MEASUREMENTS OF SELECTED TRACERS ^{18}O, ^{2}H AND ^{15}N AND NEW PRODUCTION IN THE BLACK SEA

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ABSTRACT

Sea water samples were collected in the cruises of the RV BİLİM (in January-February and April) in the Black Sea have been analyzed for ^{18}O. A cursory examination of the measurements indicates that there were no major changes of $\delta^{18}O$ in the Black Sea, as we had expected. There are some slight variations with location, however, these are immersed in the random variability resulting from natural variability or analyses errors. For example, slightly lower values of $\delta^{18}O$ can be found near the southwest Black Sea coast, which could be interpreted as being derived from the northwestern major rivers. However, even April, when the discharge was presumably high, stations visited in the northwestern region did not have a significant oxygen isotope ratio anomaly. This may be because of the rapid dilution away from the source regions.

INTRODUCTION

The scientific questions with respect to the exchange, transport and mixing processes in the Black Sea are not fully resolved by early and modern measurements alike. Fundamental scientific investigations of these processes are essential, and the use of radiotracers provide a powerful method leading to a basic understanding of the mixing and renewal mechanisms. Only detailed measurements and models developed from them can lay the groundwork for management decisions in the this medium of rapid environmental deterioration. On the other hand, recent years have seen a great number of studies in the Black Sea; among them a great number of tracer and radionuclide measurements, especially following the Chernobyl disaster.

Seasonal/annual surveys coordinated under the National Monitoring and Research Program sponsored by the State Planning Office (SPO) and Turkish Scientific and Technical Research Council (TUBITAK) and multinational CoMSBlack research program and covering the Black Sea with full series of high resolution hydrographic and hydrochemical measurements represents a unique opportunity to collect and analyze data on selected tracers modelling basic processes of primary importance.

A coordinated Research Program of the International Atomic Energy Agency entitled 'Measurements of Selected Tracers Modelling Exchange, Transport and Mixing Processes in the Black Sea' aims to use radiotracer measurements for process and pollution studies in the Black Sea. The main working document for this activity, Fabry and Fröhlich, (1992) can be obtained from the IAEA. The research program aims to have integration with the CoMSBlack Program.

The first level of information on the physical mechanisms of horizontal and vertical cross-isopycnal transport/mixing and can be extracted from high resolution measurements of temperature, salinity, light transmission. Stable isotopes and some basic chemical parameters described below complement this information, and involve a relatively simple set of measurements.

Measurements of stable isotopes ^{18}O, ^{2}H can be used to characterize the effects of freshwaters reaching south from the major rivers (*e.g.* the Danube), the formation and spreading of the Cold Intermediate Water (CIW), and the fluxes of Mediterranean water from the Bosphorus. ^{15}N isotopic ratios in the water column can be used to assess relationships between particulate and dissolved Nitrogen, the relative roles in new production of the cross-nutricline fluxes and the riverine and atmospheric influxes reaching the photic zone.

Measurements indicate that the river waters of the Danube has a clear signature of ^{18}O. The outflowing Danube waters have ^{18}O -10.3 %o, with a strong signal of ~ 2%o amplitude (Rank, 1992). Measurements in the Black Sea indicate a large variation within the upper 200m, *i.e.* approximately in the surface and Cold Intermediate Layer (CIL) above the halocline, and furthermore a characterization of Mediterranean Waters (MW) based on ^{18}O and ^{2}H isotopic ratios (Swart, 1991a,b). The ^{18}O for surface waters are on the order of -4 to -2, with large variations, and the deep waters have values of -1.65. The surface ^{2}H anomaly also has large deviations from the cluster of other data (Swart, 1991a,b). Although exchange with the atmosphere (rainfall and evaporation) seems to dominate the oxygen and deuterium isotope ratios (rainfall ^{18}O -6 to -8), their horizontal distribution especially on the western shelf region can give information on the spatial distribution of river effects if sampled closely across the shelf. The Danube source definitely constitutes a detectable signal. Similarly, the Mediterranean Water in the Marmara Sea has a positive anomaly of ^{18}O 1 to -2, and therefore its diluted intrusion in the Black Sea could still have a detectable signal.

Murray *et al.* (1992) indicate that no new nitrogen seems to reach the euphotic zone from the deep water, and this may be one of the peculiarities of the Black Sea, leaving the atmospheric and riverine supply as the only other sources of new production. A number of other studies (*e.g.* Altabet, 1988) show that ^{15}N isotopic ratios can be important indicators of trophic structure and recycling of Nitrogen.

MATERIALS AND METHODS

Samples were collected in three cruises of the RV BİLİM in January-February and April 1993. While the sampling was done mainly in the Black Sea, some oxygen isotope samples were taken in the Sea of Marmara during December 1993. Sampling locations

Water samples were collected by 2.5 L Niskin Bottles from selected stations and depths for analyses of ^{18}O and ^{2}H isotopes and were stored in 0.5L dark bottles till the analysis time. For N^{15} analysis the sufficient amount of water sample was filtered though a 0.2 pore size GF/C glass fiber filters and dried at 60°C. For Pb^{210} analyses sediment samples were collected with gravity corers and preserved in plastic bags after frozen.

O^{18} and H^{2} analysis were performed with the aid of a Micromass 602 C Model mass spectrometer. For O^{18} analysis an aliquot of the sample was placed on a 3mL volume flask and vacuum was applied after freezing the sample in order to evacuate any trace of air. CO_2 gas was introduced to the samples at 600 mbar and kept over night in a shake bath. this way oxygen exchange is achieved analyzed by mass spectrometer. CO_2 is used as reference. For the H^{2} analysis 8 L of the sample was placed together with 0.25 g of Zn in a glass vial and evacuated. At 400°C water is reduced into H_2 gas and analyzed with the mass spectrometer to determine the D/H ratio.

The O^{18} and H^{2} contents were calculated from the below equation:

$$= \frac{R_{samp.} - R_{ref.}}{R_{ref}} \quad \text{SMOW } (‰)$$

Where, $R_{ref} = O^{18}/O^{16}$ and $R_{samp.} = O^{18}/O^{16}$ for O^{18}
$R_{ref} = D/H$ and $R_{samp.} = D/H$ for H^2
SMOW : Standard Mean Ocean Water

RESULTS AND DISCUSSIONS

Oxygen isotopes in seawater:

The samples from January-February and April cruises have been analyzed for ^{18}O, and the results are given Table 1. ^{2}H analyses for these samples were scheduled for the second part of the year, and therefore they can not be reported at this time. The analyses for the August samples will be carried out in the first half of 1994.

A cursory examination of the measurements indicates that there were no major changes of ^{18}O in the Black Sea, as we had expected. There are some slight variations with location, however, these are immersed in the random variability resulting from natural variability or analyses errors. For example, slightly lower values of ^{18}O can be found near the southwest Black Sea coast, which could be interpreted as being derived from the northwestern major rivers. However, even April, when the discharge was presumably high, stations visited in the northwestern region did not have a significant oxygen isotope ratio anomaly. This may be because of the rapid dilution away from the source regions.

Measurements in the Turkish Straits System (i.e. the Dardanelles, Bosphorus Straits and the Marmara Sea) evidently show the effects of transition between the Black Sea and the Mediterranean, Rapid changes are evident especially within the Straits. Upper layer variability exists along the entire system.

^{15}N *in particulate matter:*

Samples have been collected in almost all stations. Filtered extracts of particulate matter have been saved for analyses.

Because it was not possible to carry out the analyses in Turkey, the samples have been sent to Dr. M. Altabet of the Woods Hole Oceanographic Institution for analyses. He has promised to make analyses of a limited number of samples. The results will be reported when they become available.

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TABLE 1
$\delta^{18}O$ Measurements in the Black Sea and Marmara Sea

Station	Location	Date	Sample No	Depth	$\delta^{18}O$
I1	41°22′15″*N* 28°38′00″*E*	17/01/93	D1	5	-3.45
			D31	5	-3.26
			D25	50	-3.35
I2	41°34′00″*N* 28°32′70″*E*	17/01/93	D39	5	-3.60
			D21	15	-3.59
			D29	50 (?)	-3.20
I3	41°40′00″*N* 28°30′00″*E*	17/01/93	D6	5	1.13 (?)
			D41	15	-3.17
			D46	25	-3.34
			D34	50	-3.28
I4	41°43′20″*N* 28°41′20″*E*	17/01/93	D23	(?)	-3.48
			D47	15	-3.50
			D44	50	-3.34
I5	41°45′60″*N* 28°50′00″*E*	17/01/93	D5	5	-3.30
			D16	5	-3.34
			D19	5	-3.29
			D30	15	-3.48
			D42	25	-3.64
			D3	100	-3.39
B15	41°12′55″*N* 29°07′22″*E*	11/02/93	D15	0-	-3.85
			D11	40	-3.39
			D13	50	-1.05
B0	41°01′54″*N* 29°00′53″*E*	11/02/93	D17	0	-3.23
			D27	30	-2.66
45C	40°46′00″*N* 29°00′00″*E*	13/02/93	D12	0	-2.17
			D20	10	-1.61
K50K40	40°50′00″*N* 28°28′00″*E*	14/02/93	D2	2	-1.71
			D8	10	-1.64
			D4	50	-4.66 (?)
K50K00	40°50′00″*N* 28°00′00″*E*	15/02/93	(?)	(?)	-2.13
			D7	200	-3.21 (?)
			D9	1000	1.21
K36J18	40°36′00″*N* 27°18′00″*E*	17/02/93	D35	5	-2.00
			D10	8	-0.98 (?)
			D32	20	-1.28
			D22	40	0.87

Station	Location	Date	Sample No	Depth	$\delta^{18}O$
D1	40°26′18″N 26°45′42″E	18/02/93	D38	2	-1.37
			D26	30	-1.02
			D28	75	1.07
C0	40°01′38″N 26°11′23″E	18/02/93	D40	5	-0.88
			D24	18	0.64
			D36	50	0.93
R4	43°50′00″N 30°15′00″E	04/04/93	28	1	-3.36
			20	25	-3.42
			35	50	-3.23
			26	100	-3.30
R6	43°55′00″N 29°30′00″E	04/04/93	30	1	-3.57
			37	15	-3.34
			29	15	-3.34
			34	25	-3.34
			22	50	-3.35
U8	45°30′00″N 32°00′00″E	04/04/93	19	1	-3.27
			9	15	-3.42
			23	25	-3.34
R17	45°00′00″N 30°30′00″E	11/04/93	25	1	-3.42
			32	10	-3.16
			24	25	-3.49
M08Q15	42°08′00″N 33°15′00″E	11/04/93	31	1	-3.56
			21	15	-3.40
			15	25	-3.15
			33	50	-3.23
M30Q15	42°30′00″N 33°15′00″E	14/04/93	7	5	-3.31
			16	15	-3.24
			8	55	-3.23
M10P15	42°10′00″N 33°15′00″E	14/04/93	5	1	-3.45
			1	17	-3.30
			3	48	-3.39
L55K12	41°55′00″N 28°40′00″E	14/04/93	14	1	-3.61
			12	15	-3.35
			11	20	-3.07
			13	50	3.09

Station	Location	Date	Sample No	Depth	$\delta^{18}O$
L59.5K33	41°59′05″N 28°33′00″E	14/04/93	6	1	-3.62
			10	15	-3.64
			2	25	-3.41
			4	50	-3.41
L305M15	41°30′00″N 30°45′00″E	14/04/93	36	1	-3.28
			18	10	-3.32
			27	25	-3.08
			17	50	-3.09

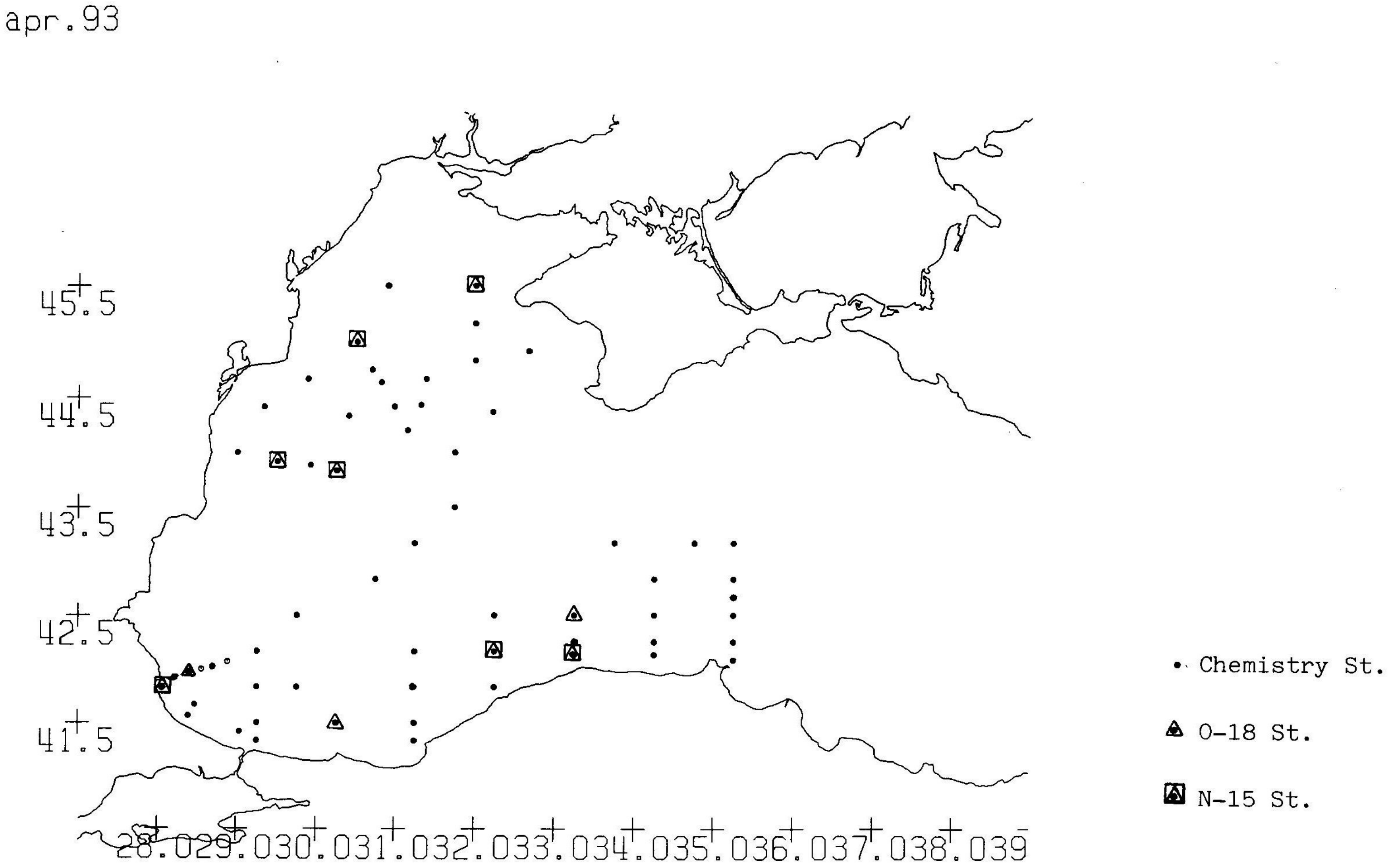


Figure 1. Sampling Sites in the Black Sea

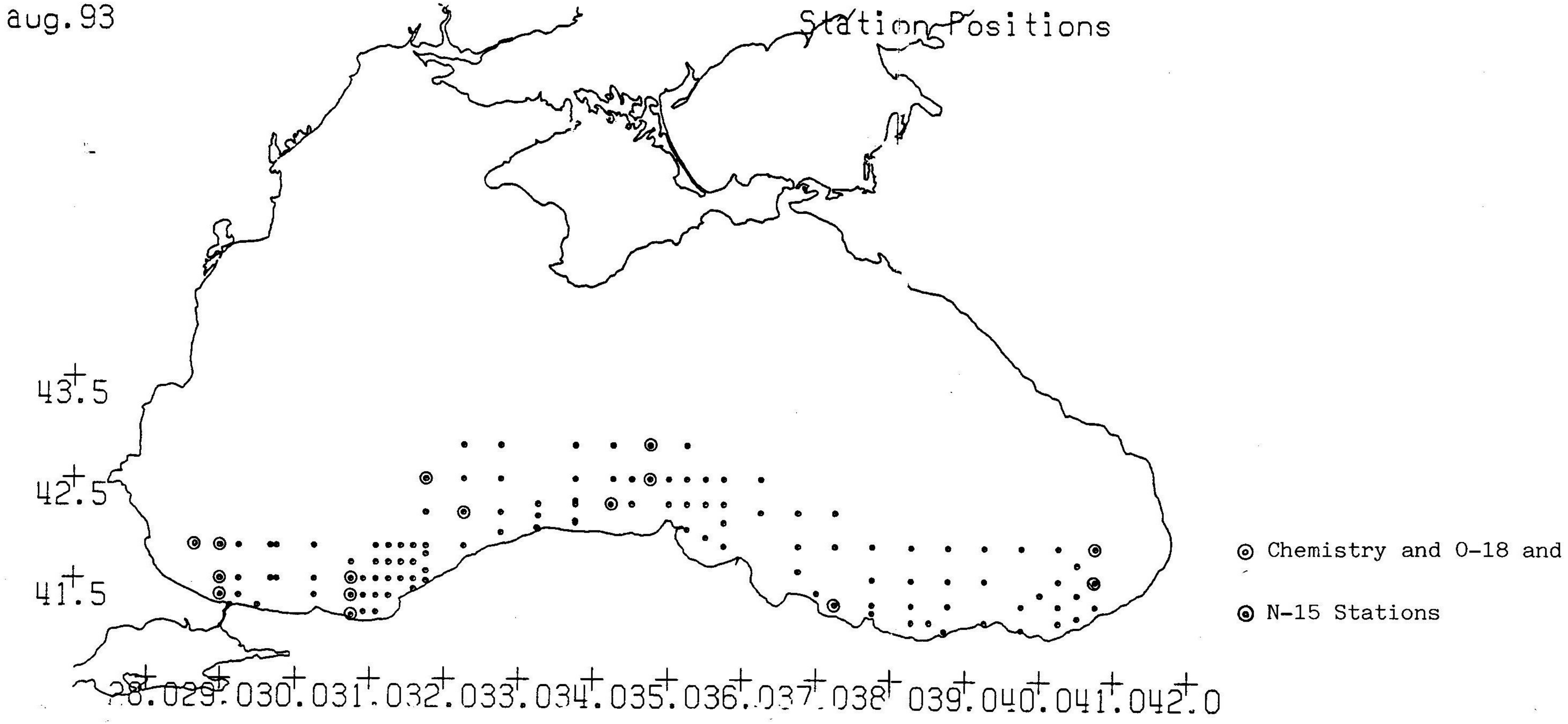
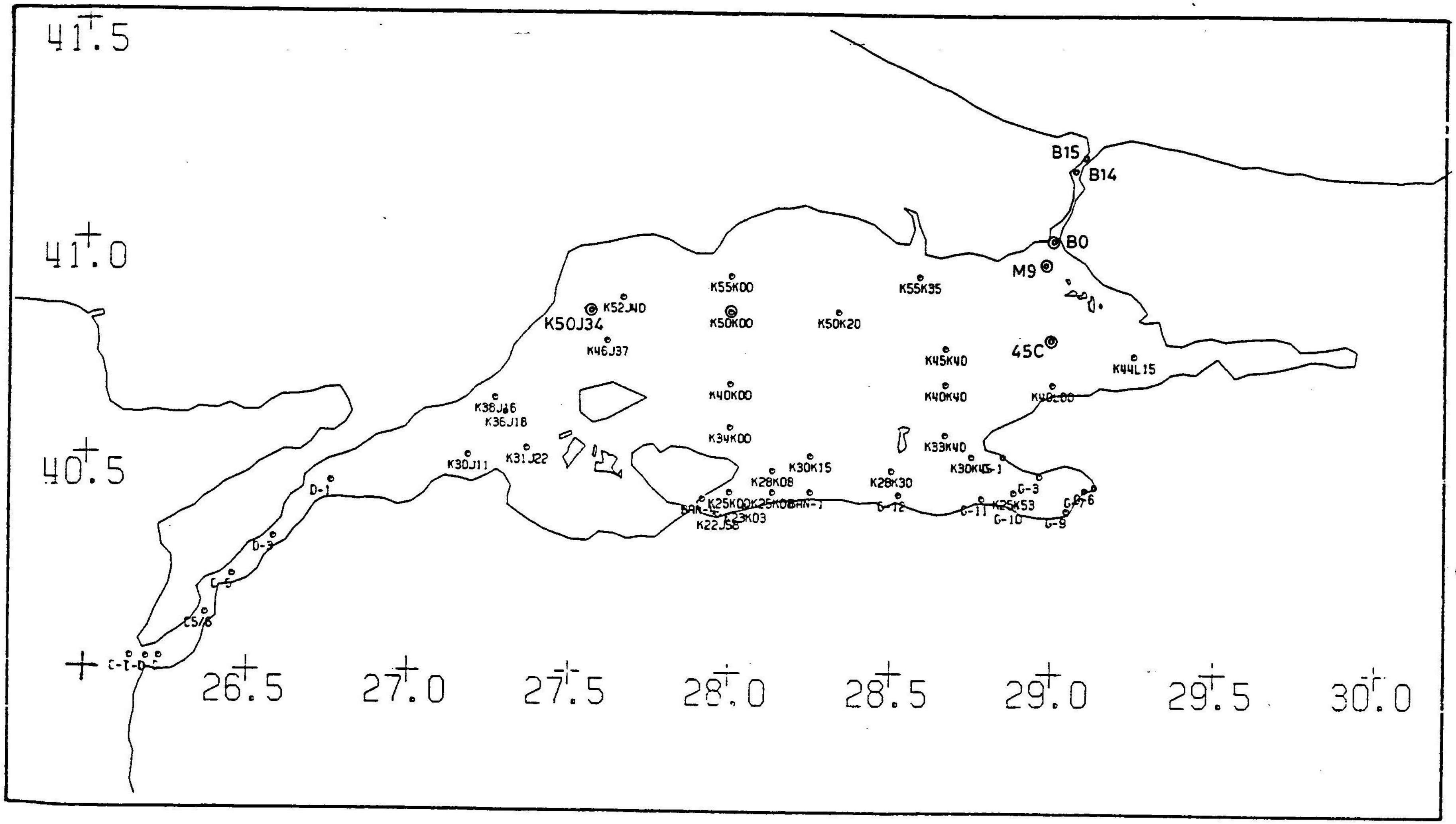


Figure 2. Sampling Sites in the Black Sea



◎ O-18 and N-15 Stations

Figure 3. Sampling Sites in the Marmara Sea