survey and Development Administration, Prime Ministry General Directorate of environment, Turkey

accumulate information from a large variety of sources. Both valid and invalid data are entered into storage. Both are retrievable from storage, but since they cannot be distinguished from one another, they are essentially useless except for bibliographical and historical purposes.

On the other hand, there are existing strategies which can identify good from bad experimental numbers with a high degree of confidence. One can call upon partners and colleagues for the creation of systems to validate data (VD) such that the evolving numbers can be screened before entry into data banks or reports. This is an especially important venture in environmental science where much information is used for "decision-making".

Many studies conducted in the various counties are aimed at evaluating normal and elevated levels of trace metals in different media. Unfortunately, most published reports and papers lack quality assurance data, and valid comparisons cannot, be made. Furthermore, results from several inter-laboratory comparisons amplify the need for quality control.

Three groups of non-radioactive contaminants:

- Metals
- Organohalogens
- Hydrocarbons

are currently monitored by the environmentalists in different phases of the environment to varying degrees

of accuracy and precision.

2.3.1. Results Of Poor Data

The elucidation of environmental biogeochemical processes, the understanding of the effects of anthropogenic discharges on the environment, the production of mass balances and fluxes for marine systems, and determination of the uptake of contaminants through consumption of edible fish and shellfish, all require representative sampling of the system under investigation and accurate analysis of the samples collected. The inability of measure low levels of trace metals in sea water has, until recently, prevented environmentalist from understanding the role played by plankton in distribution and concentrations of these elements in the water column. In the mid-70's, Topping, (1974) and Brewer, (1975) calculations made on the possible uptake of metals by plankton showed that only a few percent of the metals present in sea water were likely to be removed by plankton. With the advent of less contamination such as better sampling bottles, more careful pretreatment of samples on-situ and laboratory environments (i.e. to reduce level of background contamination) and careful quality control procedures, the level of metals in the environment such as in seawater, have been shown to be much lower (10-1000 fold) than was previously considered, Bruland, (1983). In 1983 two different studies showed that not only have these "new" data allowed more realistic calculations of

the uptake of metals from seawater by phytoplankton, but measurements in the open ocean using these improved procedures have clearly demonstrated the relationship between phytoplankton activity and ambient levels of some metals. This is one example where improvements in data quality have provided support for a previously held hypothesis concerning environmental processes, Boyle, (1983) and Bruland and Franks, (1983).

In a recent review of trace metal measurements in European coastal waters it is concluded that concentrations of some metals were at least an order of magnitude higher than those in the open ocean. However, they were unable to state what these concentrations were since there was tremendous variability in the data reported by different investigators for the same waters. Topping et al., (1980) Recent measurements, however, in European coastal waters, using the careful sampling and analytical procedures adopted for open ocean studies, have shown that levels are not as high as workers previously believed. Levels of Cu and Cd are only 2 - 3 times higher than those in open ocean surface waters. Indeed, for an elevation of an order of magnitude to be observed, samples have to be collected very closely to the actual sources of trace metal discharges, Balls, (1985).

2.3.2. State Of The Art Of The Trace Metal Measurements

1. Seawater

The current consensus among environmental scientist is that most of the published data are virtually useless with respect to establishing baseline levels of metals in seawater or understanding processes which influence the concentration and distribution of these elements in seawater. Prior to 1960 it was not unusual to find values of 10-100 μg/l being reported for some metals in coastal waters and open sea values of a few micrograms per liter were often quoted. During the early to mid 70s, some reduction of these values was observed but, in general, the range of data reported for individual metals by investigations at that time was still very large (>*10), Brewer, (1975), Topping et al., (1980). From the late 70s onwards however some measure of agreement was achieved but then only for a small number of metals, Cu, Zn, Cd and Hg, (Bruland, 1983). The extent of the lack of agreement, or compatibility of data, over the last 20 years can best be illustrated by examining the accepted representative values for a number of selected metals which were reported by principle reviewers during this period. The accepted representative values are given in Table 2.5.

Table 2.5 Summary Of Reported Values For Trace Metals In The Open Ocean Waters During 60s-80s

ELEMENT	Accepted representative values (µg/l) 1965[a]	1975[b]	1983[c]
Cadmium	0.11	0.1	0.078
Zinc	10	4.9	0.39
Lead	0.03	0.03	0.002
Copper	3.0	0.5	0.25
Mercury	0.03	0.03	0.001
Nickel	2.0	1.7	0.46

[a]Goldberg(1965), [b]Brewer(1975), [c]Bruland(1983)

It is interesting to compare the ranges of values reported by the scientists with the range of values reported by participants in interlaboratory comparison studies at these times. The range of values and results of intercomparison studies are given in Table 2.6 and Table 2.7 respectively. The data in Table 2.7 reveal that laboratories produced values for some metals for the same sample which differ by one or two orders of magnitude. On the basis of these results it is little wonder that scientists were confronted with the large range of published values over the period of 1960-1975 (Topping,1986).

Table 2.6 Summary of Range of Values For Trace Metals In The Open Ocean during 60s-80s.

Element	Range of values (µg/l)		
	1963-74[a]	1970-77[b]	1983[c]
Cadmium	0.01 - 0.60	0.025 - 0.11	0.0001 - 0.123
Zinc	0.6 - 22	0.72 - 7.4	0.003 - 0.58
Lead	0.002 - 0.11	0.04 - 0.07	0.001 - 0.036
Copper	0.05 - 12	0.12 - 1.5	0.031 - 0.38
Mercury	0.03 - 0.4	0.04 - 0.25	0.0004 - 0.002
Nickel	0.29 - 1.8	0.10 - 2.0	0.11 - 0.70

[a](Jones,1977) [b](Bewers,1979) [c](Bruland,1983)

In summary, today, relatively few laboratories have the expertise to conduct reliable measurements of trace metals in open-ocean and coastal waters. In order to improve this situation, more environmentalists will need to implement currently accepted procedures for sampling, storage and analysis. All scientists need to participate in well structured interlaboratory comparison studies so that their co-workers and users of their results are reassured as to the quality of data they produce.

2. Biological Tissue

Improvements in the measurement of trace metals in marine organisms over the last 15 years has mirrored the advances made in the respective measurements for sea water. The rapid growth of data, particularly for edible fish and shellfish, dates back to the 70s when people became increasingly concerned over the possible

Table 2.7 Intercomperison Exercises for Metals In Sea Water

Element	No.of lab	Range of values	Mean	CV*	Ref.
Cadmium	12	0.03-2.1	0.5	40	1
	26	0.03-1.9	0.25	160	2
	13		0.059	34	3
	20		0.97	97	3
	10		0.047	23	3
	16		0.068	59	3
	-		0.035	41	4
	48	0.01-2.9	0.02	24	5
Copper	12	0.8-15	3.5	120	1
	25	0.2-88	1.1	151	2
	19		0.92	78	3
	6		0.33	67	3
	17		0.42	115	3
	12		0.19	53	3
	6		0.13	30	4
	46	0.0066-3.3	0.12	19	5
Lead	13	0.42-14.1	5	114	1
	21	0.11-11.2	1.4	201	2
	14		0.64	95	3
	6		0.45	17	3
	18		0.79	70	3
	9		0.41	39	3
	40	0.010-3.32	0.049	55	5
Mercury	10	114-200	137	23	6
	14	114-300	161	35	6
	14	4.5-87	35	82	6
	5	4.5-9.5	6.6	30	6
Nickel	3		0.22	50	1
	7	0.88-8.9	3.5	63	1
	12	0.8-24.2	4.3	176	2
	3		0.25	40	3
	4		0.42	80	3
	8		0.35	66	3
	29	0.07-0.38	0.2	30	5
Zinc	15	0.2-99	4.9	93	1
	22	3.8-30	10.9	47	2
	7		5.7	22	3
	15		3.7	38	3
	16		6.5	30	3
	11		4	33	3
	-		0.35	51	4
	39	0.12-15.6	0.39	38	5

* Coefficient of variation

1- (Brewer and Spencer,1970)
2- (Jones,1977)
3- (Bewers at al.,1981)
4- (Bewers and Windom,1983)
5- (Berman et al.,1984)
6- (Olafsson,1978)

effects of anthropogenic discharges on human health through the consumption of contaminated foods. The deaths and deformations associated with the consumption of mercury-contaminated fish and shellfish by the Japanese at Minamata is a striking example of this concern. This concern forced the authorities to establish a series of surveillance programmes, and these in turn required the development or modification of analytical procedures for metals in biological tissue (Topping,1983a). Most of the methods were based on atomic absorbtion spectrophotometry which had gained general acceptance and application during the mid 60s and early 70s. The subsequent production of data by different laboratories raised the question of the comparability and accuracy of these data. This in turn led to a series of interlaboratory comparisons to assess the accuracy and comparability of analyses (Topping,1983b).

The results of the early International Council for the Exploration of the Seas (ICES) intercomparisons in 1971-1972 Topping and Holden, (1978) indicated that most laboratories were not producing reliable data for some of the more important toxic metals such as Hg, Cd and Pb. Not surprisingly this forced environmentalists to examine their analytical methods to identify where errors could be arising. Although subsequent ICES intercomparisons provided evidence of improved analytical performance, it was clear that a large number

of analysts were not meeting desired targets of precision and accuracy for some metals in some matrices (Topping,1983b).

An examination of results of the international intercomparison programme which was carried out during 1970-1980 showed that, with a few exceptions, the level of agreement between participating analysts was not good enough to allow them all to take part in a multi-laboratory monitoring programme (Holden et al.,1982). Also in this study it was stated that the analysts were unable to meet the standards required for the monitoring of contaminant level in foodstuff in relation to human health, or for the comparison of contaminant levels in fish and shellfish collected by individuals in different countries from their own coastal and offshore waters.

The position of laboratories outside Europe and North America is more serious, as was shown by Topping, (1984) in a recent intercomparison study organized for West Pacific countries on behalf of the Intergovermental Oceanographic Commission (IOC).

The current state of the art for most of the investigators in the ICES and other international organized monitoring programmes can be summarized as:

- Analysts have little difficulty in producing accurate data for Cu, Zn and Hg in marine tissue for concentrations in fish and shellfish.
- Although in a few studies accurate data for Cd at concentrations about 0.01 ppm were produced, in most of

the studies accurate data is obtained for concentrations >0.5 ppm in marine tissue.

-Pb concentration < 0.5 ppm causes problems for all analysts but some produce inaccurate data even for the range 1-5 ppm.

Results of intercomparison exercise for metals in reference materials (RM) based on marine tissue is given in Table 2.8.

3. Sediments

Although sediments have been identified as a necessary component of environmental studies from the quality of data point of view, they have received less attention than either water or organisms. In the recent past agencies such as IOC, ICES and United Nations Environmental Programme (UNEP) have established working groups to evaluate the use of sediments within their respective monitoring programmes. At the present time, therefore, there are no generally accepted guidelines for the sampling of sediments, nor is there agreement on the analytical methods to be used for this relatively heterogeneous phase. This situation is clearly unsatisfactory in view of the fact that sediments represent the single largest repository of metals in the environment, and that fluxes of metals to and from sediments are important considering mass balance calculations for trace metals (Kullenberg,1986).

It has been stated (Topping,1986) that, to date, only two major intercomparison studies have been

reported on the measurement of metals in sediments. These are (Brugman and Niemisto,1984) and (Berman and Boyko,1985). The first of these exercises was organized on behalf of ICES/SCOR working group on the study of the pollution of the Baltic for participants in the Baltic monitoring programme and the second one was organized on behalf of the Canadian National Research Council's Marine Analytical Chemistry Standards Programme primarily for the Canadian laboratories involved in sediments monitoring under an ocean dumping control act. A summary of the results of these exercises is given in Table 2.9. Both exercises demonstrated that at the most participants can produce comparable and accurate data for Cu, Zn and Pb at levels found in inshore and estuarine sediments. However, the results for Cd and Hg particularly those submitted by ICES participants, suggest that a minority of participants are not producing comparable data at levels normally encountered in sediments.

Table 2.8. Results Of Intercomperison Exercise For Metals In RMs Based On Marine Tissue

ELEMENT	RM[b]	No of Particip.	Range of Values	Mean	CV[c]	REF
Copper	FishFlesh	64	0.5-17.6	4.5	53	1
		20	2.7-5.7	3.8	18	2
		36	0.4-4.0	1.8	39	3
		21	1.7-11.0	4.1	40	4
		21	0.5-6.3	1.8	48	4
		49	1.0-8.1	3.1	27	5
	LobsterLiver	49	110-508	331	10	5
	Scallopmusc.	48	0.4-9.9	3.7	16	5
	Sea Plant	67	3.3-43	12.6	26	5
	Copepod	56	4.5-16.8	7.7	19	6
Zinc						
	FishFlesh	74	4.0-204	33	26	1
		21	28-53	38	16	2
		36	13-37	23	18	3
		22	25-56	42	15	4
		22	5.9-38	21	35	4
		48	19-187	93	10	5
	LobsterLiver	49	91-335	179	6	5
	Scallopmusc.	48	11-98	58	9	5
	Sea Plant	75	1.5-225	64	27	6
	Copepod	66	4.2-247	159	15	6
Mercury						
	FishFlesh	29	0.93-1.8	1.4	17	7
		29	0.03-0.2	0.1	60	7
		52	0.18-3.5	0.49	29	1
		16	0.74-1.4	0.85	7	2
		33	0.05-0.3	0.21	33	3
		34	0.01-0.2	0.06	50	3
		19	0.49-2.2	1	41	4
		20	0.04-0.8	0.23	62	4
		20	0.03-3.4	0.13	140	4
		37	<0.01-0.	0.056	16	5
	LobsterLiver	37	0.13-0.5	0.25	19	5
	Scallopmusc.	36	<0.01-0.	0.08	10	5
	Sea Plant	75	0.05-5.6	0.33	43	6
	Copepod	43	0.04-3.6	0.27	48	6

Table 2.8. (Continued)

ELEMENT	RM	No of Particip.	Range of Values	Mean	CV	REF.
Cadmium	Fish Flesh	41	0.02-1.1	0.1	150	1
		21	0.03-1.8	0.08	75	2
		35	0.005-0.99	0.033	87	3
		22	<0.1-0.77	0.22	112	4
		21	<0.1-0.65	0.19	112	4
		44	0.01-0.85	0.06	38	5
	Crab Meat	52	0.53-1.1	0.8	17	8
		22	0.39-1.9	0.87	37	4
	LobsterLiver	48	5.2-40	26	8	5
	Scallopmusc.	48	0.12-1.3	0.75	13	4
	Sea Plant	46	0.11-24	0.7	96	6
	Copepod	43	0.34-3.0	0.75	26	6
	NBS oys.tis.	35	0.4-12.0	3.7	50	9
Lead						
	FishFlesh	33	0.1-5.1	0.8	71	1
		21	0.16-4.0	1.1	83	2
		32	0.02-7.5	0.21	71	3
		22	0.13-9.6	2.4	120	4
		22	0.12-10	1.2	135	4
		38	0.1-<25	2	41	5
	Fish Meal	52	0.22-7.8	2.7	47	8
		22	0.19-15	3.9	101	4
	ObsterLiver	43	0.6-63	5.6	30	5
		32	0.11-3.2	0.75	71	8
	ScallopMusc.	39	0.06-<25	0.29	41	5
	NBS oys.tis.	35	0.1-7.0	1	124	9
Arsenic						
	Fish Fles	16	0.5-21	17	9	3
		20	0.85-8.5	4.6	35	5
	LobsterLi	21	10.2-38.5	25	21	5
	ScallopMusc.	20	2.3-13.6	7.4	29	5

[a] All outlier have been omitted from the calculation of the mean values.
b Reference Material
c Coefficient of Variation
1- (IAEA,1980)
2- (Topping and Holden,1978)
3- (Holden and Topping,1981)
4- (Berman,1984)
5- (IAEA,1984)
6- (IAEA,1978)
7- (Uthe at al,1971)
8- (Topping,1982)
9- (knowles and Burrell,1981)

2.4. Quality Of Data In Turkey

In a latest study Balkaş et al., (1988) established poor quality and quantity of available data on the concentrations of pollutants. As it is mentioned in the study, national Monitoring Programme are operational since 1983. In five years considerable effort and money was spent to continue measurements. But, results of measurement are so poor that further measurements of the same parameters with same quality will be a meaningless waste of money and man power, as the concentrations of pollutants are still not known after 5 years of monitoring.

In this study, problems with the investigated data is summarized as;

- Lack of data,
- Unusually high or low numbers reported for pollutants,
- Unit problems,
- Lack of agreement between institutes.

Results of annual Hg concentrations in the Egean Sea water between 1983-1987 is given in Table 2.10. This is quite good example to show the situation in Turkey. When the source and reference stations are compared it is seen that reference stations have about 2.5 times higher mercury concentration than source stations. Also when the Hg concentrations are considered Egean Sea looks like a Mercury mine.

Table 2.9 Summary Of Recent Intercomperison Exercises For Metals In Marine Sediments

ELEMENT	Location of Sediment	No of Particip	Range[a] (mg/kg)	Mean[b] (mg/kg)	CV[c]	REF.
Copper	Coastal	29	30-76	50	12	1
		29	16-43	28	10	1
	Estuarine	39	17-45	31	7	2
	Harbour	39	25-87	54	6	2
		39	32-158	129	7	2
Zinc						
	Coastal	28	252-529	304	8	1
		28	107-255	158	17	1
	Estuarine	39	45-128	85	9	2
	Harbour	39	87-198	130	9	2
		39	122-396	314	7	2
Cadmium						
	Coastal	27	0.27-6.2	0.99	46	1
		27	0.17-6.9	0.79	60	1
	Estuarine	35	0.1-3.3	0.71	35	2
	Harbour	35	0.16-4.2	0.98	23	2
		38	0.5-5.4	2	21	2
Mercury						
	Coastal	19	0.080-0.66	0.27	36	1
		18	0045-0.45	0.09	38	1
	Estuarine	21	0.032-0.43	0.13	18	2
	Harbour	21	0.096-0.75	0.38	17	2
		21	0.142-2.05	1.5	13	2
Lead						
	Coastal	26	29-140	94	12	1
		26	19-94	54	9	1
	Estuarine	38	7.5-67	34	14	2
	Harbour	38	18-177	115	9	2
		38	83-262	211	10	2
Arsenic						
	Estuarine	21	1.3-18.4	10.8	35	2
	Harbour	21	4-46	31.5	19	2
		21	6-33	20.2	34	2

[a]Incluces all values Submitted by participants
[b]Excludes Outlier
[c]Coefficient of Variation
1- (Brugmann and Niemisto,1984)
2- (Berman and Boyko,1985)

Table.2.10 Annual Averages of Hg in the Eagean Sea water (ng/l)

STATION	1983	Std	1984	std	1985	std	1986	std	1987
Source Stations									
11	-	-	-	-	900	700	950	580	-
12	-	-	-	-	1500	750	590	90	-
13	-	-	-	-	1200	650	660	290	-
14	-	-	-	-	-	-	-	-	-
15	-	-	-	-	980	650	500	50	-
16	-	-	-	-	1100	400	690	180	-
17	-	-	-	-	1250	1100	650	160	-
18	-	-	-	-	1800	1200	730	480	-
19	-	-	-	-	80	290	1800	1500	
Estuarine Stations									
33	-	-	-	-	3700	1100	690		11
34	-	-	-	-	1350	1100	450		17
35	-	-	-	-	4200	4900	3500	4500	22
36	-	-	-	-	1500	1400	11400	18800	30
37	-	-	-	-	1800	2100	6100	9200	17
38	-	-	-	-	1500	500	560	310	11
40	-	-	-	-	1100	800	970	370	9
41	-	-	-	-	2300	2600	270	180	14
42	-	-	-	-	1000	670	19000	33000	50
43	-	-	-	-	1000	500	730	270	10
44	-	-	-	-	1200	550	310	80	22
45	-	-	-	-	1200	850	1200	920	15
46	-	-	-	-	6100	6700	1800	1300	17
47	-	-	-	-	3700	4000	330	110	12
48	-	-	-	-	930	660	330	110	18
49	-	-	-	-	3200	2700	1600		9
50	-	-	-	-	600	170	420	200	16
Reference Stations									
57	-	-	-	-	2100	1600	180		-
58	-	-	-	-	1100	700	320		-
59	-	-	-	-	1600	900	-		-
60	-	-	-	-	500	170	19000		-
61	-	-	-	-	1500	1600	1100		16
62	-	-	-	-	1100	700	70000		
63	-	-	-	-	1300	500	-		15
64	-	-	-	-	2100	250	3100		10
65	-	-	-	-	1900	900	420	200	12
66	-	-	-	-	2000	1100	420		-
67	-	-	-	-	1900	1100	760		-
68	-	-	-	-	2200	1900	-		-
69	-	-	-	-	50	-	-		-

CHAPTER 3

EXPERIMENTAL STUDIES

3.1. Sampling and Sampling Site

As is mentioned in all environmental studies a major consideration in reliability of the study is related to the sampling quality. A number of devices have been used for sampling sediments. The selection of sampling equipment depends both on the type of environment to be sampled and the type of sample required. Although the effects of sampling is out of the scope of this study some precautions have been taken.

In this study "Göksu" River sediments were used, and in order to obtain statistically representative results, 7 previously determined sampling stations, which cover about 100 Km. from the entry of last tributary were used. Also surface sediment samples from the river delta in the Mediterranean Sea was collected. The sampling sites for river "Göksu"and "Taşucu" estuary is given in Figure 3.1 and in Figure 3.2 respectively.

For the sample collection 20 cm. gravity corers were used. The corers are made of PVC, they were all precleaned with nitric acid at least 24 hours, and then rinsed several times with mono distilled water, followed by double distilled water and up to sampling time they

were contamination protected.

At each station three core samples were taken. In order to eliminate the effect of flow patterns each of the sampling was made on the same side of the river. Taşucu estuary sediment samples were collected from five different points, such a way that they give an idea about both lateral and vertical distribution of the metals in the estuary.

The collected samples are taken to the laboratory immediately after collection, after which they are stored in refrigerator at -20 °C.

3.1.1. Sample preparation

After removing the sediment samples from the corers, 1 cm from the outer shell is whipped off and then they were oven dried at 70 °C. for 24 hours. First of all they were ground by a mortar grinder by hand. As the second step of sample preparation the most common hand method "conning and quartering" is applied. This was the first step of homogenization. They were then transferred to precleaned polyethylene bags and sealed.

3.1.2. Homogeneity and Homogeneity control

As it is known that sediments are heterogeneous phases of the environment and as the scope of the study was not covering the dating or vertical distribution of the elements in sediments, the samples must be homogenized in order to obtain representative samples and results. This is one of the most important steps in determination of pollutants in the environment. In

order to satisfy and control the homogeneity of the samples a two step homogenization is applied. In the first step as was mentioned in sample preparation section, the samples are sub divided by "conning and quartering" and a "hand made" homogeneity is attempted. In the second step these "homogenized" samples are ground in a "Tema" mechanical agate grinder for 5 minutes with a speed of 710 rpm and during this operation due to the high speed of vibration a higher degree of homogeneity is obtained. Each step of homogeneity is controlled by taking 10 different randomly selected samples from the first and second homogenized samples. The results of homogeneity control are given and discussed in chapter 4, in trace metal concentration bases.

3.1.3. Contamination control

In this study, another precaution taken was the elimination of contamination from the PVC corer used. Although PVC is used as a sampler in some studies, in order to prevent wall contamination, if present, 1 cm. from the wall of the corer is whipped off. In one of the cores taken the core is vertically divided into four separate parts without whipping off the outer layer. The results of contamination control are given in the results and discussion chapter in tabular and form.

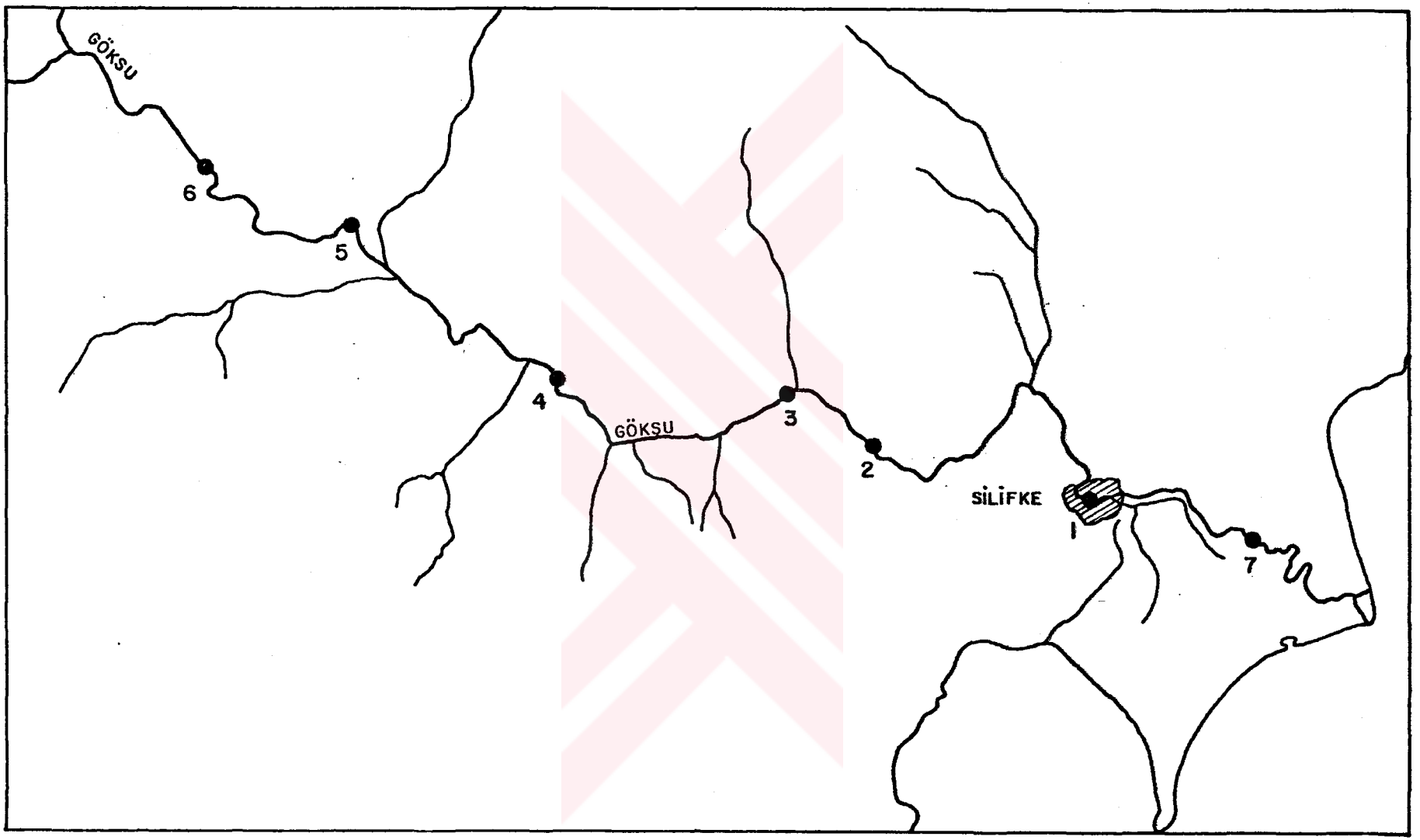

Figure 3.1. Sampling Stations on River "Göksu".

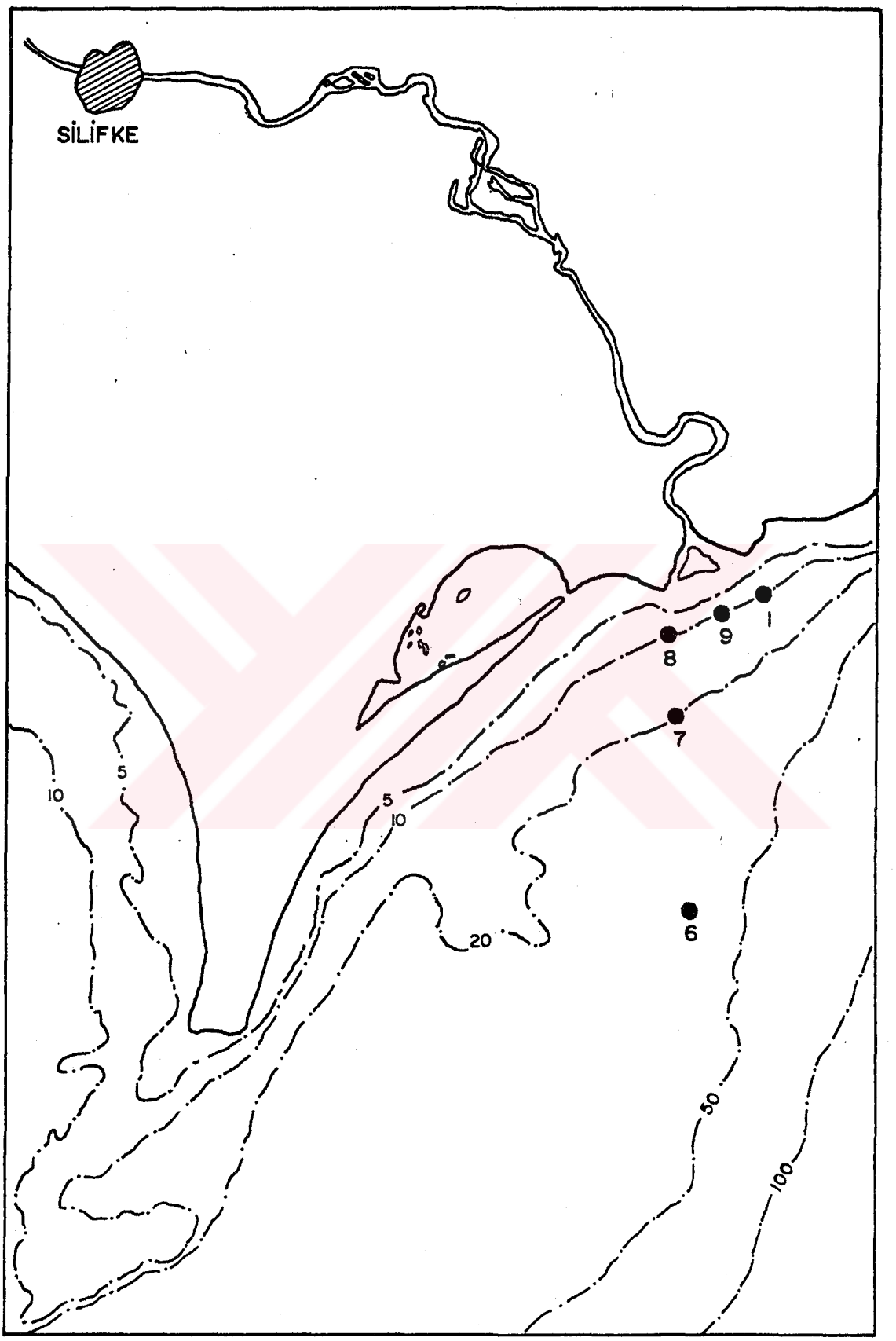

Figure 3.2. Sampling stations in Mediterranean.

3.2. Analysis

The analysis of the "Göksu" sediments are carried out with three instruments using the following methodology in digestion and analysis.

3.2.1. Inductively Coupled Plasma

Sample digestion; In the digestion of sediment samples the "decomposition with hydrofluoric acid and perchloric acid" Thompson, (1987) method is used. This method was designed to exploit the improved performance from hydrofluoric acid digestion. The procedure is described by Thompson, (1987).

Analysis; each sediment sample was divided into two sub samples and then they were analyzed in ARL 3410 Inductively coupled plasma, in the laboratories of Imperial Collage, London. Twenty one elements were detected in Inductively coupled plasma and the results and the discussion is given in chapter 4.

3.2.2. Neutron Activation Analysis

Sample preparation; Instrumental neutron activation analysis requires no sample pretreatment. The samples of about 0.1 gram are weighed then placed in precleaned quartz tubes. After sealing the tubes were sent to TAEK "Çekmece" Reactor for irradiation.

Analysis; After irradiation the quartz tubes were again cleaned in order to eliminate contamination. The activity in each sample was determined by gamma counting 0.1 gram of the sediment sample for four and twelve hours, for first and second long counts respectively,

using a lithium drifted germanium detector (Ge/Li) coupled to 4096 channel "canberra" multi channel analyzer system. The spectrums are then analyzed with the use of a software called "Sampo", which is being specially developed for "Canberra" type multi channel analyzer. The standard reference material, IAEA soil 3, contained 26 elements some of which were short lived elements so that is was not possible to determined. The Instrumental neuton activation results are given in chapter 4.

3.2.3. Atomic Absorption

Sample digestion; In order to eliminate composition differences due to differences in digestion procedures the same digestion procedures used in Inductively coupled plasma determination were used, (Thompson,1987). All the reagents used for digestion, have AnalaR Grade purity.

Analysis; The sediment samples were analyzed by the use of "Hitachi" atomic absorption instrument in TAEK. They were analyzed by the use of calibration curves, as time did not allow use of other methods such as the standard edition method. Fifteen elements were analyzed by Atomic absorption. The one which can be analyzed in flame Atomic absorption is analyzed by flame and some dilution factor are applied when necessary, for the ones with low concentration "pyro coated" furnace Atomic absorption is used. The results of atomic absorption analysis are discussed in chapter 4.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Homogeneity Test Results

The homogeneity test results are given in Table 4.1. The homogeneity control were carried out with a one-way analysis of variance (ANOVA). ANOVA table calculations were made with the use of statistical programme, statistical pagage for social sciences, (SPSS), on the main frame, at METU.

According to the ANOVA table results, all the elements except Ni, Mn and Na were homogeneous for 95 % confidence interval, Ni and Mn were homogeneous for 99 % confidence interval, Na was non-homogeneous even for 99 % confidence interval. It was thought that non-homogeneity of the Na is due to contamination which is also observable in contamination studies. This negative effect can be eliminated with precautions taken before homogeneity and analysis of the samples, such that 1 cm of the sediment sample from the outer perimeter was whipped off with a polyethelene knife.

The results of ANOVA table for 95 % and 99 % confidence interval are given in Table 4.2.

The coefficient of variation (C.V) is also

checked for Mo, Sr, Zn, P, Li, Na, K, Be, Ba, La, Cr, Co, Ni, Cu. Although C.V is a simple method it is effective enough to show the variation between results. When the coefficient of variation results were compared it was seen that all the values except Mo and Cr were less than 0.1, which means deviations of the results were very small. So the sediment samples from river "Göksu" can be considered as homogeneous.

Also when the coefficient of variation results of different studies which were mentioned in literature survey, considered it was seen that C.V values obtained in this study is one of the best ones.

The results of C.V test are shown in Table 4.2. In Table 4.1 H1 and H2 represents first and second homogeneity respectively. The numbers following 4A from 1 to 10 are the randomly selected homogeneity samples from the same corer.

Table 4.1. Homogeneity Test results (µg/g)

	H1/1	H1/2	H1/3	H1/4	H1/5
Li	13.05	13.50	13.20	13.80	13.05
Na	4105	3860	3810	3950	4040
K	7110	7020	7070	7150	7000
Rb	20	20	20	20	20
Be	0.600	0.625	0.600	0.575	0.575
Mg	21220	20100	19150	19580	20010
Ca	205900	211600	214200	211600	204500
Sr	900	958	1003	954	920
Ba	143	134	133	134	130
Al	20960	21150	20940	21530	20870
La	9.0	9.5	10.0	9.5	9.0
Ti	1110	1200	1266	1257	1149
V	38.7	41.5	43.0	41.2	39.7
Cr	167	270	284	238	242
Mo	3.0	3.0	2.5	1.5	2.5
Mn	389	397	386	391	386
Fe	16380	16550	16720	16540	16130
Co	12.5	12.0	12.0	12.0	12.0
Ni	129	109	104	107	116
Cu	18.2	17.2	17.0	17.5	16.5
Ag	1	1	1	1	1
Zn	26.5	26.5	26.5	26.0	25.5
Cd	0.5	0.5	0.5	0.5	0.5
Pb	7.5	5.0	5.0	5.0	5.0
P	378	362	380	366	350

Table. 4.1.(Continued)

	H1/6	H1/7	H1/8	H1/9	H1/10
Li	13.05	13.20	13.05	12.75	13.05
Na	3755	3828	3965	3983	4098
K	6900	7000	7110	6950	7270
Rb	20	20	20	20	20
Be	0.550	0.575	0.550	0.575	0.575
Mg	19260	19100	19670	19450	20620
Ca	209300	209900	206600	208600	208400
Sr	983	980	969	963	949
Ba	130	140	146	131	135
Al	20820	20900	20880	20730	21340
La	9.0	10.0	9.5	10.5	10.0
Ti	1224	1299	1188	1275	1206
V	40.5	42.7	40.5	42.5	41.0
Cr	232	302	265	281	205
Mo	1.5	2.0	1.5	2.0	1.5
Mn	380	379	384	381	389
Fe	16180	16640	16290	16360	16560
Co	11.5	11.5	11.5	11.5	12.0
Ni	104	104	110	103	116
Cu	17.2	17.0	16.0	15.7	16.7
Ag	1	1	1	1	1
Zn	26.0	27.0	25.0	26.5	26.5
Cd	0.5	0.5	0.5	0.5	0.5
Pb	5	5	5	5	5
P	382	370	372	368	342

Table 4.1. (Continued)

	H2/1	H2/2	H2/3	H2/4	H2/5
Li	13.20	13.20	13.20	10.80	13.35
Na	3708	3825	3795	3278	3778
K	7070	7070	7100	5870	7020
Rb	20	20	20	20	20
Be	0.575	0.600	0.575	0.475	0.575
Mg	19500	19100	19540	17320	19650
Ca	210800	211900	209500	178100	213600
Sr	995	997	1005	849	1007
Ba	130	134	157	109	129
Al	20760	21170	21160	17830	21030
La	9.5	10.5	9.5	9.0	9.5
Ti	1287	1278	1308	1068	1338
V	42.2	44.5	41.5	36.2	43.0
Cr	308	377	270	319	212
Mo	2.0	2.5	1.0	2.0	2.0
Mn	381	384	384	329	381
Fe	16410	16750	16670	14280	16500
Co	12.0	12.0	12.0	10.5	12.0
Ni	103	102	106	92	104
Cu	16.5	16.7	16.7	14.5	16.7
Ag	1	1	1	1	1
Zn	26.5	28.5	26.0	22.5	26.0
Cd	0.5	0.5	0.5	0.5	0.5
Pb	5	5	5	5	5
P	350	382	376	298	368

Table 4.1. (continued)

	H2/6	H2/7	H2/8	H2/9	H2/10
Li	12.9	12.45	12.9	12.75	12.75
Na	3713	3703	3710	3630	3753
K	6930	6910	6790	6690	6750
Rb	20	20	20	20	20
Be	0.575	0.575	0.575	0.575	0.575
Mg	19010	18780	19550	19290	19030
Ca	211900	209300	211000	206200	209400
Sr	985	978	988	967	999
Ba	127	127	125	127	124
Al	20700	20260	20490	20000	20500
La	9.5	10.5	11.5	10.0	9.0
Ti	1245	1233	1266	1236	1251
V	41.5	40.2	41.7	39.7	41.7
Cr	224	213	337	209	231
Mo	2.5	2.5	3.0	2.5	2.0
Mn	373	367	376	373	376
Fe	16240	15770	16430	16130	16290
Co	11.5	11.5	12.0	12.0	11.5
Ni	102	101	108	110	99
Cu	16.2	16.0	17.2	16.0	16.0
Ag	1	1	1	1	1
Zn	25.0	25.0	26.5	25.5	26.0
Cd	0.5	0.5	0.5	0.5	0.5
Pb	5	5	5	5	5
P	364	352	376	352	372

* H1 and H2 represents 1st and 2nd homogenity test

Table 4.2 Analysis Of Variance Results

	Calculated F Value	%95 Interval	%99 Interval	Coeff.Of Variation H1	H2
Li	2.804	+	+	0.22	0.06
Na	16.059	-	-	0.031	0.042
K	3.944	+	+	0.015	0.053
Be	0.949	+	+	0.04	0.05
Sr	0.822	+	+	0.031	0.062
Ba	2.478	+	+	0.04	0.09
La	0.71	+	+	0.05	0.08
Cr	0.848	+	+	0.16	0.23
Mo	0.15	+	+	0.292	0.244
Mn	6.795	-	+	0.01	0.04
Co	0.648	-	+	0.03	0.04
Ni	5.89	-	+	0.07	0.05
Cu	3.875	+	+	0.04	0.05
Zn	0.609	+	+	0.022	0.058
P	0.851	+	+	0.035	0.067

* H1 and H2 represents 1st and 2nd homogenity respectively

4.2. Contamination Control Results

Contamination control were carried out with inductively coupled plasma analysis. According to the results of the contamination test there is 0.67 deviation between inner and outer slices for Cr, for Mg although there is no statistical deviation between slices (ratios are all greater than 0.98) graphically it shows a contamination profile and for Na results

concentration ratios are greater than 0.80 so there may be contamination; for the other elements it is hard to say there is contamination but for most of the elements, according to the % concentration results there may be a loss of concentration from inner slices to outer slices. Mo, Ag, Cd, and Pb concentrations are under Inductively coupled plasma detection limit so no comment can be made on these metals.

The results of the contamination test is given in Table 4.3. The results showed that precautions taken to prevent contamination were justified and statement "PVC corers must not be used especially for Cr, Mg and Na sampling in sediments", is correct. However there is a certain amount of doubt for PVC if metal sampling is going to be considered. Percent concentration ratios are given in Table 4.4. Graphical repserentation of Na, Sr, Cr and Mg contamination test results are given in Fig 4.23 to Fig 4.26 respectively.

4.3 Analytical Results

4.3.1. Inductively Coupled Plasma Results

The results of "Göksu" sediments which were obtained by the use of Inductively coupled plasma technique are given in Table 4.5. The results of Inductively coupled plasma analysis showed that Rb, Cd and Ag concentrations in the "Göksu" sediments are under Inductively coupled plasma's detection limit. Mo concentrations in the Mediterranean delta is under detection limits, where as there is detectable Mo

concentration in the river sediments; contrary to this there is Pb seen in the sea sediments but not in the river sediments.

When the detection limits are considered Inductively coupled plasma is less sensitive to Rb compared to Mo, Ag, Cd and Pb. The detection limits of these elements are 20, 1, 1, 0.5 and 5 micrograms per gram respectively.

Table 4.3. Results of Contamination Test (µg/g)

	1/1	1/2	1/3	1/4
Li	22.3	30.1	25.7	20.4
Na	3821.5	3135.5	3564.0	4140.5
K	9960	13070	11245	9930
Rb	-	30	25	-
Be	0.83	1.06	0.95	0.81
Mg	21150	20920	21235	21610
Ca	176250	156350	172250	171850
Sr	756.0	609.0	727.5	661.5
Ba	472.75	209.15	383.65	264.65
Al	30445	42130	35480	31085
La	13.75	17.75	15.25	14.75
Ti	1795	2307	2016	1860
V	59.9	74.8	66.8	58.25
Cr	194.0	131.15	131.0	201.5
Mn	477.8	523	502.5	475.9
Fe	21020	27675	23980	22080
Co	15.5	19.5	17.5	16.25
Ni	123.00	135.25	129.75	130.5
Cu	21.5	27.6	24.7	22.0
Zn	40.25	49.25	45.00	37.50
P	436	406	422	374

Table 4.4. Concentration ratios between slices (ug/g)

	1/2	3/2	4/3
Li	74.06	85.54	79.30
Na	82.05	87.98	86.08
K	76.21	86.04	88.31
Rb	-	-	-
Be	77.65	89.41	85.53
Mg	98.91	98.52	98.26
Ca	88.71	90.77	99.77
Sr	80.56	83.71	90.93
Ba	44.24	54.52	68.98
Al	72.26	84.22	87.61
La	77.46	85.92	96.72
Ti	77.83	87.39	92.26
V	80.08	89.30	87.20
Cr	67.60	99.89	65.01
Mn	91.36	96.08	94.71
Fe	75.95	86.65	92.08
Co	79.49	89.74	92.86
Ni	90.94	95.93	99.43
Cu	77.83	89.59	88.89
Zn	81.73	91.37	83.33
P	93.12	96.21	88.63

Table 4.5 Inductively Coupled Plasma Results

	STATION 1		STATION 2		STATION 3	
	CONC (µg/g)	D.M*	CONC (µg/g/)	D.M	CONC (µg/g)	D.M
Li	17.28	3.54	14.05	0.22	13.13	0.43
Na	4255	316	3947	158	3833	84
K	8640	933	7441	106	6906	305
Rb	20.00	0.00	20.00	0.00	20.00	0.00
Be	0.72	0.08	0.62	0.01	0.55	0.02
Mg	21632	57	19678	599	19900	380
Ca	177383	1464	195700	6936	197800	7041
Sr	704	40	858	93	922	40
Ba	315	115	315	68	193	32
Al	26808	2584	22715	166	20705	754
La	13.17	0.42	11.58	0.31	10.67	0.24
Ti	1684	78	984	686	1257	49
V	52.05	6.10	43.33	0.86	41.21	1.18
Cr	230	36	180	35	275	145
Mo	-	-	2.17	0.42	2.08	0.24
Mn	459	13	406	5	379	3
Fe	19848	828	17247	166	16370	32
Co	15.00	0.35	12.67	0.24	12.08	0.12
Ni	124	1	107	3	108	6
Cu	19.54	1.39	17.92	0.31	16.54	0.65
Ag	-	-	-	-	-	-
Zn	33.33	5.02	28.00	0.89	25.92	1.12
Cd	-	-	-	-	-	-
Pb	-	-	-	-	-	-
P	372	45	361	17	351	2

Table 4.5. (Continued)

	STATION 4		STATION 5		STATION 6	
	CONC (µg/g)	D.M	CONC (µg/g)	D.M	CONC (µg/g)	D.M
Li	13.01	0.04	17.29	0.64	14.83	0.15
Na	3979	178	4122	13	4835	102
K	6932	137	8752	247	8723	970
Rb	20.00	0.00	20.00	0.00	20.00	0.00
Be	0.55	-	0.70	0.02	0.64	0.02
Mg	19720	300	20975	155	21857	1258
Ca	203525	6875	181225	4825	177783	4809
Sr	902	78	672	70	646	48
Ba	130	2	143	6	167	24
Al	20808	253	26563	458	24747	843
La	9.88	0.63	12.75	1.00	12.42	0.82
Ti	1260	18	1630	81	1546	49
V	41.50	0.25	53.40	0.60	50.52	1.16
Cr	303	32	360	47	554	83
Mo	2.13	0.38	1.50	0.25	2.00	0.20
Mn	394	4	483	23	767	405
Fe	16495	30	19742	287	19278	588
Co	12.25	0.00	14.63	0.38	14.50	0.54
Ni	106	1	117	2	118	7
Cu	15.94	0.69	18.88	1.25	17.67	0.42
Ag	-	-	-	-	-	-
Zn	25.88	1.38	33.00	1.25	30.67	0.42
Cd	-	-	-	-	-	-
Pb	-	-	-	-	-	-
P	361	23	371	-	324	16

Table 4.5. (Continued)

	STATION 7	
	CONC (µg/g)	D.M
Li	13.75	0.13
Na	4027	121
K	7311	30
Rb	20.00	0.00
Be	0.60	0.03
Mg	19922	568
Ca	193917	5924
Sr	824	42
Ba	482	95
Al	22478	71
La	11.67	0.31
Ti	1490	37
V	43.83	0.47
Cr	267	46
Mo	2.00	0.20
Mn	421	2
Fe	17321	115
Co	13.17	0.31
Ni	110	2
Cu	16.83	0.26
Ag	-	-
Zn	27.42	0.51
Cd	-	-
Pb	-	-
P	344	18

* Deviation from the mean

4.3.2. Instrumental Neutron Activation Analysis Results

The results of instrumental neutron activation analysis are given in Table 4.6. IAEA Soil 3 is used as reference material. It can be seen from the results of the analysis that most of the elements are rare earths. Although the peak of environmentally important elements such as V, Fe, Cr, Mg, etc. were observed on the spectrum, as the reference material used did not have certified values for these elements, it was not possible to convert the activities to concentrations.

On the other hand there are certified elements such as Al, as the first short and second short count are not able to do due to transportation problems, it was not able to obtain their concentration values in the sediments. A second reason why we were not able to obtain results for some elements was that the , second long counts took long a time and during that time the activity of the element died, as can be easily seen from the Instrumental neuton activation results table.

Table 4.6. Instrumental Neutron Activation Analysis Results

	STATION 1		STATION 2		STATION 3	
	CONC	D.M	CONC	D.M	CONC	D.M
	(µg/g)		(µg/g)		(µg/g)	
As	4.96	0.53	-	-	5.19	0.70
Br	3.26	0.54	-	-	3.47	1.07
K	7211	641	-	-	7317	692
La	13.66	0.58	11.35	1.04	13.37	0.41
Lu	-	-	0.17	0.02	-	-
Na	4292	304	3916	316	4047	204
Sm	2.61	0.20	-	-	3.32	0.25
Ce	-	-	-	-	222.13	41.99
Cs	-	-	-	-	16.93	3.07
Eu	-	-	-	-	4.54	0.59
Hf	-	-	-	-	17.38	3.54
Sc	-	-	-	-	47.77	2.52
Sr	-	-	-	-	-	-
Ta	-	-	-	-	-	-
Tb	-	-	-	-	-	-
Yb	-	-	-	-	-	-

Table 4.6. (Continued)

	STATION 4		STATION 5		STATION 6	
	CONC	D.M	CONC	D.M	CONC	D.M
	(µg/g)		(µg/g)		(µg/g)	
As	5.97	0.89	4.19	0.65	4.55	0.40
Br	2.49	0.29	-	-	1.83	0.26
K	-	-	-	-	8353	717
La	10.57	0.96	12.23	0.58	12.92	0.38
Lu	0.14	0.02	-	-	0.11	0.02
Na	4059	299	3359	244	4725	240
Sm	2.04	0.16	2.57	0.21	2.37	0.13
Ce	221.01	20.45	226.31	41.47	214.69	13.95
Cs	25.40	2.40	-	-	-	-
Eu	4.67	0.53	-	-	5.06	0.46
Hf	21.87	1.48	18.97	3.49	18.36	1.69
Sc	59.65	3.12	51.44	2.67	53.30	1.96
Sr	13111	1746	-	-	4364	815
Ta	-	-	-	-	-	-
Tb	-	-	-	-	3.26	0.72
Yb	10.38	1.60	-	-	10.99	2.00

Table 4.6 (Continued)

	STATION 7	
	CONC	D.M
	(µg/g)	
As	5.18	0.56
Br	-	-
K	-	-
La	13.78	0.54
Lu	0.16	0.02
Na	4037	291
Sm	2.27	0.19
Ce	241.93	21.96
Cs	-	-
Eu	4.83	0.46
Hf	34.95	2.79
Sc	60.22	3.12
Sr	-	-
Ta	-	-
Tb	-	-
Yb	-	-

* Deviation from the mean

4.3.3. Atomic Absorbtion Analysis Results

15 elements were analyzed by Atomic absorption and the results given in Table 4.7. Zn, Cr, Ni, Mn, Fe, Na, K, Mg, Ca and Sr are analyzed by the use of flame atomic absorption where as Co, Cu, Pb, Cd and Al are analyzed

by the use of furnace atomic absorption. For the elements analyzed by flame atomic absorption a matrix similar to the sediment solution is tried to obtained by the use of Inductively coupled plasma results. For the ones analyzed with furnace, furnace conditions were optimized.

Table 4.7. Atomic Absorption Results

STATION NO	Mg (µg/g) CONC.	STD.DEV	K (µg/g) CONC.	STD.DEV
1	21100	508	9348	283
2	19386	500	8467	213
3	20317	813	8185	509
4	18846	540	7853	179
5	20434	-	10261	178
6	21714	1530	9731	780
7	20148	543	9018	898
D1	19703		1969616	12258
D6	19513		1185925	16064
D7	20910		1773694	17057
D8	19703		1885649	11500
D9	20783		1503133	11891

NO	Mn (µg/g) CONC.	STD.DEV	Na (µg/g) CONC.	STD.DEV	Zn (µg/g) CONC.	STD.DEV
1	461	13	1736	272	39.16	1.42
2	415	3	1021	286	37.20	4.38
3	409	3	1011	890	30.46	0.61
4	397	9	1023	279	29.56	0.14
5	475	10	1564	164	66.63	30.88
6	682	263	2004	357	52.08	13.88
7	453	33	1225	967	35.53	3.78
D1	503		9986		53.25	
D6	425		9971		66.30	
D7	480		11022		62.80	
D8	423		7011		43.79	
D9	497		6361		47.20	

Table 4.7. (Continued)

STATION NO	Cr (µg/g) CONC.	STD.DEV	Fe (µg/g) CONC.	STD.DEV	Ni (µg/g) CONC.	STD.DEV
1	156	25	1044	9	132	1
2	153	-	1199	14	112	4
3	660	237	1207	15	116	10
4	160	2		1	111	2
5	155		1033	42	126	1
6	189	56	990	95	131	10
7	171	23	1111	78	121	2
D1	136		738		134	
D6	136		591		134	
D7	119		532		131	
D8	170		932		127	
D9	141		879		120	

STATION NO	Cd (µg/g) CONC.	STD.DEV	Sr (µg/g) CONC.	STD.DEV	Al (µg/g) CONC.	STD.DEV
1	2043	55	557	17	22200	2750
2	1613	651	686	79	18032	230
3	1682	349	796	34	18352	1029
4	1608	108	756	72	17328	629
5	2013	214	543	64	24216	432
6	2331	486	693	169	24424	3375
7	2099	231	662	22	20760	2774
D1	2135		583		33984	
D6	1613		386		34104	
D7	2438		516		39744	
D8	2136		625		28080	
D9	1288		421		27528	

NO	Sb (µg/g) CONC.	STD.DEV	Pb (µg/g) CONC.	STD.DEV	Co (µg/g) CONC.	STD.DEV
1	5.34	1.18	163	56	0.48	0.01
2	3.85	0.46	237	233	0.51	0.01
3	4.96	0.28	194	186	0.46	0.03
4	3.92	0.66	88	13	0.47	0.05
5	3.94	0.26	106	2	0.50	0.05
6	5.63	1.66	105	23	0.51	0.03
7	4.75	0.35	112	31	0.60	0.16
D1	5.51		213		0.52	
D6	6.58		76		0.54	
D7	4.73		85		0.57	
D8	5.26		123		0.51	
D9	4.60		59		0.60	

4.3.4. Comparison of The Results of Methods

The results of sediment samples obtained by the use of three analytical techniques are compared statistically. SPSS statistics program is used for correlation between each result with pearson correlation at METU, at main frame.

According to the correlation results for atomic absorption and inductively coupled plasma techniques zinc, potassium, magnesium, aluminum, manganese, nickel and iron results give a correlation greater than 0.80. On the other hand strontium, calcium and chromium result correlations are less 0.80 which means detection limits, chemical and physical interferences must be considered if these elements are going to be studied. The results are given in Table 4.8. At this point as the results give such a high correlation some other factors must be considered for the method to be selected and used. These factors are economy and simplicity to operate and if these are also considered atomic absorbtion gains much more importance.

On the other hand if Co and Cd data is analyzed it is as if there is a contamination problem. When the laboratory and analyze conditions are considered it seems as though the problem rises from the analysis carried out by atomic absorption instrument which can only be a personal guess until the samples are analyzed by Instrumental neuton activation as its analytical approach is quite different than either Atomic

absorption or Inductively coupled plasma. There is a similar situation for Na, The obtained concentrations in the sediments by Inductively coupled plasma, varies between 3800 and 4800 μg/g, on the other hand Atomic absorption results varies between 1000 and 2000 μg/g, which is about four times the Atomic absorption. Sodium concentrations obtained by Inductively coupled plasma which are in good agreement with the Instrumental neuton activation results.

Table 4.8. Correlation coefficients of some elements between atomic absorption and Inductively coupled plasma

ELEMENT	CORRELATION
Zn	0.80
K	0.92
Sr	0.75
Mg	0.89
Al	0.84
Ca	0.17
Mn	0.99
Fe	-0.92
Ni	0.95
Cr	0.07

For atomic absorption, inductively coupled plasma and neutron activation analysis results comparisons there are only two common elements. These elements are Na and K.

When Atomic absorption and Instrumental neuton activation are compared it can be seen that Na concentration results gave a 0.43 correlation and for K this correlation decreased to 0.15 .

Comparison of Inductively coupled plasma and Instrumental neuton activation results gave a 0.65 and 0.33 correlation for Na and K respectively.

When the correlation results were screened atomic absorption and inductively coupled plasma resluts gave the best correlation. The correlation of the results between atomic absorption and neutron activation analysis and also inductively coupled plasma and neutron activation analysis were not as good as atomic absorption and inductively coupled plasma.

Inductively coupled plasma test was run in the United Kingdom at the Imperial Collage which is well organized. They have very well organized cleaning and digestion laboratories and trained analysts. Although there was trained analysts for atomic absorption, and attempts are made to achieve the best working conditions they were not competable with Imperial Collage. On the other hand the results can be considered quite good although the analysis conditions were not.

Other advantages of atomic absorption are, the simplicity of the instrument, which can be learned in a months time whereas Instrumental neuton activation and Inductively coupled plasma requires about six months training.

4.4. Göksu Sediments

The results of Inductively coupled plasma analysis, for selected elements are used to indicate trace metal finger prints of "Göksu" sediments. Inductively coupled plasma results were used as those were a complete set of metals and more representative compared to other methods.

Graphical representation of the elements (Ca, Sr, Al, Be, Co, Zn, Fe, V, Li, K, La, Cu, Mn, Na, Ni, Mg, Ba, Ti, P, Pb, Cr) at the river and Taşucu estuary are given in Fig 4.1. to Fig 4.22.

Enrichment ratios (ER) at each sampling point are calculated by the use of the following formula;

$$ER = \frac{(X / Al)_s}{(X / Al)_c}$$

where; ER = The crustal enrichment ratio,
$(X/Al)_s$ = The ratio of the concentration of element X to the concentration of Al which is a crustal reference element in the sediment sample,
$(X/Al)_c$ = The same ratio in the average crustal material,

and this is used to decide if there is pollution or not; this pollution may be anthropogenic or natural. Taylor's (1972) crustal abundance pattern is used in this study. Enrichment ratio values are given in Table 4.9.

When enrichment ratios are considered the highest of these was seen at station 1 with a value of 37.58. This is an indicator of independent, non-crustal, concentration of the enriched V concentration at that

point.

As the enrichment ratios give a rough idea about pollution at that point, on the average, enrichment ratios greater than 10 are considered as an indicator of pollution in this study. Although the values between 1 and 10 indicates a non-crustal contribution they must be considered carefully. Also it may be a mistake to define that "non-crustal" pollution as "anthropogenic", because it may be a natural pollution, such as erosion, sediment transport etc.

Calcium and Cr are the only two elements which give an enrichment ratio above 10, so only these two elements can be considered as exact pollution indicators in "Göksu".

As mentioned in the introduction chapter, "Göksu" is one of the "non-polluted" rivers, there being only a few domestic settlements along the river. So theoretically the enrichment ratios must be around unity. This situation is satisfied for most of the elements; Na, Rb, Be, Ti have enrichment ratios less than 1 and Al, La, V (except station 1), Mn, Fe, Co, Cu, Zn, P, K have enrichment ratio values around 1 or 1.5. From the above point of view of the above elements it would not be wrong to say that "Göksu is a non-polluted river.", this satisfying the approach mentioned in chapter 1.

Another interesting point, which is also contradicting with the introduction chapter, is;

although the elements can be used as fertilizers, herbicides, insecticides etc. the effect of irrigation can not be clearly seen for these elements so only just a rough approach can be made for them.

Table 4.9. Enrichment ratios

St.No	7	1	2	3	4	5	6
Li	2.52	2.65	2.55	2.61	2.57	2.68	2.47
Na	0.62	0.55	0.61	0.65	0.67	0.54	0.68
K	1.28	1.27	1.29	1.31	1.31	1.30	1.39
Rb	0.81	0.68	0.81	0.88	0.88	0.69	0.74
Be	0.79	0.79	0.80	0.77	0.78	0.77	0.76
Mg	3.13	2.85	3.06	3.39	3.35	2.79	3.12
Ca	17.11	13.12	17.09	18.95	19.40	13.53	14.25
Sr	8.05	5.77	8.30	9.78	9.52	5.55	5.73
Ba	4.15	2.28	2.69	1.81	1.22	1.04	1.31
Al	1.00	1.00	1.00	1.00	1.00	1.00	1.00
La	1.42	1.35	1.40	1.41	1.30	1.32	1.38
Ti	0.96	0.91	0.63	0.88	0.87	0.89	0.90
V	1.19	37.58	1.16	1.21	1.22	1.23	1.24
Cr	9.79	7.08	6.55	10.97	12.00	11.16	18.44
Mo	-	-	-	-	-	-	-
Mn	1.62	1.48	1.55	1.59	1.64	1.58	2.69
Fe	1.13	1.08	1.11	1.16	1.16	1.09	1.14
Co	1.93	1.84	1.84	1.92	1.94	1.81	1.93
Ni	5.39	5.09	5.17	5.77	5.62	4.84	5.24
Cu	1.12	1.09	1.18	1.20	1.15	1.06	1.07
Ag	-	-	-	-	-	-	-
Zn	1.43	1.46	1.45	1.47	1.46	1.46	1.46
Cd	-	-	-	-	-	-	-
Pb	-	-	-	-	-	-	-
P	1.20	1.09	1.25	1.33	1.36	1.09	1.03

Table 4.9. (Continued)

	D1	D6	D7	D8	D9
Li	2.75	2.89	2.89	2.85	2.72
Na	1.27	1.03	1.05	1.35	1.19
K	1.32	1.31	1.33	1.36	1.33
Rb	0.56	0.75	0.67	0.61	0.56
Be	0.85	0.83	0.84	0.83	0.84
Mg	2.20	1.65	1.79	2.34	2.29
Ca	10.90	7.43	7.90	12.41	10.65
Sr	4.48	2.97	3.21	5.95	3.77
Ba	1.80	0.63	0.90	2.61	1.14
Al	1.00	1.00	1.00	1.00	1.00
La	1.37	1.28	1.33	1.37	1.51
Ti	0.90	0.82	0.84	0.90	0.89
V	1.10	1.08	1.06	1.13	1.07
Cr	2.73	1.78	1.96	2.81	3.08
Mo	-	-	-	-	-
Mn	1.26	0.85	0.95	1.20	1.32
Fe	1.01	0.93	0.92	1.02	1.00
Co	1.57	1.36	1.38	1.64	1.59
Ni	4.04	3.26	3.12	4.39	3.91
Cu	1.06	0.91	0.91	1.07	0.99
Ag	-	-	-	-	-
Zn	1.37	1.29	1.30	1.39	1.36
Cd	-	-	-	-	-
Pb	-	-	-	-	-
P	0.98	0.83	0.87	1.09	0.90

According to the trends that they show, elements can be categorized into five groups, these are;

1st group; Ni, Mg

2nd group; Mn, Na

3rd group; Ca, Sr

4th group; Li, La, Cu

5th group; Be, Co, Al, Zn, Fe, K, V

Barium, Ti, P, Pb, Cr are showed different trends so it was not possible to group them.

Strontium, Ca, Cr, Mn, Pb, V, Ni and Mg were selected as the elements to be considered in this study. These elements were selected to show some special cases such as non natural trends and natural trends of the river.

The results of lead concentration in "Göksu" sediments according to the Inductively coupled plasma analysis was quite straight forward. Lead was not detected in river sediments so "Göksu" can not be considered as a land based pollutant source for lead. In the Mediterranean sediments lead concentrations of 8.75 and 6.25 μg/g was observed at up to 20 meters depth. This lead in concentration at the Mediterranean sediments could be due to marine traffic and atmospheric transport.

Calcium and Mg are known to be the most popular hardness and crustal parameters and they show the same or a similar mechanism and trend in the environment. According to the results of this study there is a quite

an interesting contradiction between Calcium and Mg results. At each river sampling station there was an increase of calcium concentration where as there was a decrease for Mg concentration. This situation was the same for the two stations for Mediterranean sediments up to 20 meters depth, but after this depth their trends showed a similarity. Also as it was mentioned in the above paragraphs, the enrichment ratio of Calcium shows a non-crustal character with a value greater than 10, but Mg enrichment ratios are about 2 and 3. As the enrichment ratio can not be considered as an accurate indicator of pollution, the Mg concentration can be considered as natural whereas Calcium can not.

"Göksu basin" naturally has a calcareous structure and as the average reference crustal elements are used to calculate enrichment ratios, Calcium showed a high ER value.

According to McKee and Wolf, (1971) Sr occurs largely with Calcium and Ba minerals. So the similarity of the trends through out the river is a natural occurrence. Enrichment ratios greater than 5 at each station, may show a "non-crustal" contribution. Speculating on this situation due to irrigation like the other elements may not be wrong as the river passes through fields.

Crhromium is the only element which showed an "anthropogenic" pollution at "Göksu" sediments. Station 6 is the first station after the last tributary to the

river "Göksu" from station 6 on Cr concentration decreases from 554.58 μg/g to 180.83 μg/g at station 2, it increases up to 267.5 μg/g at the final station. High Cr concentration at the station 6 may be due to the tributary which is joining to the "Göksu" river. The effect of Silifke is seen and continued up to the sea. At the Mediterranean delta Cr concentrations decreases with depth, from 103 μg/g at 10 meters depth to 92.5 μg/g at 50 meters depth. The trend is also satisfied with the enrichment ratio changes.

Nickel and V are the indicators of "anthropogenic" pollution especially for traffic and combustion pollution. Ni pollution was observed through the river whereas V had its peak value at "silifke" station.

When the enrichment ratio of 2.69 for Mn, at station 6, is considered it indicates a pollution but as the other stations are only about 1.5 and "Göksu" appears non-polluted, as mentioned previously.

For most of the elements the effect of Silifke is seen as a peak. For Calcium and Sr a sink is observed at the Silifke station.

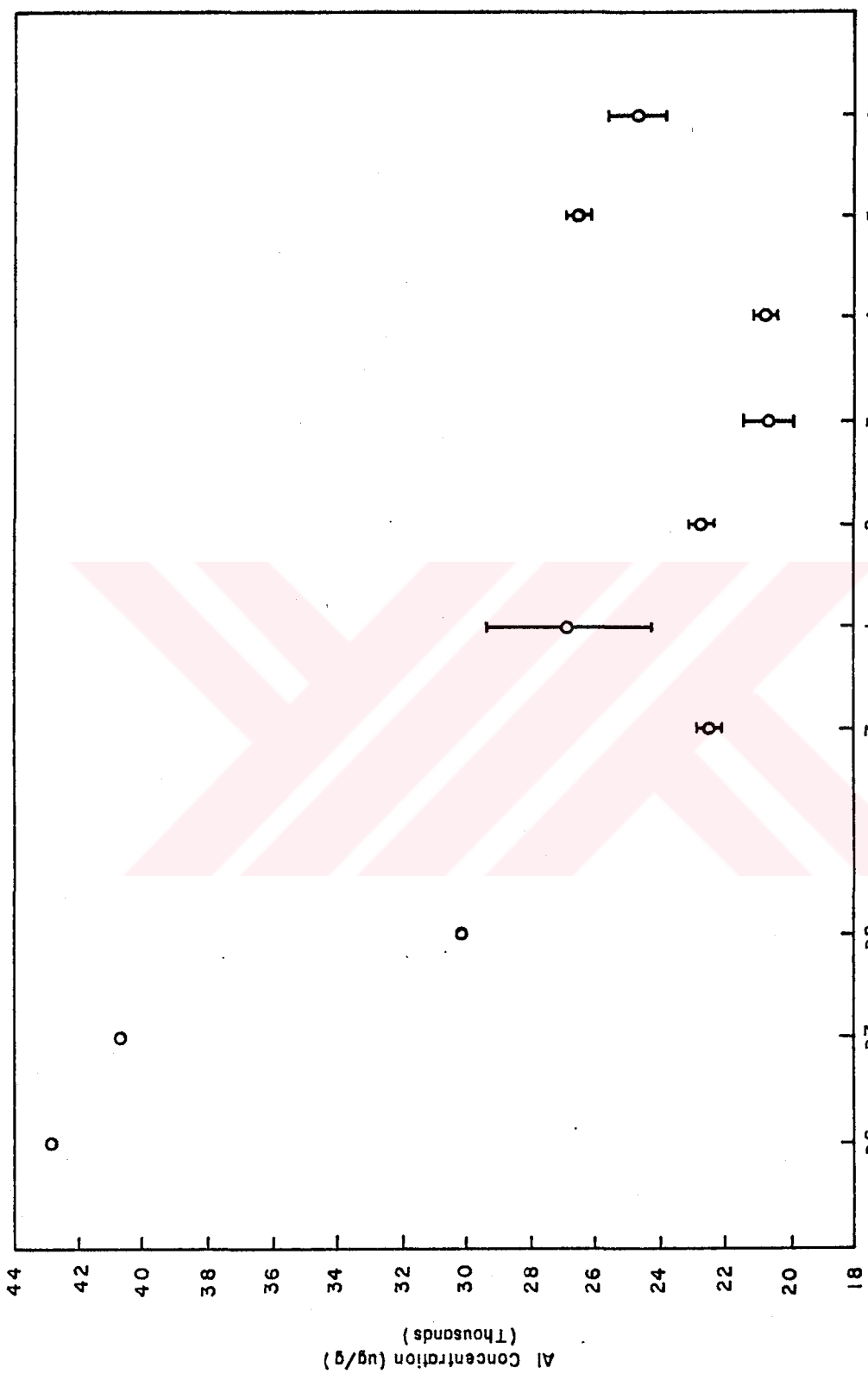

Figure 4.1. Al Concentration in "Göksu" river sediments and Taşucu estuary.

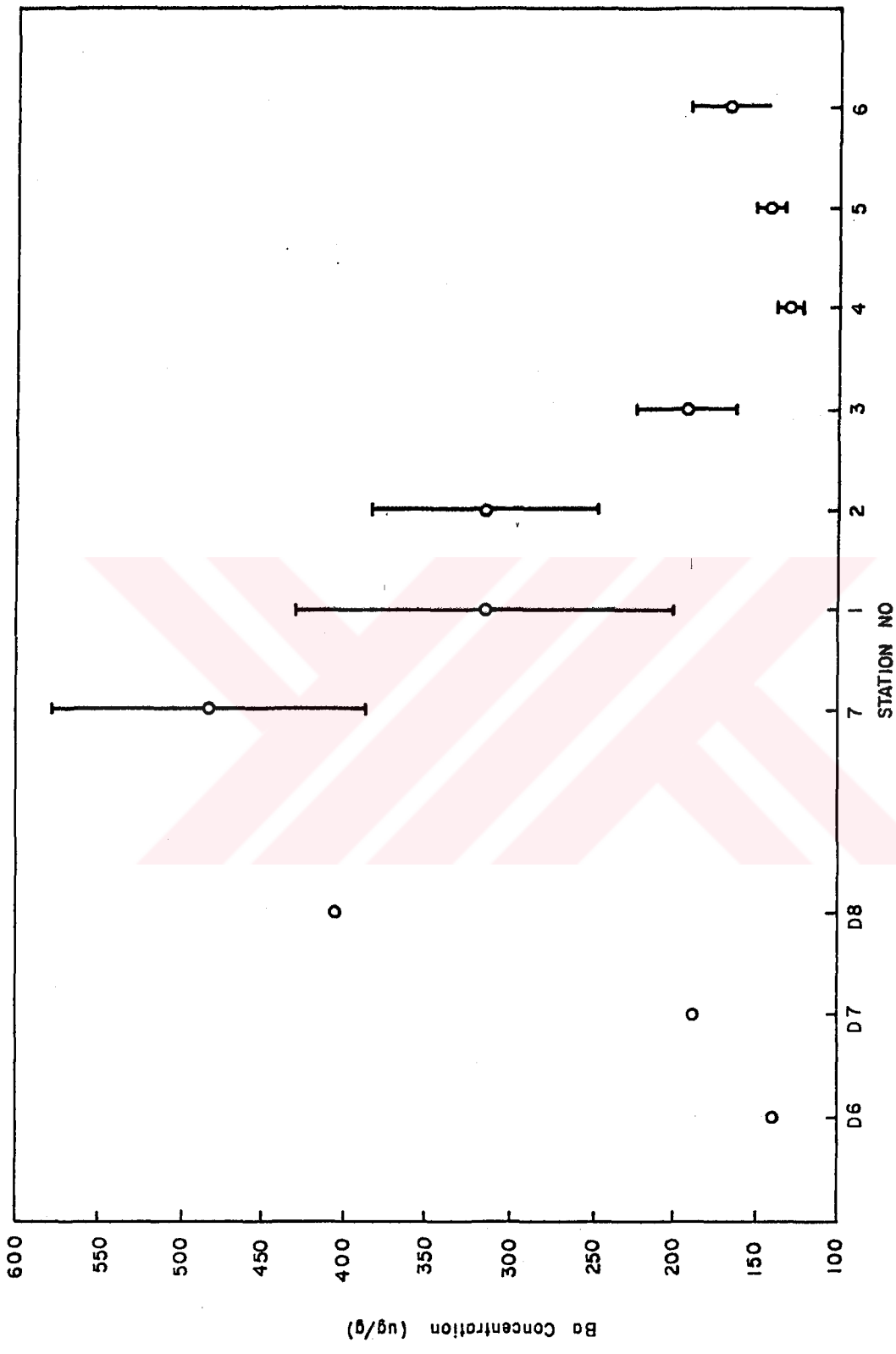

Figure 4.2. Ba Concentration in "Göksu" river sediments and Taşucu estuary.

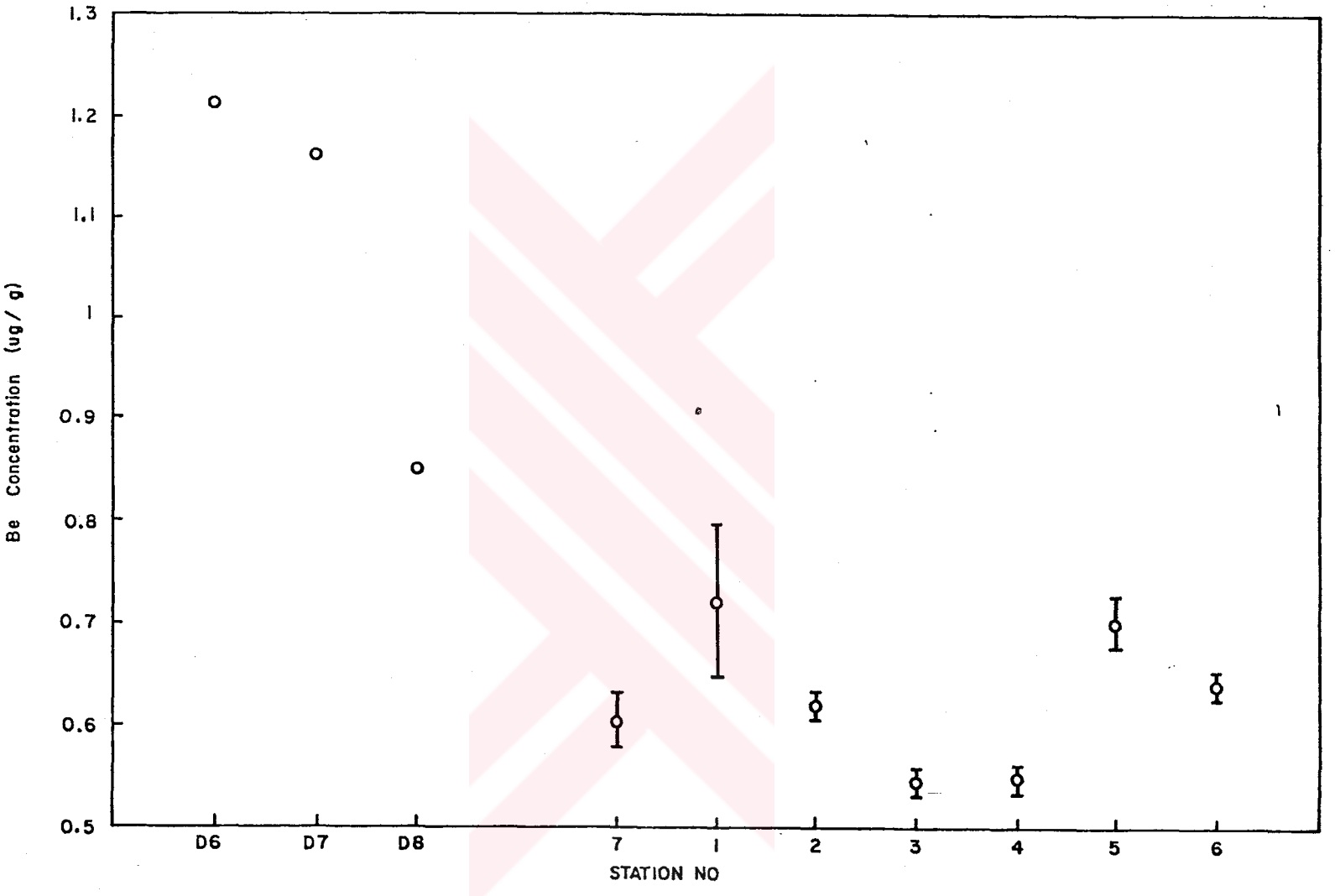

Figure 4.3. Be Concentration in " Göksu " river sediments and Taşucu estuary.

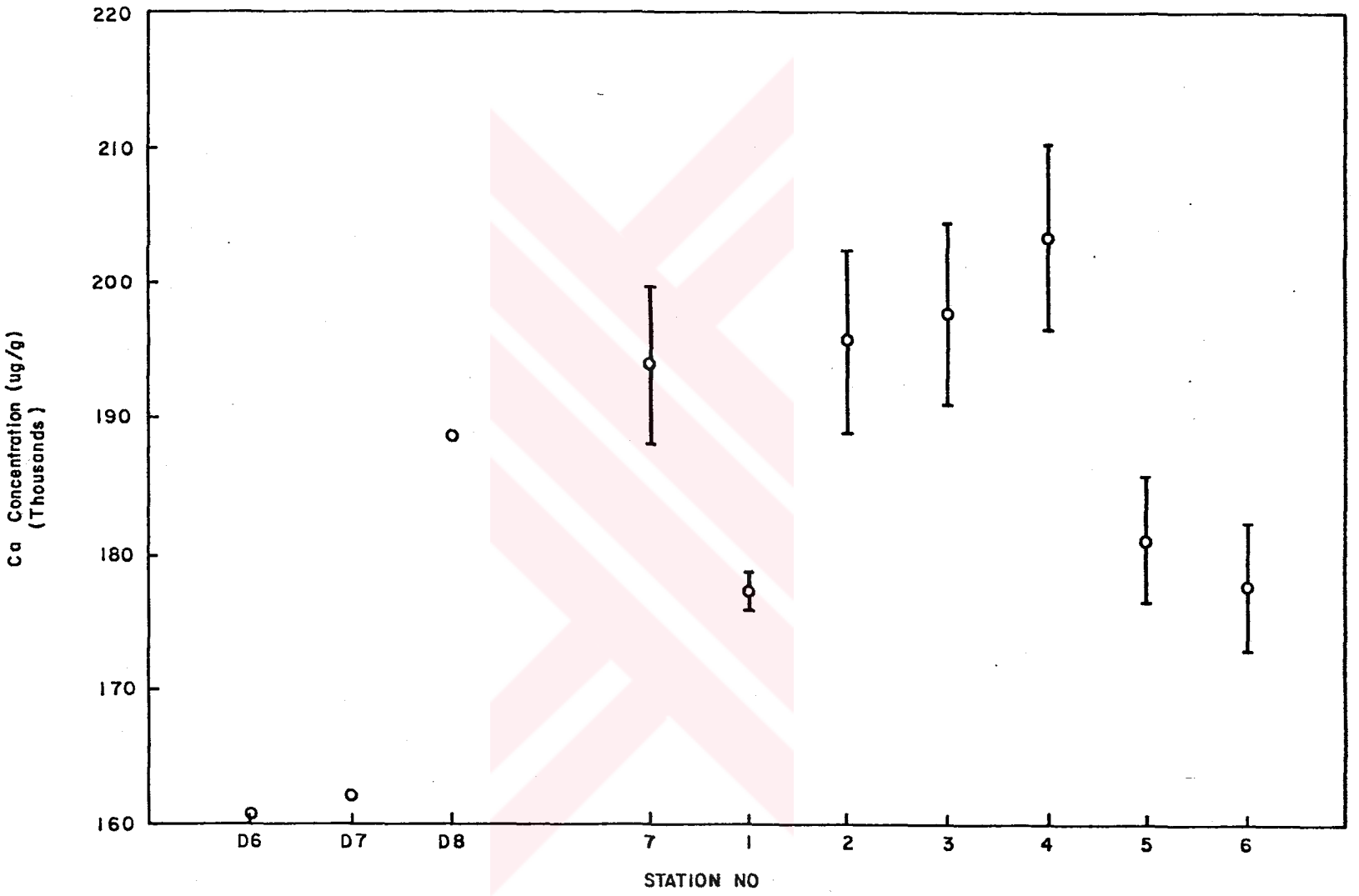

Figure 4.4. Ca Concentration in "Göksu" river sediments and Taşucu estuary.

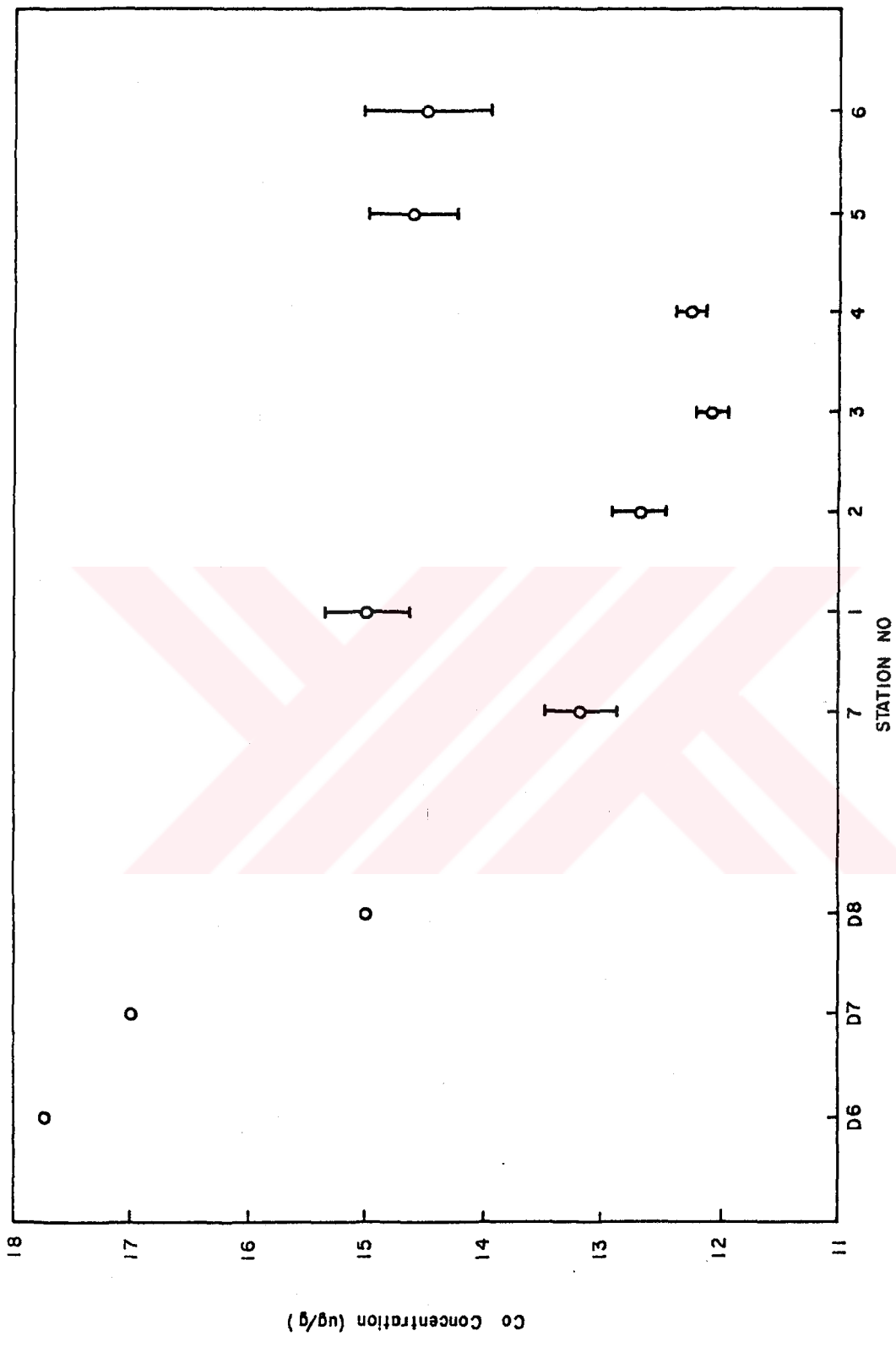

Figure 4.5. Co Concentration in "Göksu" river sediments and Taşucu estuary.

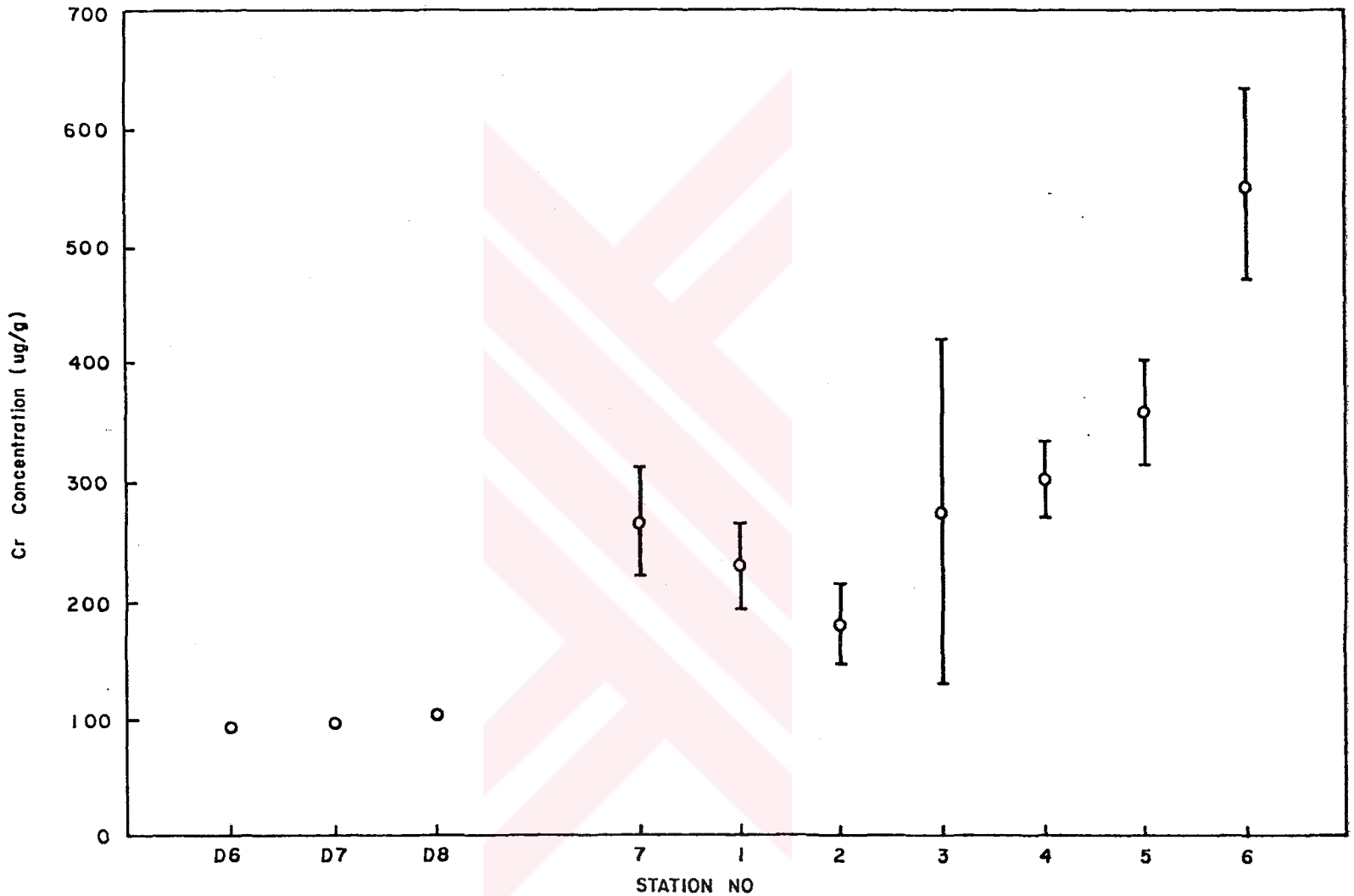

Figure 4.6. Cr Concentration in "Göksu" river sediments and Taşucu estuary.

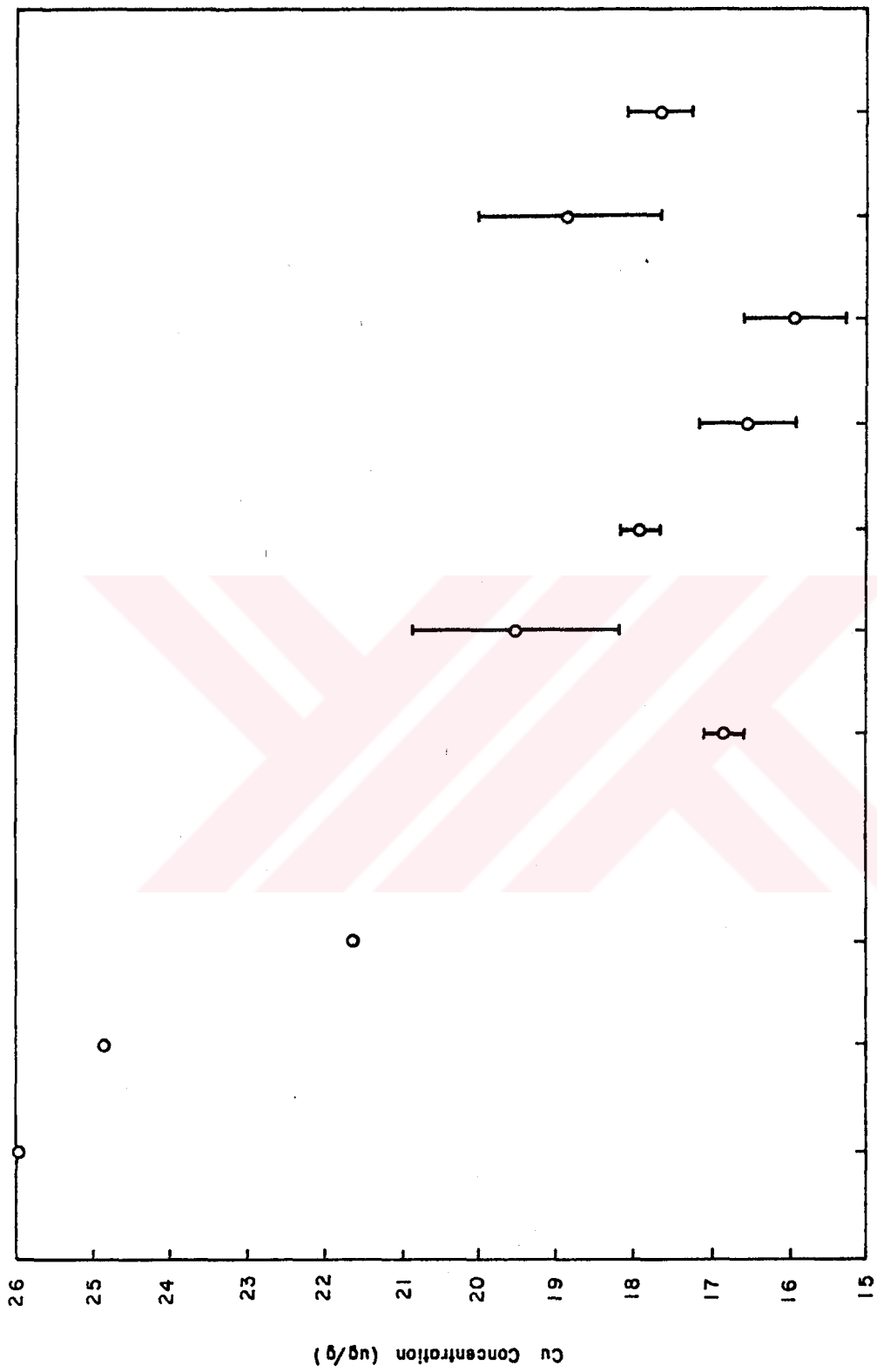

Figure 4.7. Cu Concentration in "Göksu" river sediments and Taşucu estuary.

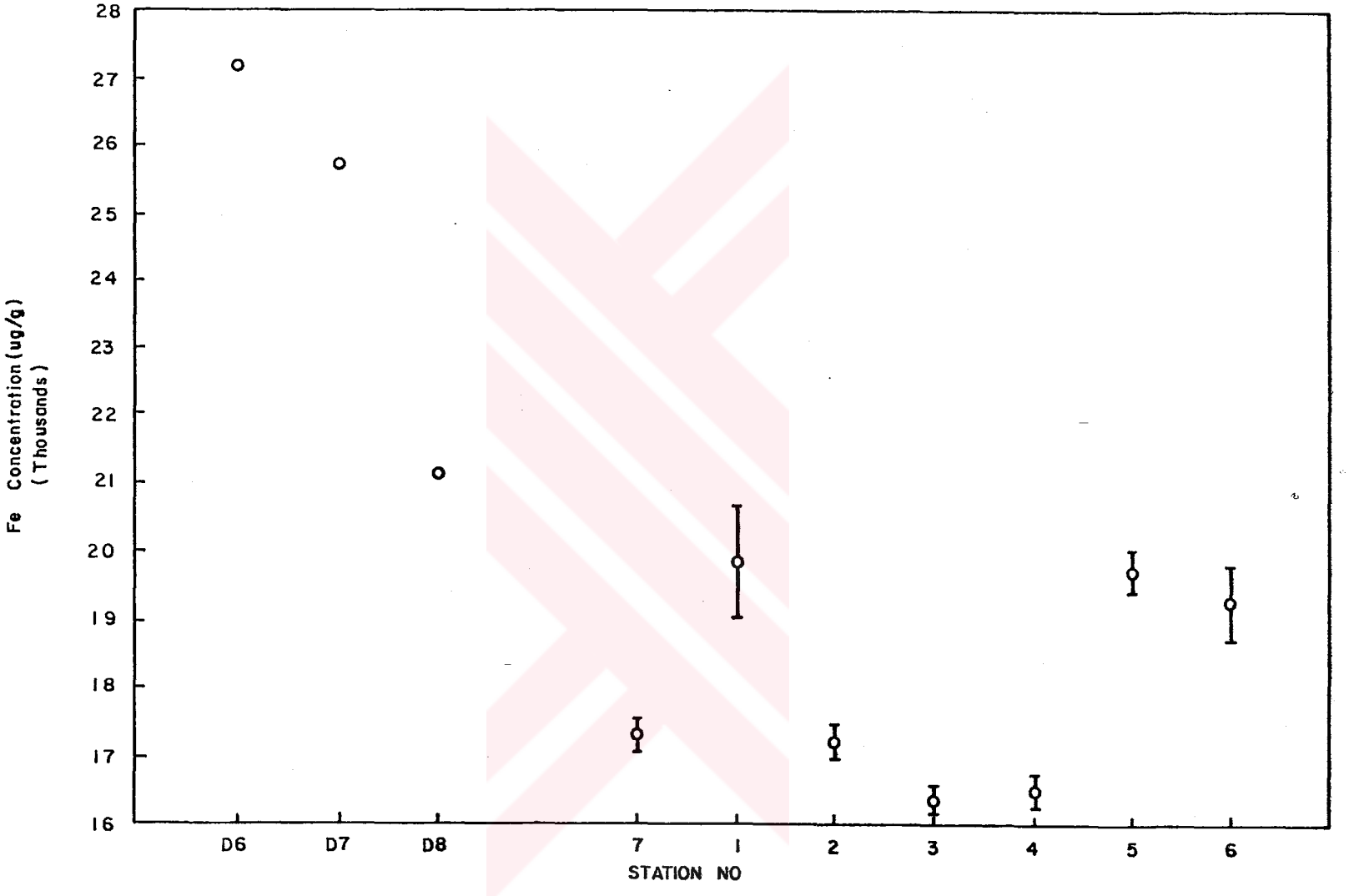

Figure 4.8. Fe Concentration in "Göksu" river sediments and Taşucu estuary.

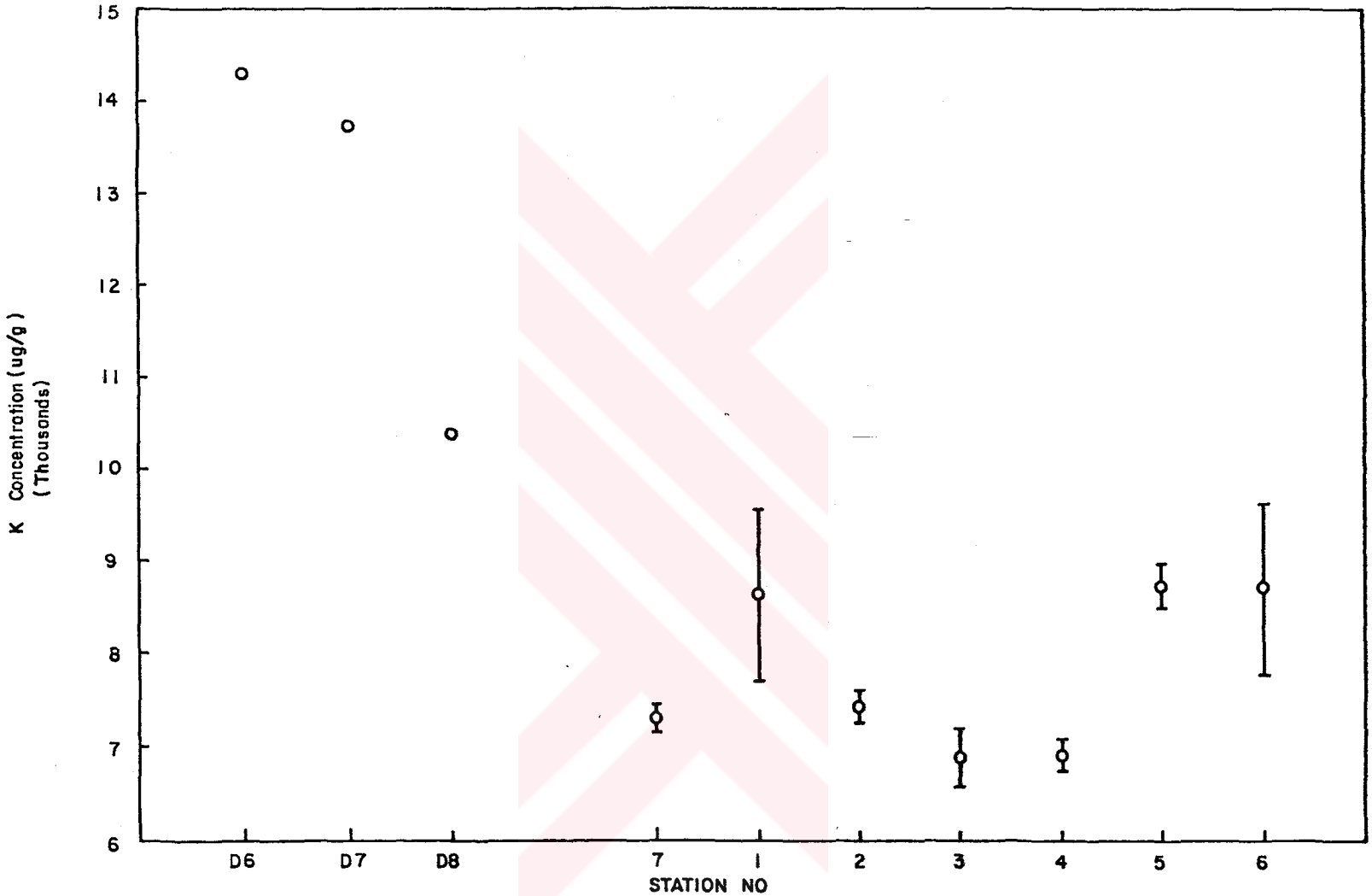

Figure 4. 9. K Concentration in "Göksu" river sediments and Taşucu estuary.

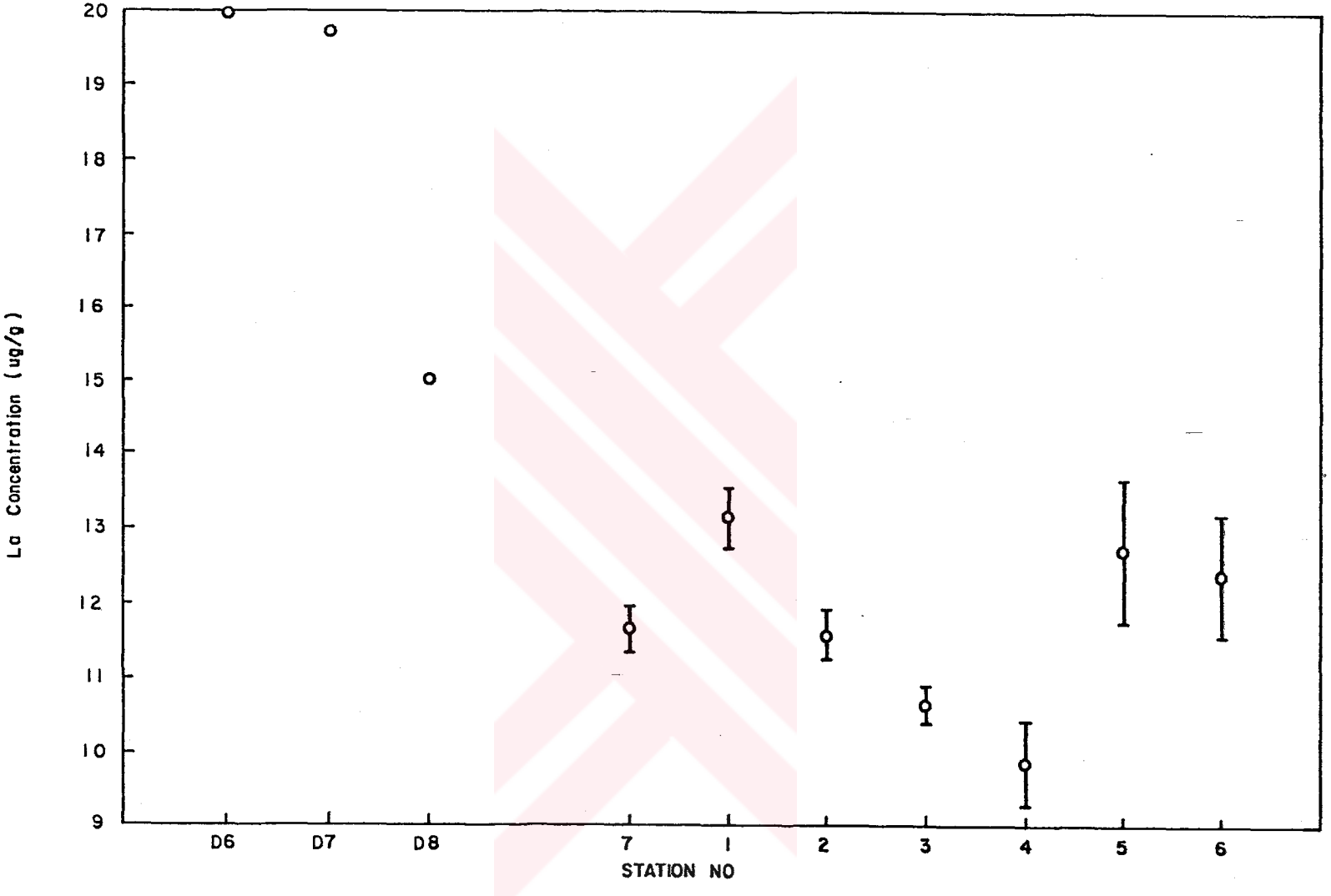

Figure 4.10. La Concentration in "Göksu" river sediments and Taşucu estuary.

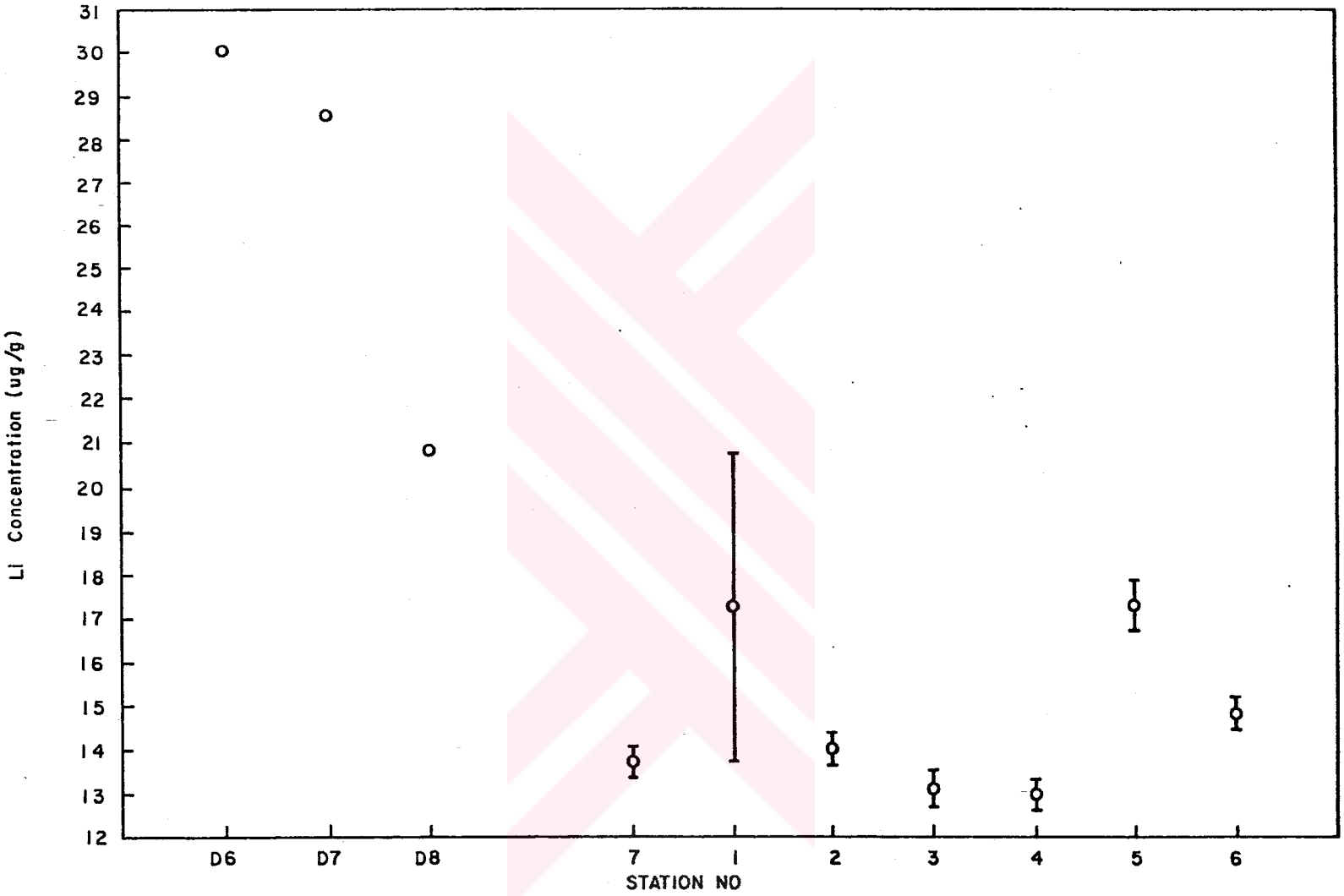

Figure 4.11. Li Concentration in "Göksu" river sediments and Taşucu estuary.

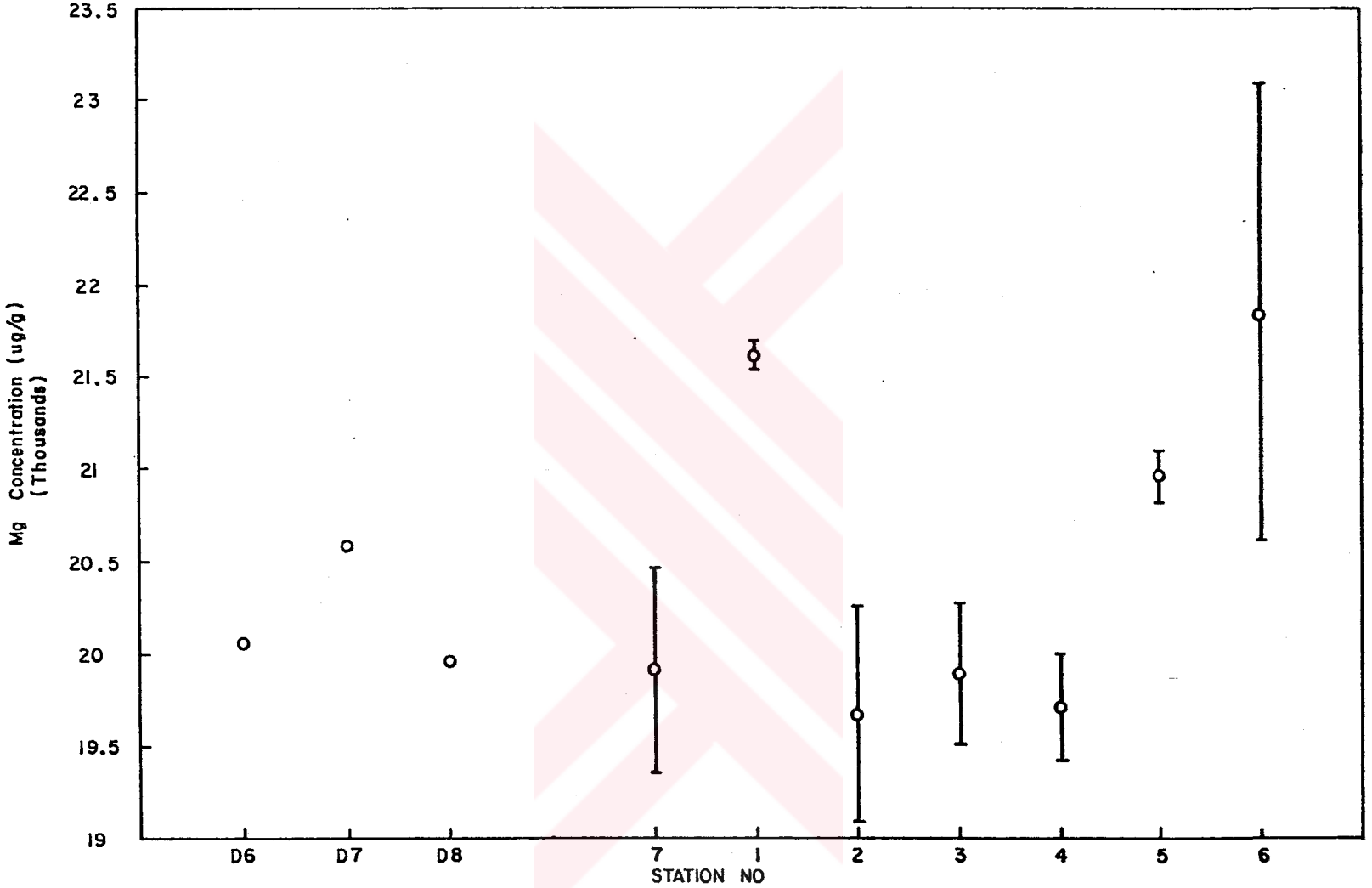

Figure 4.12. Mg Concentration in "Göksu" river sediments and Tasucu estuary.

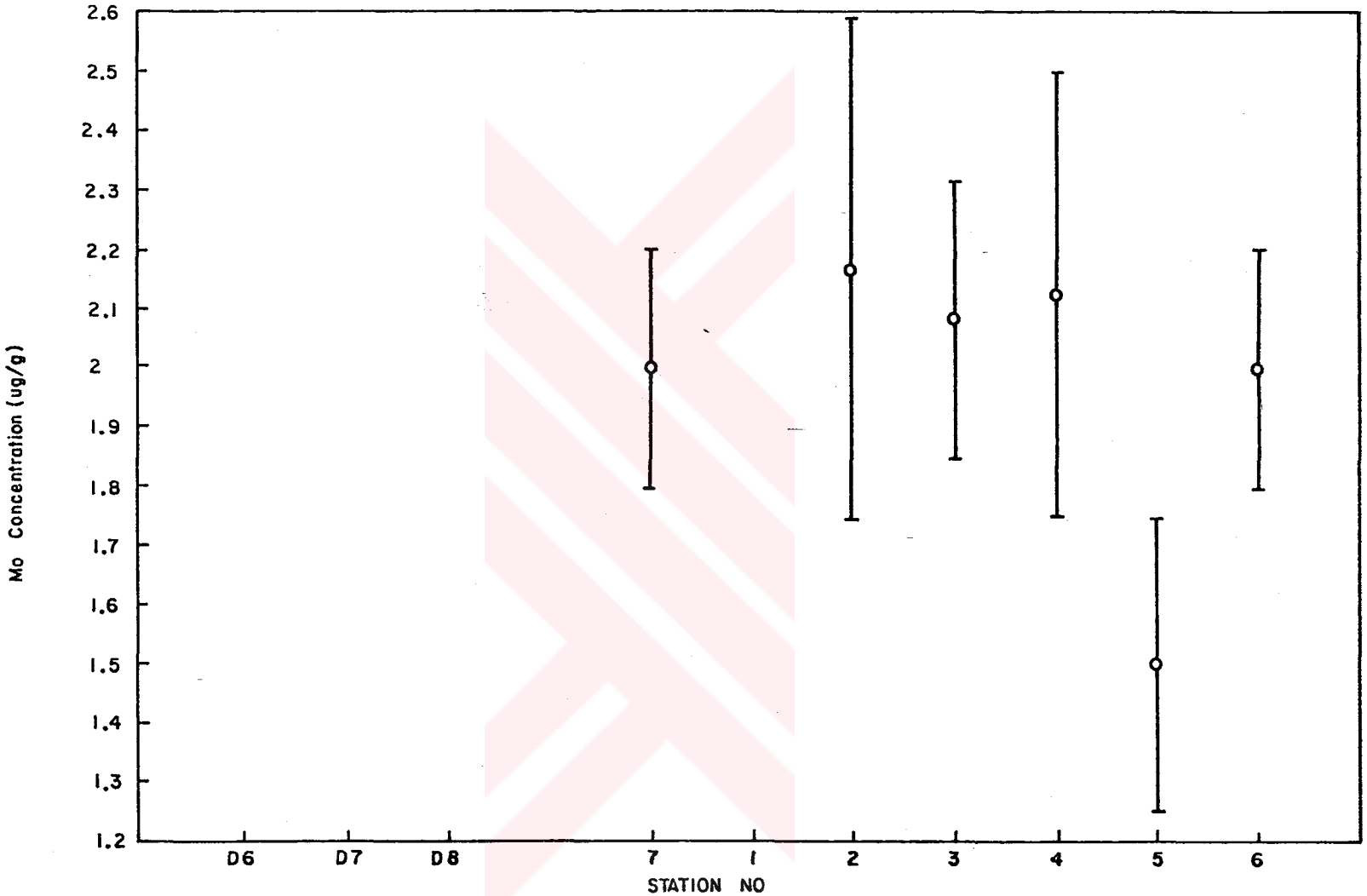

Figure 4.13. Mo Concentration in "Göksu" river sediments and Taşucu estuary.

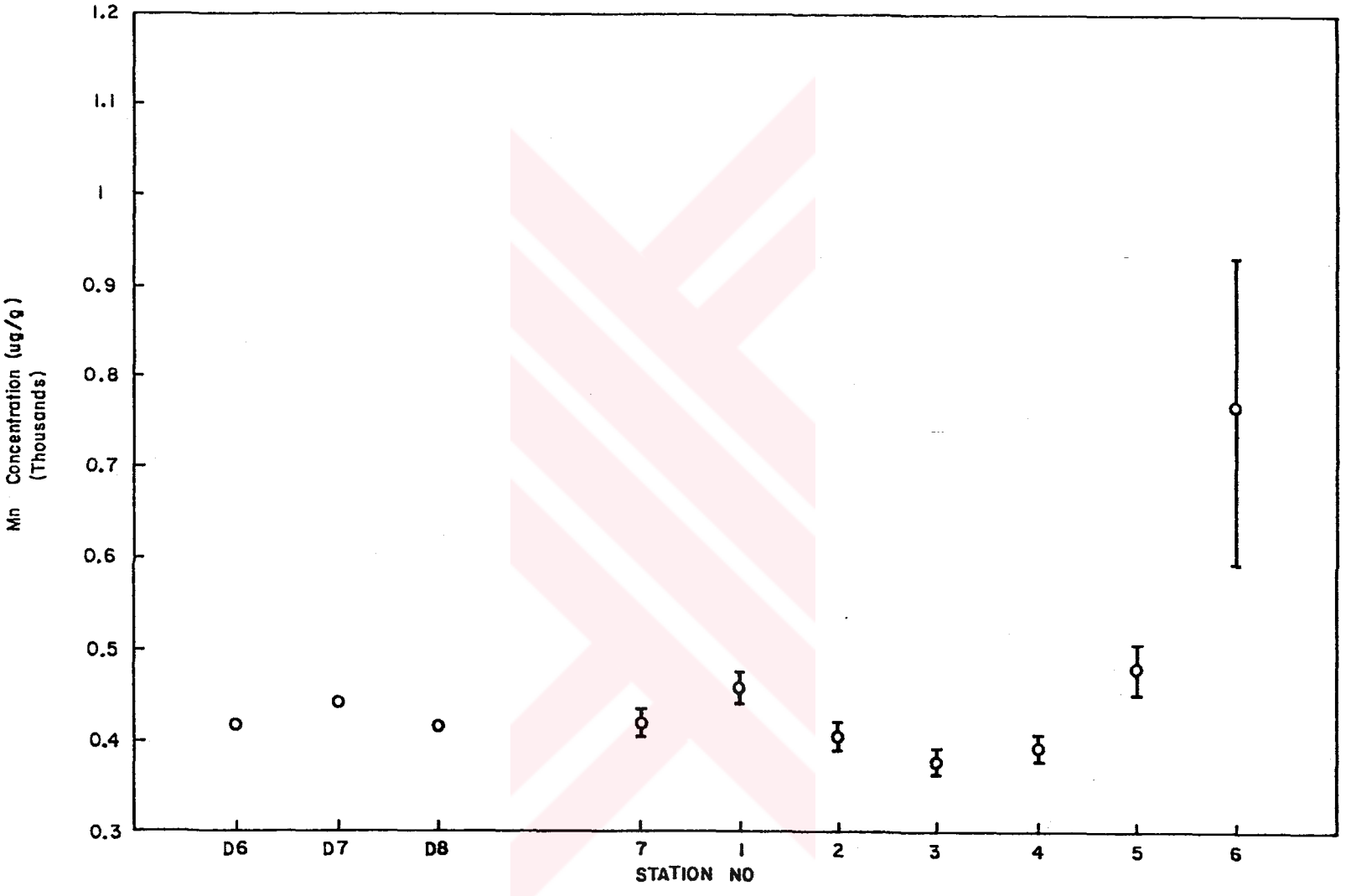

Figure 4.14. Mn Concentration in "Göksu" river sediments and Taşucu estuary.

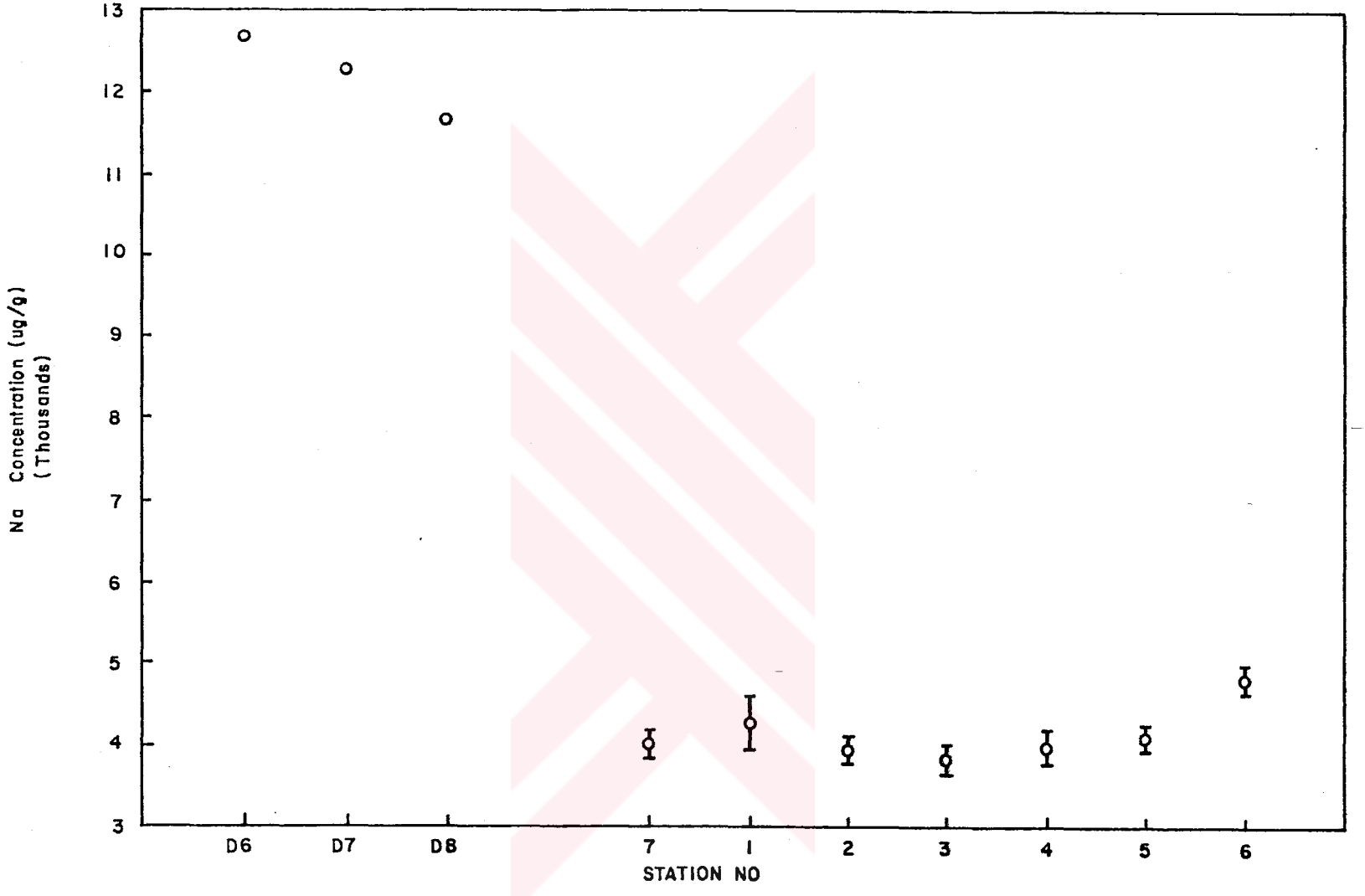

Figure 4.15. Na Concentration in "Göksu" river sediments and Taşucu estuary.

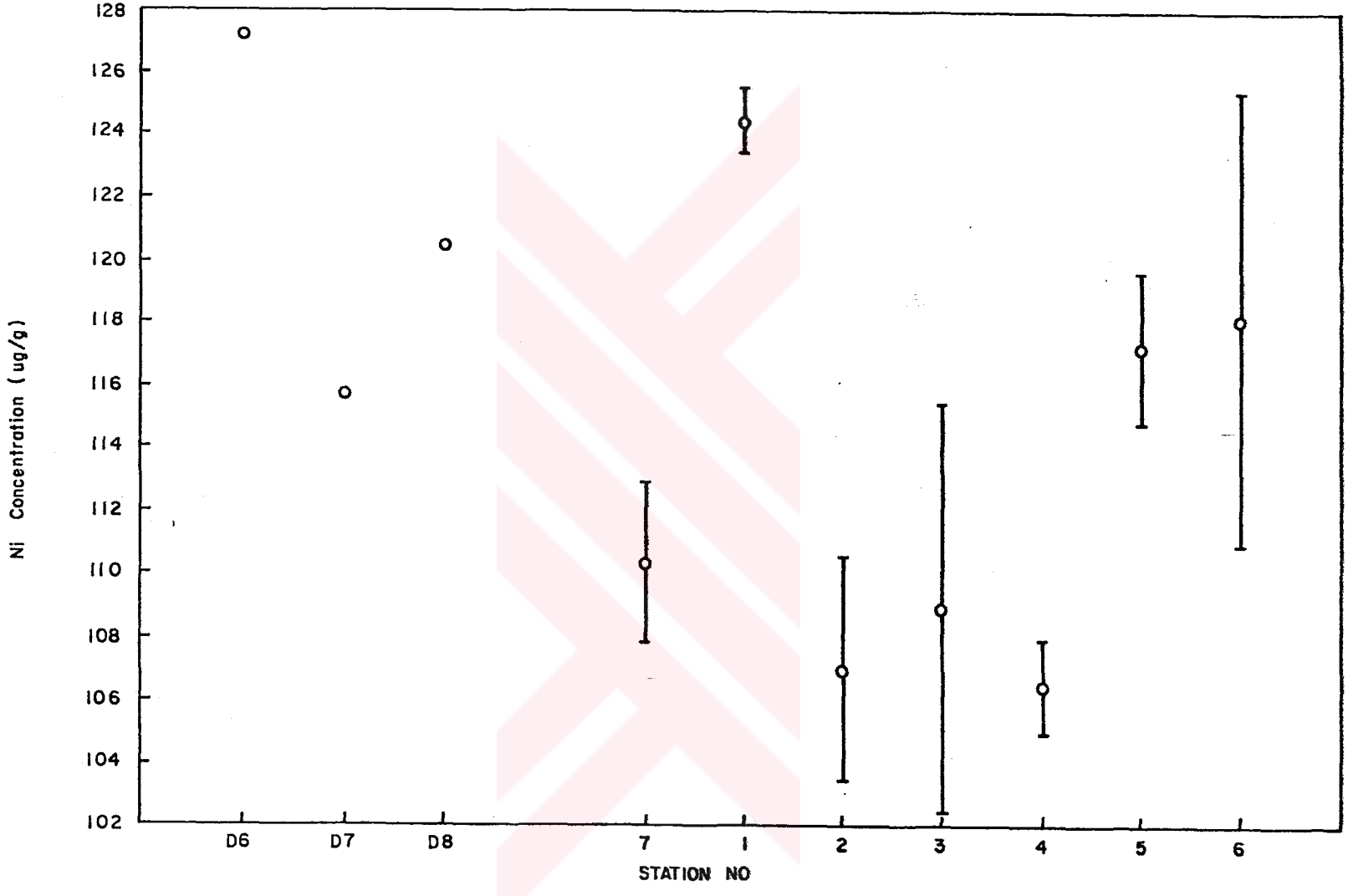

Figure 4. 16. Ni Concentration in "Göksu" river sediments and Taşucu estuary.

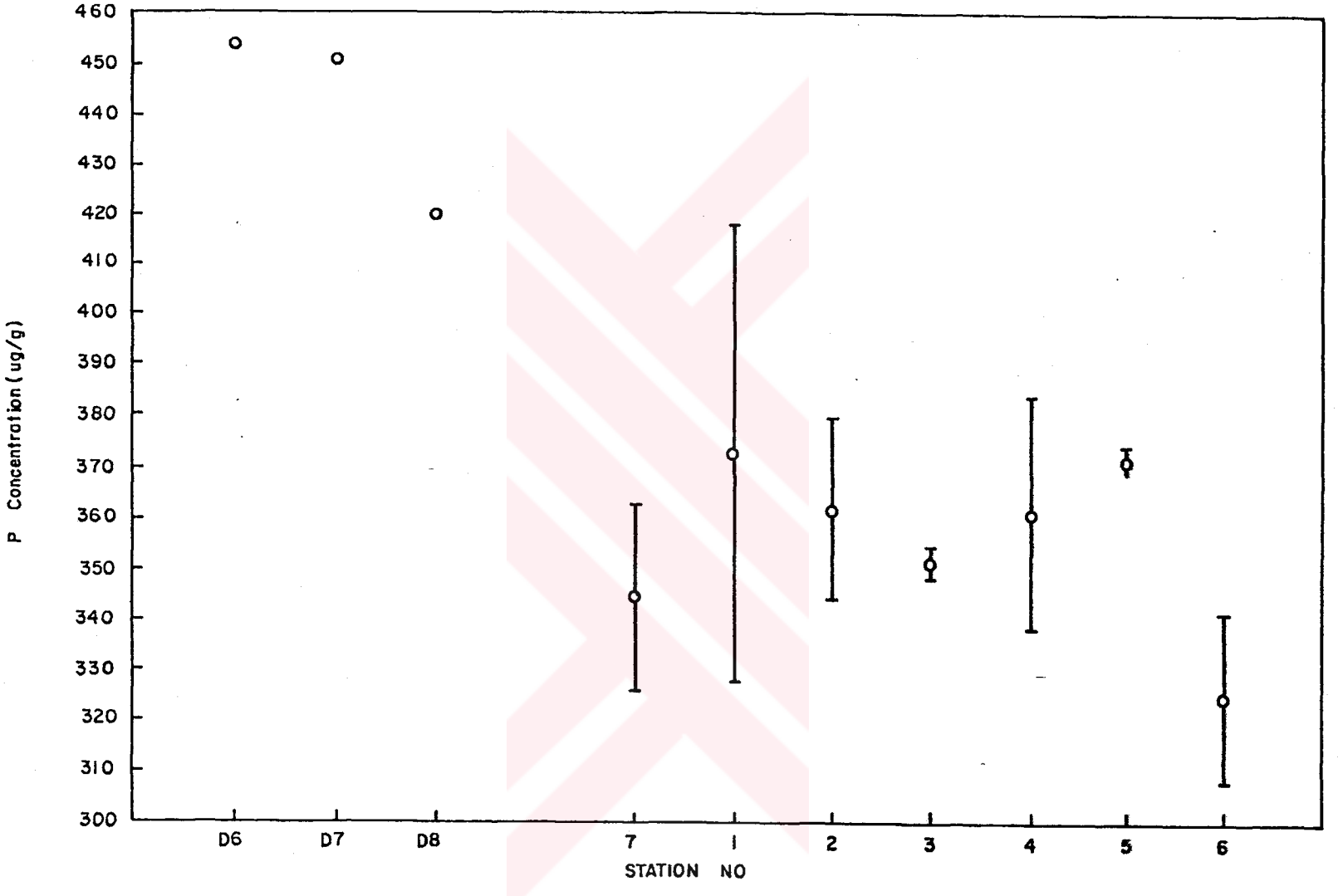

Figure 4.17. P Concentration in "Göksu" river sediments and Tasucu estuary.

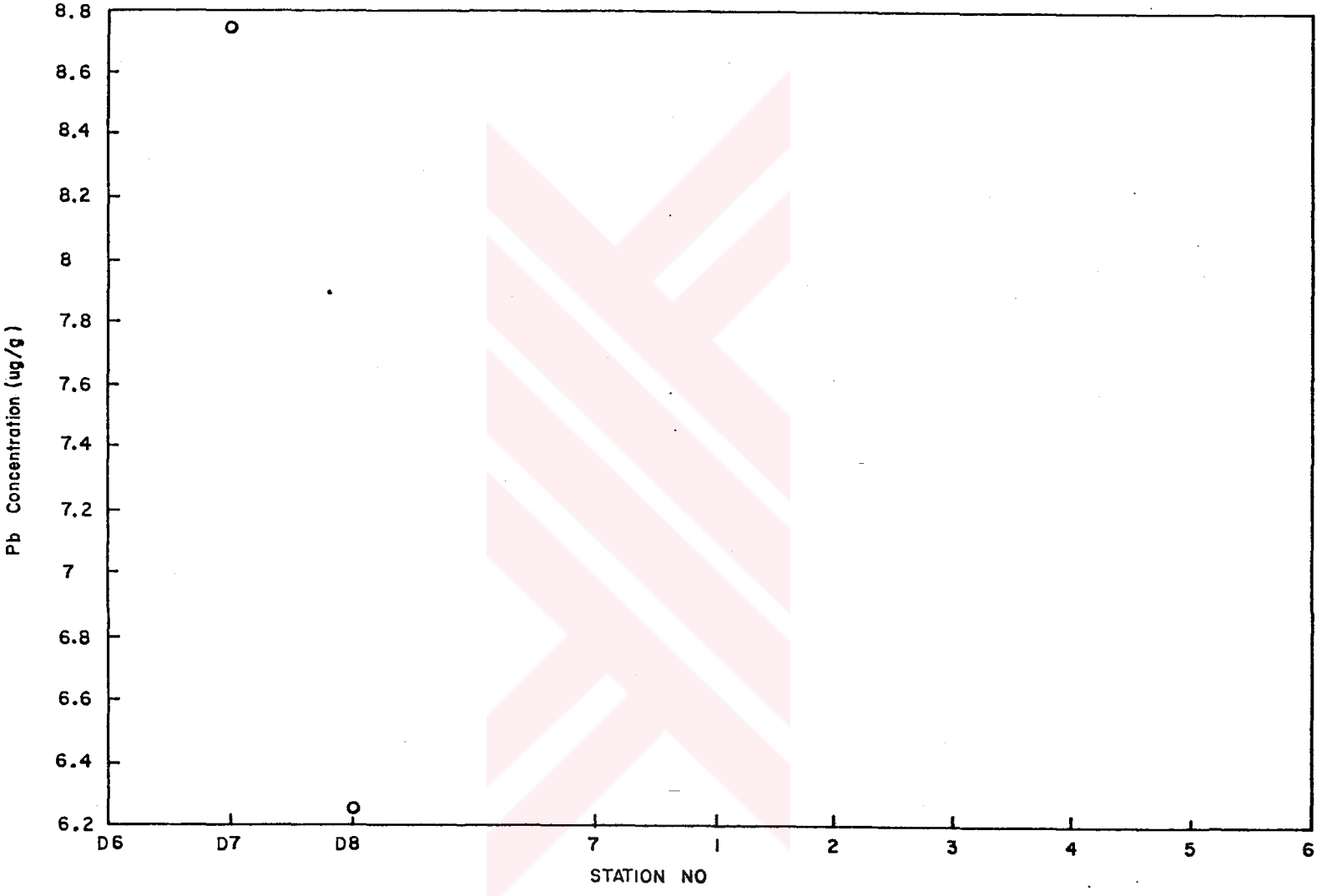

Figure 4.18. Pb Concentration in "Göksu" river sediments and Taşucu estuary.

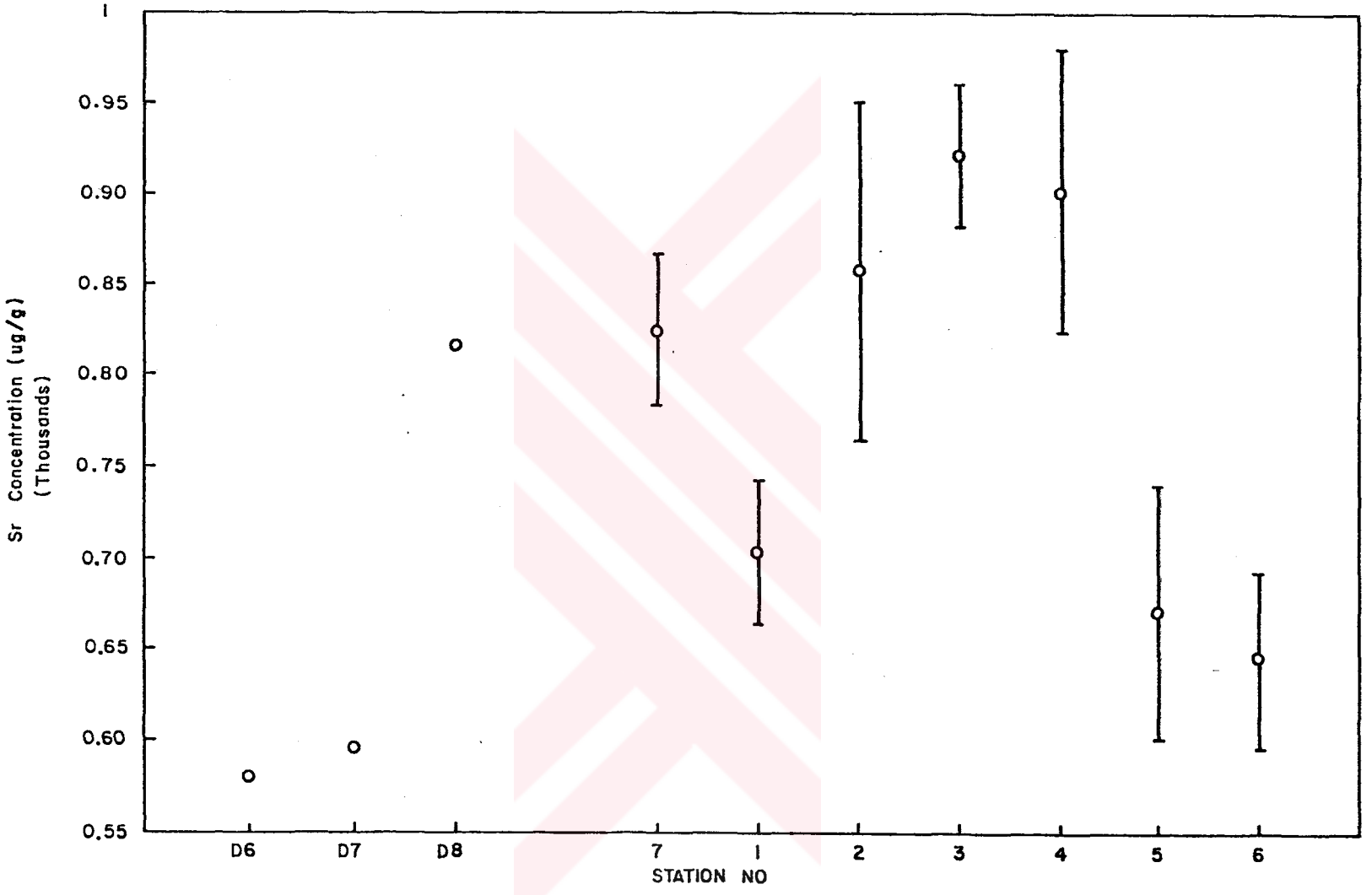

Figure 4.19. Sr Concentration in "Göksu" river sediments and Taşucu estuary.

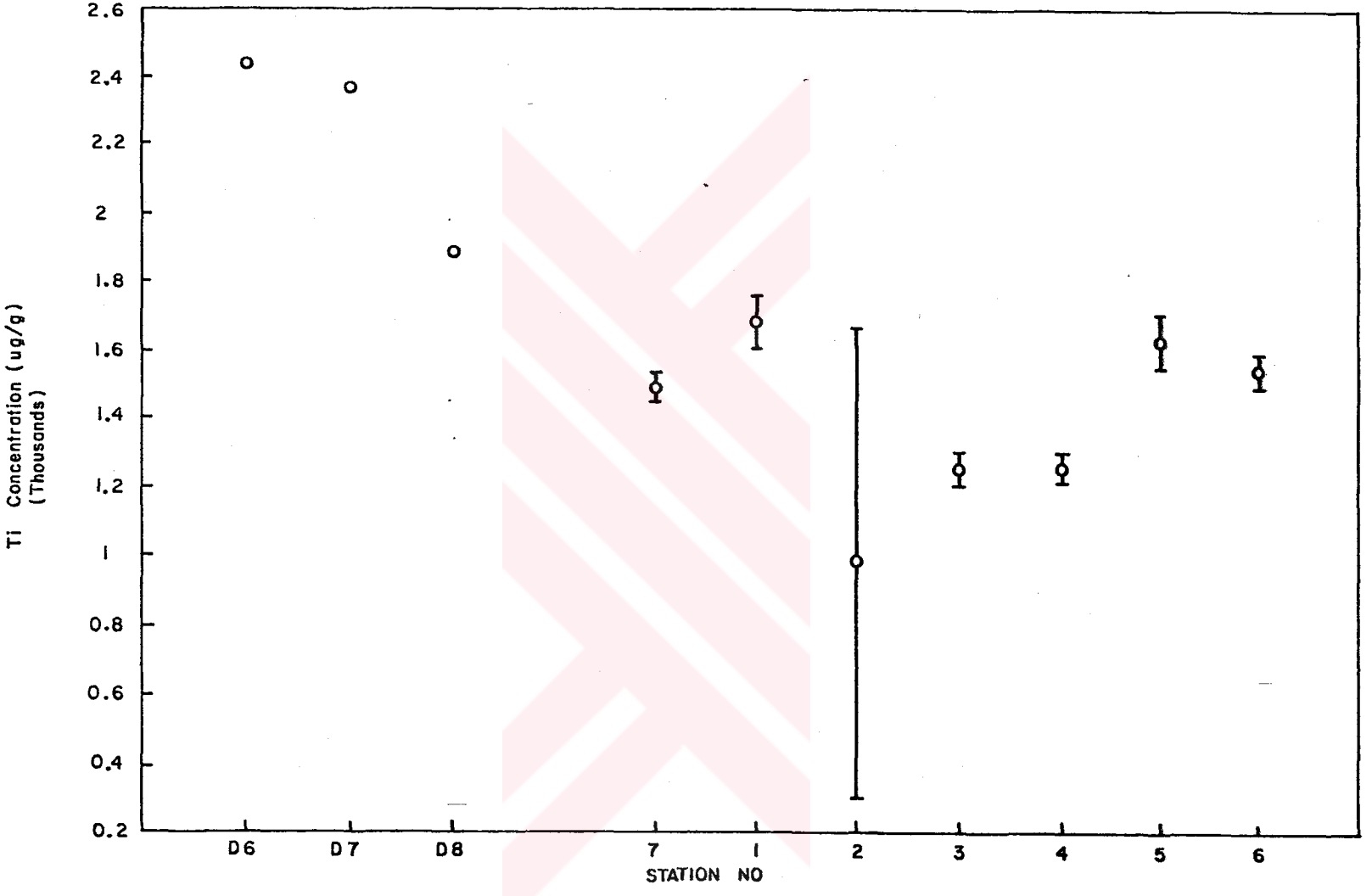

Figure 4.20. Ti Concentration in "Goksu" river sediment and Taşucu estuary.

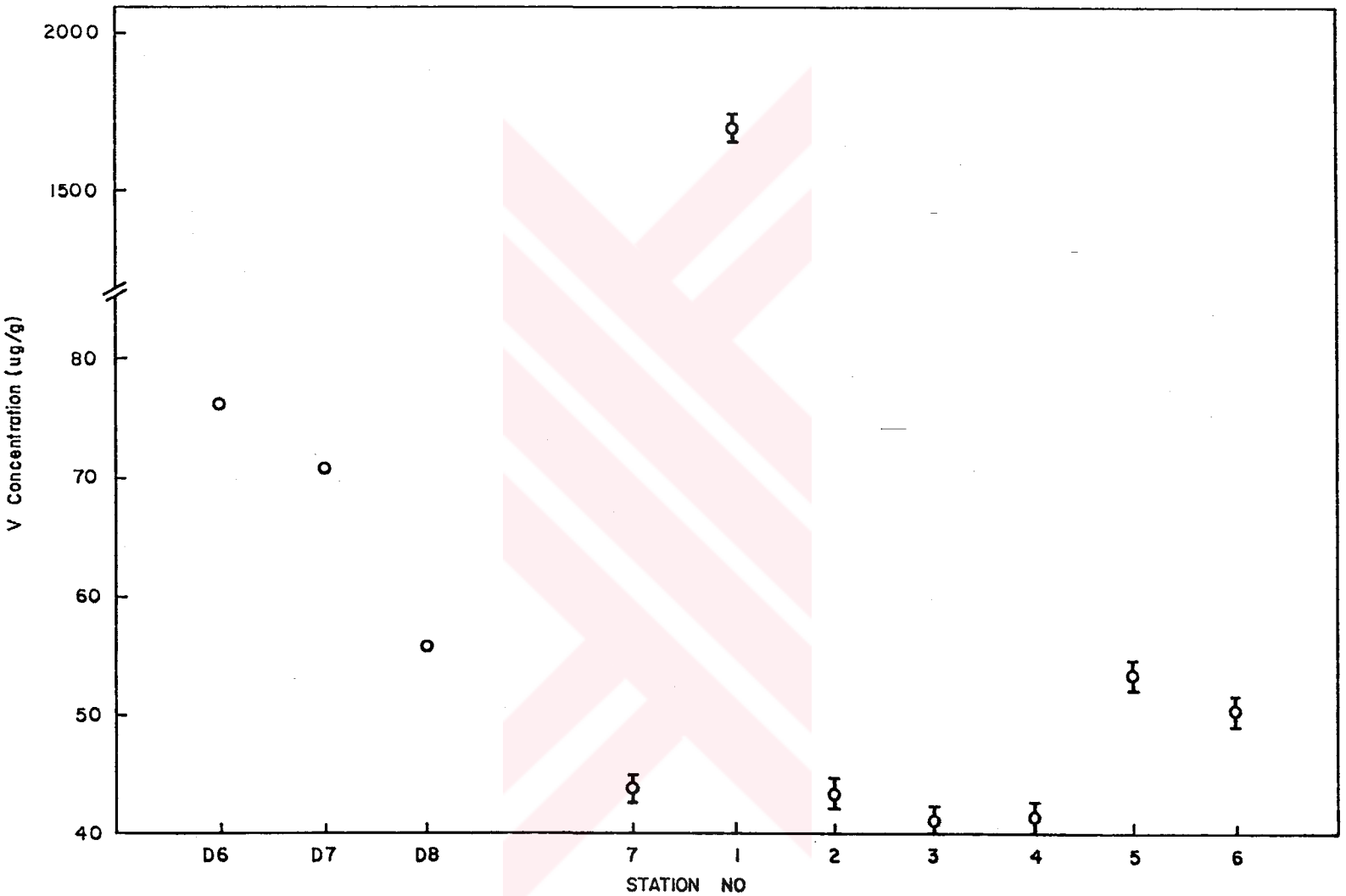

Figure 4.21. V Concentration in "Göksu" river sediments and Taşucu estuary.

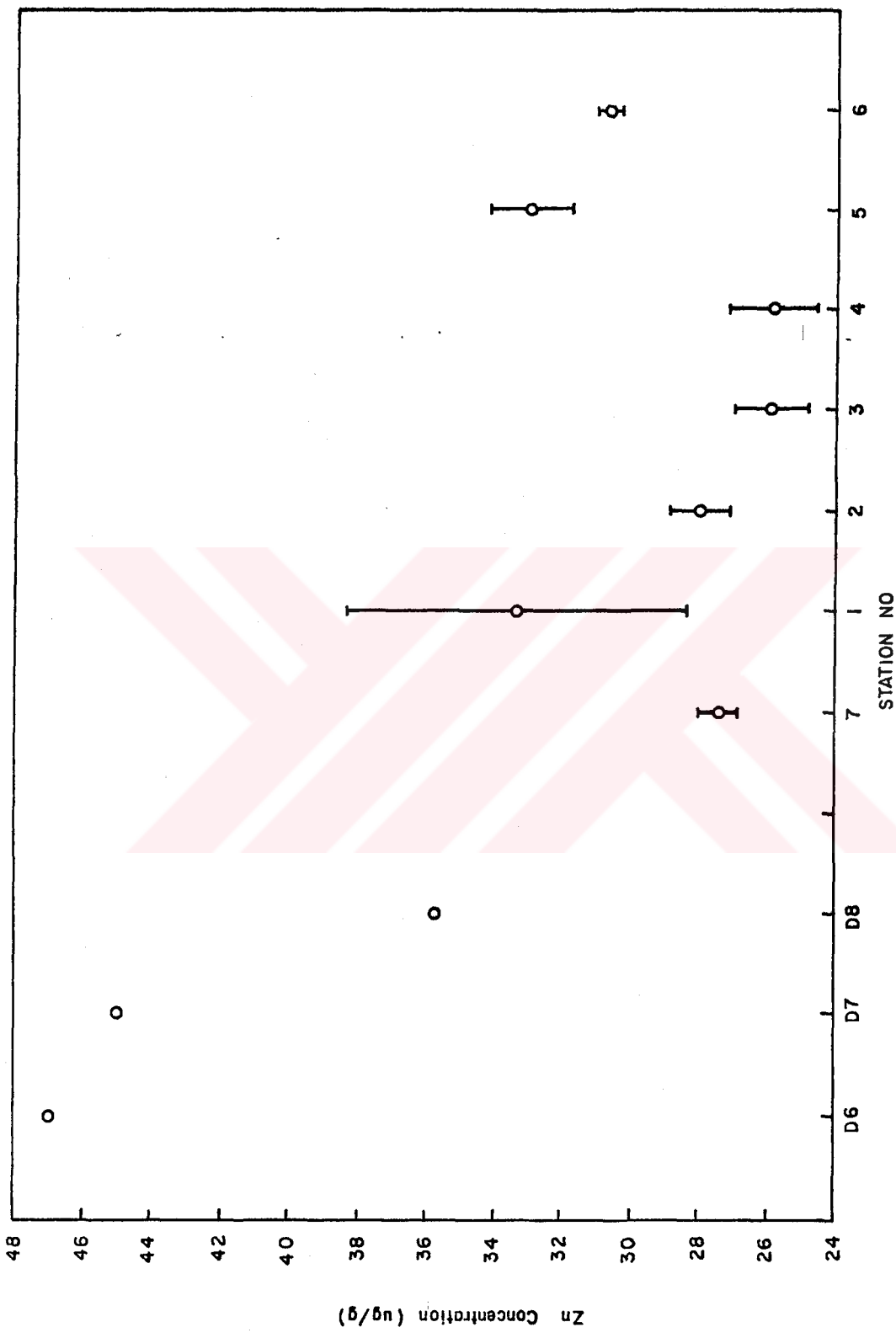

Figure 4.22. Zn Concentration in "Göksu" river sediments and Taşucu estuary.

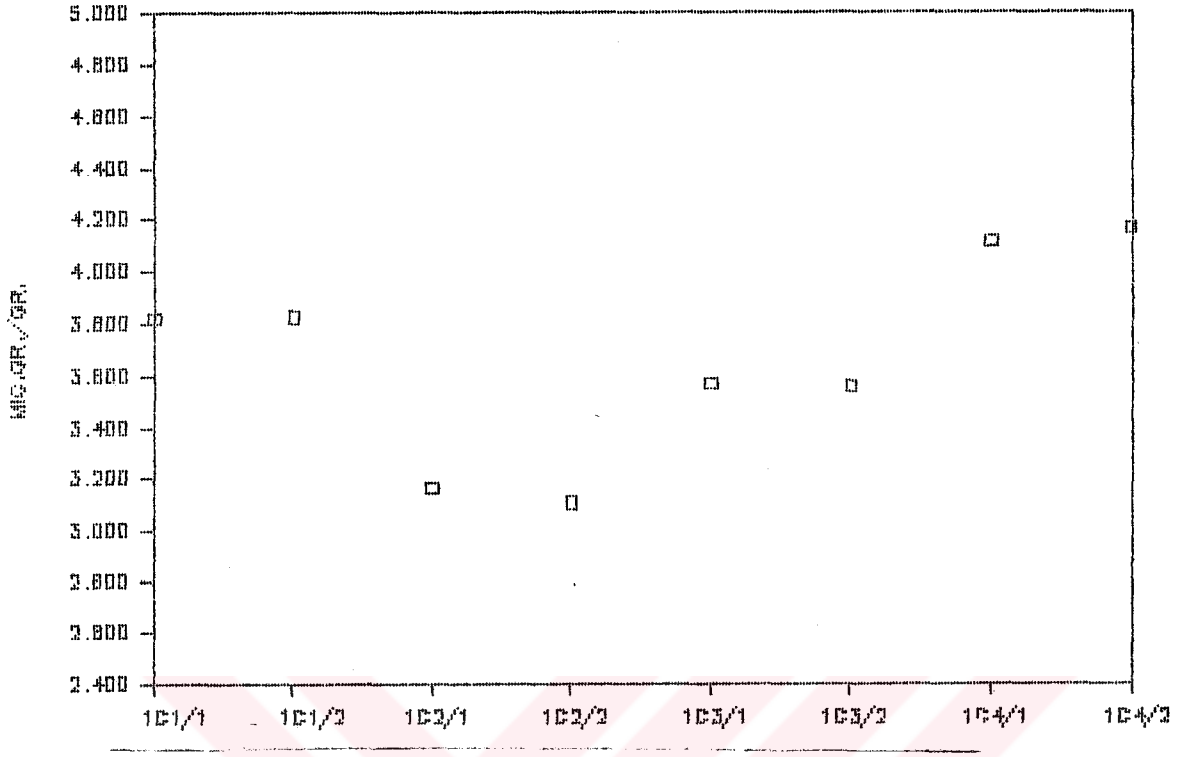

Figure 4.23. Na Contamination control Test results

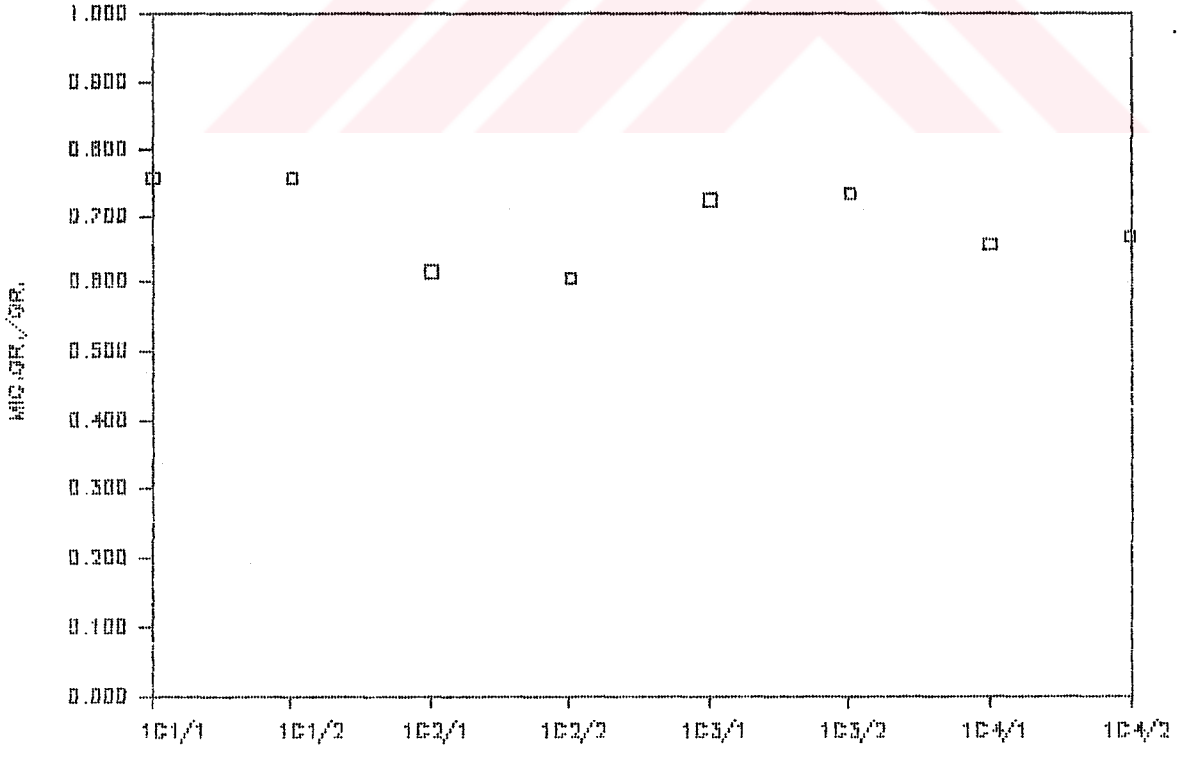

Figure 4.24. Sr Contamination control test results

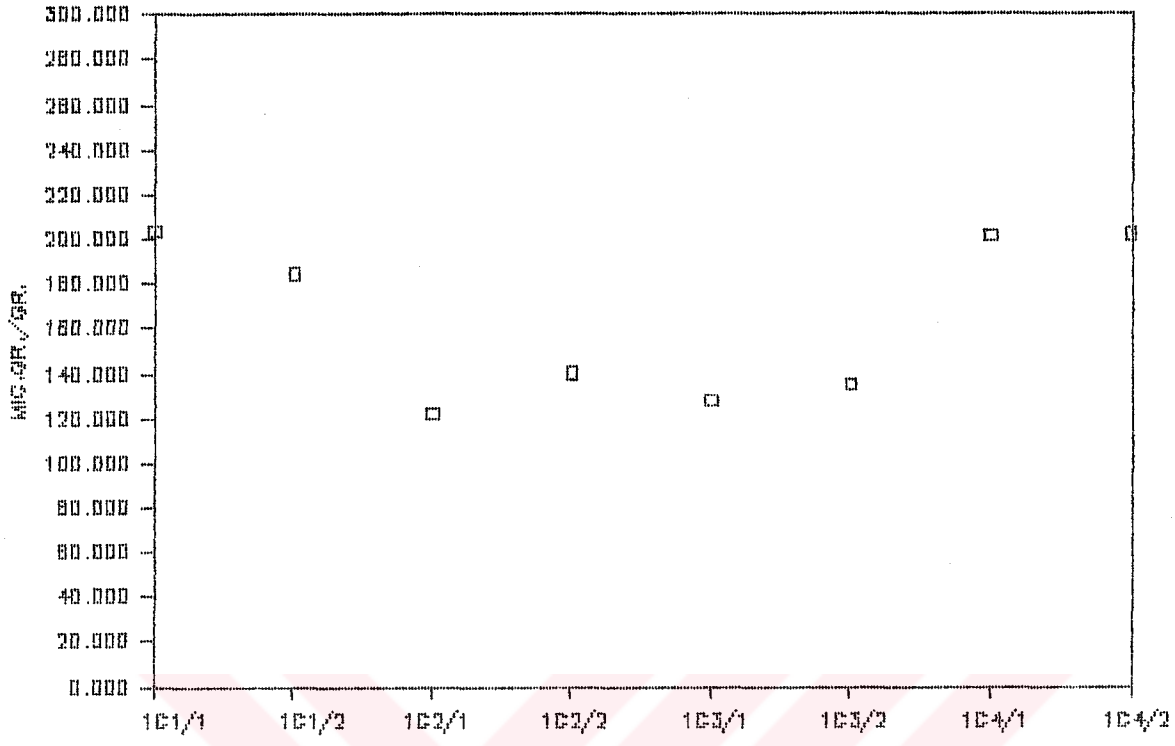

Figure 4.25. Cr Contamination control test results

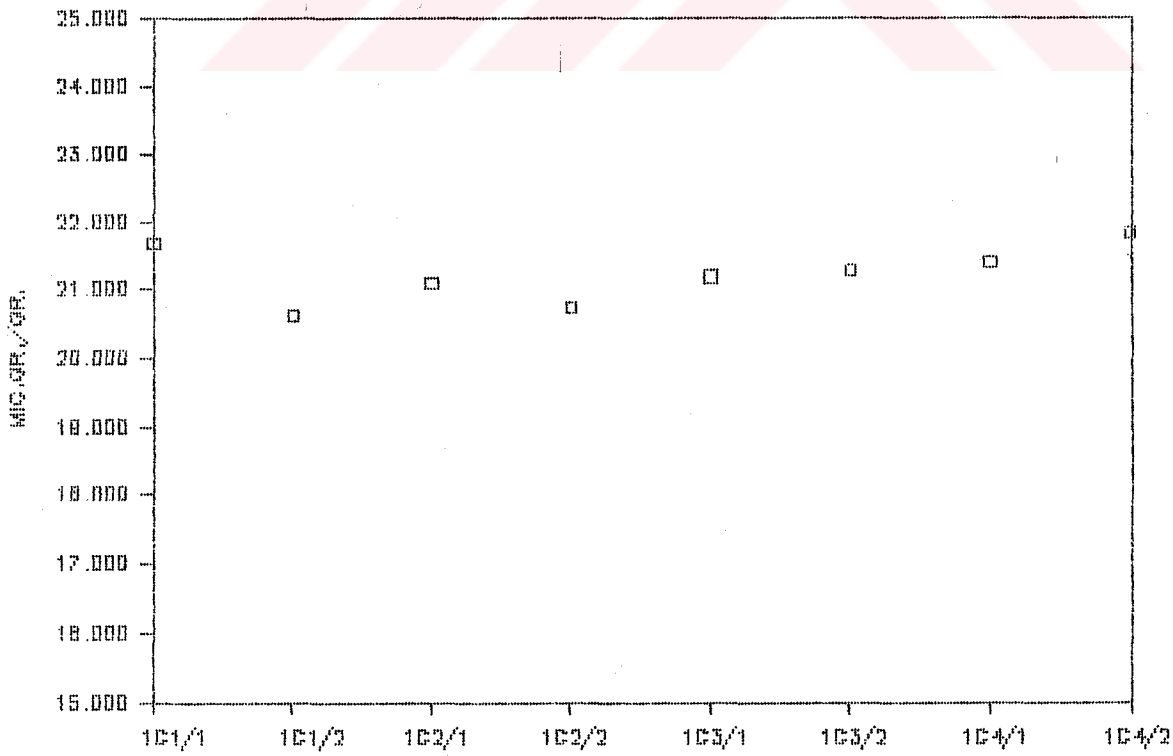

Figure 4.26. Mg Contamination control test results

CHAPTER 5

CONCLUSIONS

The conclusions of this study, can be classified into two groups; the first relating to the analytical results obtained, and the second the "Göksu" river sediments.

When the analytical results are considered;

* Inductively coupled plasma and Instrumental neuton activation requires a trained and experienced analyst in order to obtain meaningful results. At the same time although Atomic absorption requires such necessities, it easier to use compared with other methods;
  * The expected levels of concentration must be well defined;
  * If the levels of concentration are not too low, Inductively coupled plasma is preferable as it is faster. It is to be processed quite an economic method, if there is high number of data.
  * For neutron activation analysis, SRM which is going to be used must be selected very carefully reference materials for environmental must be used;

According to the "Göksu" river sediments results as a selected basin;

* Sediments must be considered as an indicator of pollution
* River "Göksu" is not pollution source for Pb;
* Although it is a "non-polluted" river for most of the analyzed element, effect of irrigation is observed;
* Silifke is a point source, for Mediterranean on the river;
* The effect of geological structure on the sediments is strong especially for Calcium.

CHAPTER 6

RECOMMENDATIONS FOR FUTURE WORK

The results of this study can be use for modelling of the basin. The relation between sea and the river must be studied.

Geochemistry of the sediment can be a topic of an environmental study.

Analytical methods used in environmental studies can be coupled to improve the quality of the obtained data.

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