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Migration amd transformation of Organic Chemical Compounds n Polluted Turkmenistan Water Bodies

AID/CDR First Annual Report

D. Wynne & R. Parparova (Israel)
Viskrebentsev V.P. & Y.N. Fedorov
(Turkemenistan)

T18/96 May 1996

REPORTS

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AID/CDR Project No. TA-MOU-94-CA-13-005

"Migration and transformation of organic chemical compounds in polluted Turkmenistan water bodies."

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Abstract

The Gara-Gum canal, situated in Turkmenistan, is 1000 km long and supplies water to a large proportion of the population for domestic and agricultural purposes. Crops grown in the vicinity of the canal include cotton, wheat and grapes and there is a concomitantly high use of pesticides in these regions which may directly enter the canal. Moreover, several towns and cities along its route can contribute toxic chemicals to the canal waters. This problem may , therefore, pose a direct threat to human health.

During the period of this project covered by this report, we have completed the following tasks: i. The types and quantities of pesticides used in several areas along the Gara-Gum canal have been obtained, ii. analytical techniques for the determination of pesticides in water, soil and sediments have been evaluated for the actual field conditions encountered, iii. seasonal and spatial distributions of organochlorinated pesticide residues in the waters of the canal and in the soil in its vicinity have been determined; highest water concentrations were generally found in the spring (and summer) although a 60 fold range in levels between stations was observed, iv. by following the same body of water along the entire length of the canal, we noted that concentrations of several organochlorinated compounds dropped rapidly but then increased again at other stations.

In addition to the scientific accomplishments, noted above, the Turkmenistan Principal Investigators visited the Kinneret Limnological Laboratory at the beginning of the project to discuss plans for the sampling of the canal and to develop analytical techniques for the analysis of pesticide residues in the canal waters. Towards the end of the first year of the project, the Israeli PI's paid a reciprocal visit to the Center of Environmental Monitoring in Ashgabat, Turkmenistan. During this visit the Israeli PI's visited the Gara-Gum canal, near Ashgabat, and learnt first hand of some of the problems encountered in these analyses.

Introduction

Turkmenistan is situated in the southern Central Asian region of the former Soviet Union, adjacent to Iran and Afganistan (Fig. 1). The country, the capital of which is Ashgabat, is about 500,000 km^2 in area and has a population of approximately 4.5 million people. Turkmenistan became independent in 1991.

Much of the land in Turkmenistan appears to be desert. However, some regions have an agricultural potential which was not utilised, solely because of the lack of water. Consequently, the Gara-Gum canal was built to supply water to those areas of possible agricultural significance but where natural sources of water were scarce. Constructed in 1956, the Gara-Gum canal had returned building costs by 1962, mainly from the sale of water for agricultural purposes, although water has also been sold to some domestic users. Only 10% of the Gara-Gum canal water is used for industry.

The Gara-Gum canal , which is approximately 1000 km in length, is considered to be the longest canal built through desert-like regions. It takes water from the Amudarya river, at Chardzou, and supplies agricultural and domestic water to various cities and settlements en route to Hazanje, close to the Caspian Sea (Fig. 1). About 60% of the population of Turkmenistan now live in the vicinity of the canal; indeed some villages in the surrounding area have seen a two fold increase in size because of their proximity to the canal.

Cotton, melon and wheat are among the major crops grown in the region around the Gara-Gum canal, and, consequently, large amounts of different types of pesticides are used in this area (some of these pesticides and the quantities used in various regions along the Gara-Gum canal, are summarised in Table 1). Since this poses a potential direct or indirect danger to human health, the problem of pesticide residues in the canal is of utmost concern. This project is being carried out in order to investigate the problem in more detail and to propose recommendations to the Turkmenistan government to reduce, or eliminate, pollution in the canal.

[Note: The Amudarya river is not only a major source of water for the Gara-Gum canal but also for the Aral Sea, situated at the end of the river (Fig. 1). Flow of water into the canal might, therefore, have been thought to have contributed to the drying up of the Aral Sea. Only about 15% of the canal water comes from the river (the Gara-Gum canal also obtains water from agricultural run-off and from other rivers). Furthermore, the level of the Aral Sea began to drop only 5 years after operation of the canal. Scientists in Turkmenistan believe that these observations suggest that other causes, rather than the operation of the Gara-Gum canal, have contributed to the "Aral Sea crisis" and are beyond the scope of the current co-operative research project.].

Materials and Methods

Samples (1 liter of water; 10g $_{(dry\ weight)}$ of soil or sediment or 10g $_{(wet\ weight)}$ of biota) were extracted with an organic solvent (usually hexane), reduced in volume on a rotary evaporator and analysed by gas chromatography (GC). Polychlorinated biphenyl compounds (PCBs), which interfere with the analysis of organochlorinated pesticides, were dechlorinated with potassium hydroxide before injection into the GC.

GC analyses were carried out on a Sviet gas chromatograph, fitted with an electron capture detector (ECD) and 1-2m glass columns (0.2-0.4cm i.d.). Various column packings were used in this work, including 5% SE30 or XE60 on Chromatone N-AW-DCMS; mixtures of QF1, OV1 (or OV11 & OV17) and XE60 on Chromosorb W-HP, in order to obtain the best separation of the pesticide mixtures actually found in the canal and also to confirm the identities of the different peaks obtained. Standards of α-HCB, γ-HCB, Heptachlor, Heptachlor epoxide Aldrin, Dieldrin, n,n'-ddd; n,n'-dde; o,n-ddt and PCBs (Arochlors 1221, 1242, 1254, 1260 or their analogues) were used to quantitate the analytical results.

At the Kinneret Limnological Laboratory, GC analyses were also carried out on a Perkin-Elmer Turbocrome gas chromatograph, fitted with an ECD and a nitrogen-phosphorus specific detector (NPD). Glass capillary columns (30m; 0.32mm i.d.) with SE54 or AT1701 liquid phases (both

obtained from Alltech, Inc.) were used to separate and quantitate the pesticide residues detected. In addition to the extraction of organochlorinated compounds with hexane, organophosphorus and organonitrogen compounds were extracted from samples with dichloromethane.

Acknowledgements

We thank Prof. Boris Shteinman for preparation of the figures used in this report.

Results and Discussion.

Seasonal and spatial distribution of organochlorinated pesticide concentrations in the Gara-Gum canal.

Samples were taken at regular intervals from different places in the Gara-Gum canal and analysed for organochlorine pesticides as described above. Both seasonal and geographical differences in pesticide concentrations were observed (Table 2). Highest pesticide concentrations were generally found during spring (and sometimes stretching into summer). A 50-60 fold range in concentrations was noted between stations. For example, concentrations of both α-and γ-HCB at Zachmet, Mary and Dushak were about 0.01μg l^{-1} ; whereas at Kodj, water concentrations of α-HCB and γ-HCB reached 0.6 and 0.2μg l^{-1}, respectively.

The above results probably reflect the types of pesticides used and the crops grown at the sites sampled. The soil types and agricultural products grown, along the Gara-Gum canal, together with the pesticide concentrations in soil are shown in Fig 2a-d. A large range in soil types, with concomitant differences in crops grown and types and quantities of pesticides used, were noted. However, for certain compounds, the soil:water ratios were constant, even though there were changes in the absolute concentrations found at these sites (Table 3.). Furthermore, although DDT (and DDE, to a lesser extent) levels in soil were quite high, the concentration of these chemicals in water, at the same sites, were below the limit of detection. These results suggest that at least some of the toxic chemicals found in soil will not be released into the surrounding aquatic environment when the soil particles reach the canal waters.

Transformation of toxic agricultural products in the Gara-Gum canal.

In order to obtain preliminary information on the possible decomposition and/or transformation of chemicals in the Gara-Gum canal, a major sampling was carried out as follows: Samples were taken at the regular sampling site (Halounoe) where the Amudarya river enters the canal, then the same body of water was followed the approximate 1000km to Gazanjik. The regular 9 water sampling stations, as well as 3 reservoirs, were sampled and analysed for organochlorine pesticides as well as a number of other parameters, such as oxygen content, BOD & COD and petroleum content. Temperature and water velocity were also measured at each sampling site. The results are summarised in Table 4. We observed little change in water temperature (averaging 22.9°C) and water velocity (averaging 0.5 m s^{-1}) along the canal, although water flow tended to be higher at the beginning of the canal. However, several places showed peaks in pesticide concentrations. For example, γ-HCB concentrations were high at the beginning of the canal, then dropped only to rise again around the cities of Kaaka and Ashgabat; DDE (a breakdown product of DDT) levels peaked at the Kopetdag station (Fig 3). These data suggest that there was an input of such chemicals into the water at these places, a supposition supported by the increases of organic matter (as measured by the changes in COD) at the different stations (Fig 4). It should be noted, however, that the COD measurements are at least three orders of magnitude higher than the pesticide concentrations, suggesting that large amounts of other organic compounds, much of which is not biologically available, enter the canal at various points along its route.

Visits of Turkmenistani and Israeli Principal Investigators

The Turkmenistan PI's visited the Kinneret Limnological Laboratory at the beginning of the project to discuss work plans for the project. The possibility of using a new Perkin Elmer Gas Chromatograph, situated at the Kinneret Limnological Laboratory, in the study, was also considered. Later in the project the Israeli PI's visited Turkmenistan. They were taken round the laboratory in Ashgebat and were shown part of the Gara-Gum canal as it flows from the city towards the Kopetdag reservoir. In addition, data to be incorporated into the first yearly report to

AID was discussed and first hand information on the canal was obtained during this visit. Dried sediment samples from part of the canal and from several reservoirs were collected and taken back to Israel for comparative analysis, using the standard procedures for such materials employed at the Kinneret Limnological Laboratory. After visiting the CEM laboratory, possible problems in the analysis of pesticide residues were evaluated and various supplies and standards were arranged to be sent to Turkmenistan so that this work could be continued.

Proposed work plan for the second year.

1. Monitoring of the Gara-Gum canal, and the surrounding agricultural areas, will be continued in order to follow the multi-annual patterns of pesticide residues in such samples. Within the framework of this monitoring program, the laboratories in both Turkmenistan and in Israel will continue to develop methods to broaden the range of chemicals that can be analysed.

2. Inter-laboratory calibration studies will be carried out between both laboratories to compare methods developed in each country.

3. The influence of pesticides in use in the Gara-Gum region on the biota, and the possible biotransformations of these chemicals, will be studied. Initial studies will focus on the role of phytoplankton in these processes. Canal water will be exposed to low levels of selected chemicals and changes in chemical parameters followed. Subsamples will be brought to Israel for evaluation of any biological changes that might have occurred. In parallel, similar work will be carried out at the Kinneret Limnological Laboratory and the results of both studies compared.

4. Reports on our findings will be written and part of the data obtained so far will be prepared for presentation at an international conference on water quality to be held in Israel at the end of 1996 and for subsequent publication.

Table 1. Types and quantities of pesticides used at various sites along the Gara-Gum canal.

	Site		
	Chardgev	Mary	Ahal
Pesticide	Active ingredient (tons y^{-1})		
Lindane (HCB)*	0.35	1.73	3.07
Femidophos	1.44	1.22	2.53
Chlorafos	4.02		
Phosalon	11.14		1.56
Thiodan*	0.94	0.50	
Carbaphos		0.83	2.11
Anthio		0.91	
Phosphamid			7.88

* organochlorinated compounds

Table 2. Seasonal and spatial distribution of organochlorinated pesticide concentrations ($\mu g\ l^{-1}$) in the Gara-Gum canal.

Pesticide	Season											
	Winter			Spring			Summer			Autumn		
	min	mid	max	min	mid	max	min	mid	max	min	mid	max
Holovnoe												
α-HCB	0	0.04	0.09	0	0.159	0.161	0	0.101	0.225	0	0.047	0.082
γ-HCB	0	0.02	0.04	0	0.126	0.15	0	0.065	0.155	0	0.027	0.049
Heptachlor	-	-	0.06	0	0.045	0.069	-	-	0.012	-	-	-
Zachmet												
α-HCB	0	0.006	0.008	0	0.009	0.015	0	0.005	0.010	-	-	-
γ-HCB	0	0.005	0.005	0	0.007	0.009	-	-	-	-	-	-
Heptachlor	-	-	-	0	0.015	0.022	-	-	-	-	-	-
Mary												
α-HCB	0	0.007	0.014	0	0.005	0.007	0	0.025	0.046	-	-	-
γ-HCB	0	0.004	0.005	-	-	0.005	0	0.016	0.023	-	-	-
β-HCB	-	-	-	-	-	-	-	0.009	-	-	-	-
Heptachlor	-	-	0.012	0	0.020	0.032	-	-	0.039	-	-	-
Dushak												
α-HCB	0	0.005	0.008	0	0.007	0.012	-	-	0.010	-	-	-
γ-HCB	-	-	0.005	0	0.007	0.008	-	-	-	-	-	-
Heptachlor	-	-	-	0	0.014	0.020	-	-	-	-	-	-

Table 2., contd

Pesticide	Season											
	Winter			Spring			Summer			Autumn		
	min	mid	max	min	mid	max	min	mid	max	min	mid	max
Kaaka												
α-HCB	0	0.005	0.007	0	0.008	0.013	-	-	0.010	-	-	-
γ-HCB	-	-	0.004	0	0.006	0.008	-	-	-	-	-	-
Heptachlor	-	-	-	0	0.021	0.035	-	-	-	-	-	-
Ashgabat												
α-HCB	0	0.005	0.008	0	0.009	0.019	0	0.035	0.057	-	-	-
γ-HCB	-	-	0.003	-	-	0.013	-	-	-	-	-	-
DDE	-	-	-	0	0.009	0.013	-	-	0.005	-	-	-
Kopetdag												
α-HCB	0	0.007	0.012	0	0.003	0.004	0	0.050	0.060	0	0.007	0.012
γ-HCB	0	0.003	0.005	-	-	0.004	-	-	0.015	-	-	0.005
β-HCB	-	-	0.004	-	-	-	-	-	0.011	-	-	0.018
DDD	-	-	-	-	-	-	-	-	-	-	-	0.193
Heptachlor	-	-	-	-	-	0.087	-	-	0.021	-	-	-
Kodj												
α-HCB	0	0.023	0.053	0	0.166	0.568	0	0.183	0.615	-	-	0.014
γ-HCB	0	0.014	0.032	0	0.124	0.136	0	0.092	0.174	-	-	-
β-HCB	-	-	0.006	-	-	-	-	-	0.017	-	-	-
DDE	-	-	-	-	-	-	-	-	0.111	-	-	-

Table 2., contd

Pesticide	Season											
	Winter			Spring			Summer			Autumn		
	min	mid	max	min	mid	max	min	mid	max	min	mid	max
Gazangik												
α-HCB	-	-	0.044	-	-	0.173	-	-	0.098	-	-	0.011
γ-HCB	-	-	0.016	-	-	0.085	-	-	0.060	-	-	-
β-HCB	-	-	-	-	-	-	-	-	0.010	-	-	-
DDE	-	-	-	-	-	-	-	-	0.051	-	-	-
Hanhovus reservoir												
α-HCB	-	-	-	0	0.011	0.021	-	-	0.145	-	-	-
γ-HCB	-	-	0.007	0	0.013	0.022	-	-	0.020	-	-	-
β-HCB	-	-	-	0	0.008	0.009	-	-	-	-	-	-
Heptachlor	-	-	-	-	-	0.016	-	-	-	-	-	-
Kopetdag reservoir												
α-HCB	-	-	0.005	-	-	-	-	-	-	-	-	-
γ-HCB	-	-	-	-	-	-	-	-	0.009	-	-	0.004

Table 3. Ratio between soil and water concentrations of several pesticides, at various sites along the Gara-Gum canal*.

Station	Pesticide			
	α-HCB	γ-HCB	DDE	DDT
Halovnoe	0.0012; 0.006 0.20	0.0006; 0.017 0.035		
Mary	0.0016; 0.008 0.20	0.0009; 0 -	0.0029; 0 -	
Dushak	0.0013; 0.007 0.19	0.001; 0 -	0.0048; 0 -	0.0084; 0 -
Ashgabat	0.0019; 0.007 0.27	0.0015; 0.023 0.065	0.0084; 0.07 0.49	0.0076; 0 -
Hazularbat	0.0004; 0.014 0.28	0.0005; 0.009 0.06	0.0043; 0.001 4.3	

*Values are given for the concentration of various pesticides in soil (mg kg^{-1}) and in water (μg l^{-1}) with the soil/water ratio ($x10^{-3}$) under each pair, where applicable.

Table 4. Changes in pesticide concentrations ($\mu g\ l^{-1}$), and other parameters, in a body of water flowing along the Gara-Gum canal.

Station	Date & time	T (°C)	Pesticide concentrations ($\mu g\ l^{-1}$) α-HCB	γ-HCB	β-HCB	DDT	DDD	DDE	O_2	BOD_5	COD	Oil	Water flow
									($mg\ l^{-1}$)				($m\ s^{-1}$)
Halounoe	24.08 10:00	22.2	0.006	0.017	0	0	0	0	7.85	0.93	17.3	0.256	0.7
Zahmet	31.08 06:00	23.4	0.009	0.007	0	0	0.006	0	7.45	1.09	9	0.256	0.56
Mary	02.09 22:00	25	0.008	0	0	0	0	0	7.5	0.83	13.5	0.113	0.56
Dushak	07.09 05:00	23.2	0.007	0	0	0	0.001	0	7.6	1.01	15.4	0.121	0.53
Kaaka	08.09 04:00	23.1	0.011	0.017	0	0	0	0.002	7.63	0.73	19.2	0.201	0.53
Ashgabat	11.09 09:00	22.9	0.007	0.023	0	0	0	0.007	8.15	1.17	13.1	0.166	0.54
Kopetdag	12.09 14:00	22.4	0.002	0.004	0.018	0	0	0.007	8.1	1.19	18.9	0.166	0.52
Kodj	16.09 17:00	22	0.042	0.026	0.018	0	0	0.005	8.2	1.06	14.9	0.096	0.33
Gazanjik	17.09 19:00	21.8	0.014	0.009	0.007	0	0	0.001	8.08	1.32	15.9	0.106	0.33

Table 4, contd

Station	Date & time	T (°C)	Pesticide concentrations ($\mu g\ l^{-1}$) α-HCB	γ-HCB	β-HCB	DDT	DDD	DDE	O_2	BOD_5	COD	Oil	Velocity ($m\ s^{-1}$)
									($mg\ l^{-1}$)				
Zeidskoe	25.08 11:00	23	0.001	0	0	0	0	0	8.85	1.3	10.7	0.038	
Hanhovuz	04.09 08:00	22.8	0.004	0.001	0	0	0	0	9.8	1.6	27.9	0.189	
Kopetdag-Skoe	11.09 16:00	22.6	0.003	0	0	0	0	0	7.81	1.06	9.3	0.063	

Figure Legends

Fig. 1. Map of Turkmenistan, showing neighbouring countries and the location of the Gara-Gum canal.

Fig. 2a-d. Soil type & pesticide concentrations, and crops grown along the Gara-Gum canal. [Pesticide residues: 1 = α-HCB; 2 = γ-HCB; 3 = β-HCB; 4 = DDE; 5 = DDT]

Fig. 3. Changes in water concentrations ($\mu g\ l^{-1}$) of DDE, α- & γ-HCB in a single water body followed along the Gara-Gum canal. [Station Nos.: 1 = Halounoe; 2 = Zahmet; 3 = Mary; 4 = Dushak; 5 = Kaaka; 6 = Ashgabat; 7 = Kopetdag; 8 = Kodj; 9 = Gazanjik].

Fig. 4. Changes in several chemical parameters in a single water body followed along the Gara-gum canal. Upper panel: BOD_5 and oil production ($mg\ l^{-1}$); Lower panel: COD ($mg\ l^{-1}$). [Station Nos as given in Fig. 3].

List of Tables and Figures.

Tables.

1. Types and quantities of pesticides used along the Gara-Gum canal.

2. Seasonal and spatial distribution of organochlorine pesticides in the Gara-Gum canal.

3. Ratio between soil and water concentrations of several pesticides along the Gara-Gum canal.

4. Changes in pesticide concentrations and other parameters, in a body of water flowing along the Gara-Gum canal.

Figures.

1. Map of Turkmenistan.

2. Soil type & pesticide concentrations, and crops grown along the Gara-Gum canal.

3. Changes in water concentrations of DDE, α- & γ-HCB in a single water body followed along the Gara-Gum canal.

4. Changes in BOD_5, oil production and COD in a single water body followed along the Gara-Gum canal.

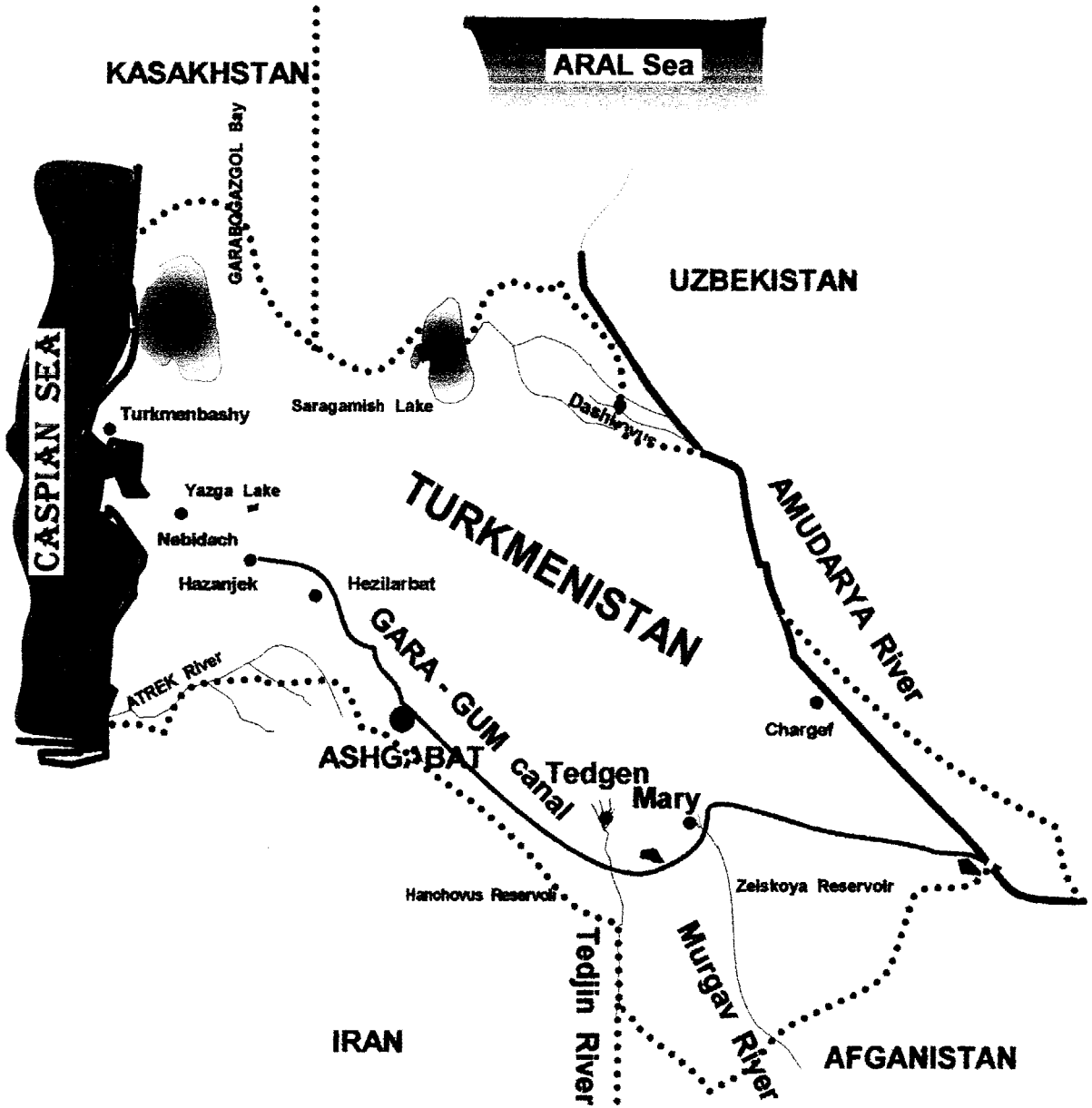
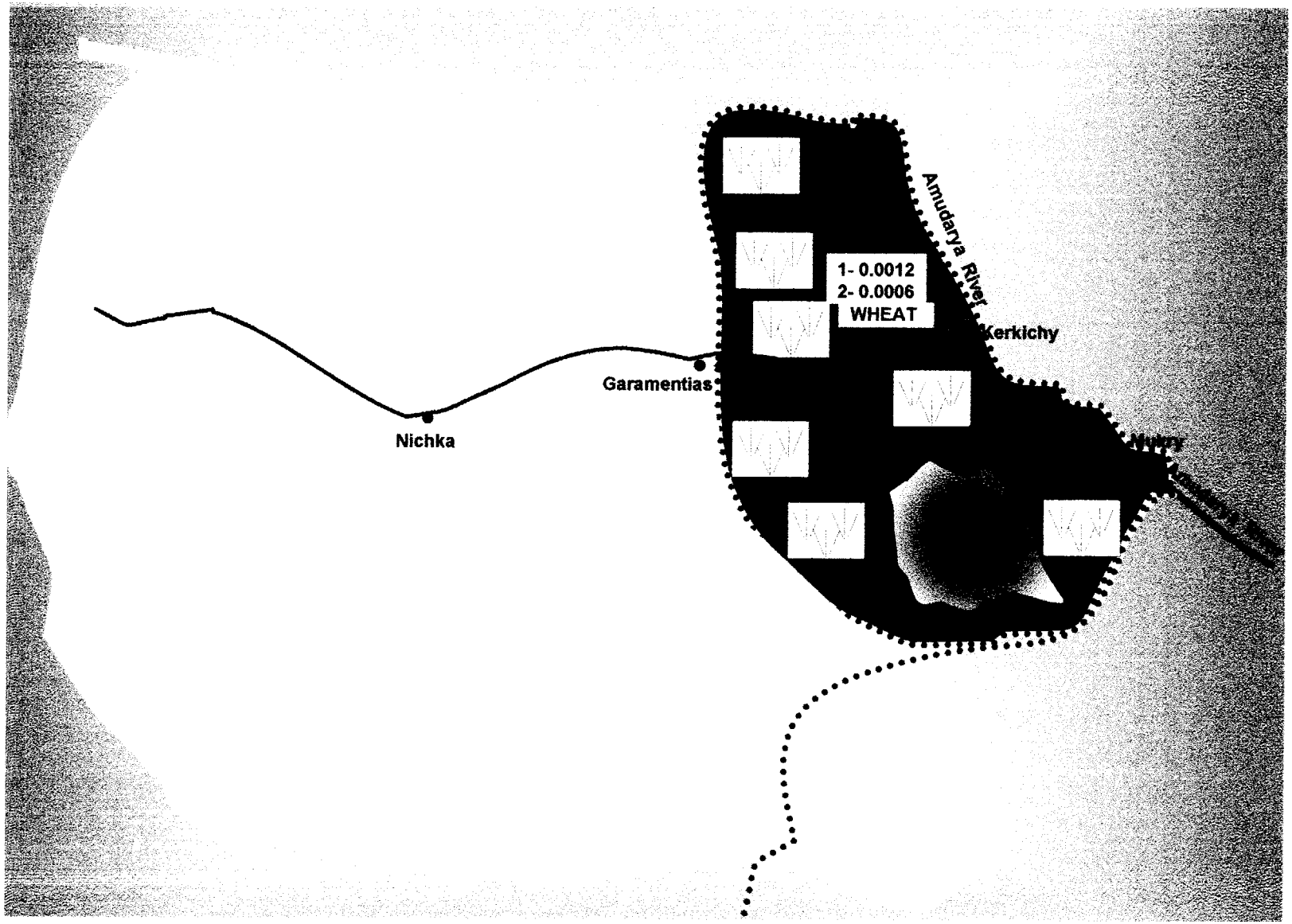

KASAKHSTAN
ARAL Sea
GARABOGAZGOL Bay
CASPIAN SEA
UZBEKISTAN
Turkmenbashy
Saragamish Lake
Dashkyuz
Yazga Lake
TURKMENISTAN
AMUDARYA River
Nebidach
Hazanjek
Hezilarbat
GARA - GUM canal
ATREK River
Chargef
ASHGABAT
Tedgen
Mary
Zelskoya Reservoir
Hanchovus Reservoir
Tedjin River
Murgav River
IRAN
AFGANISTAN

FIG. 1


1- 0.0012
2- 0.0006
WHEAT
Amudarya River
Kerkichy
Garamentias
Nichka

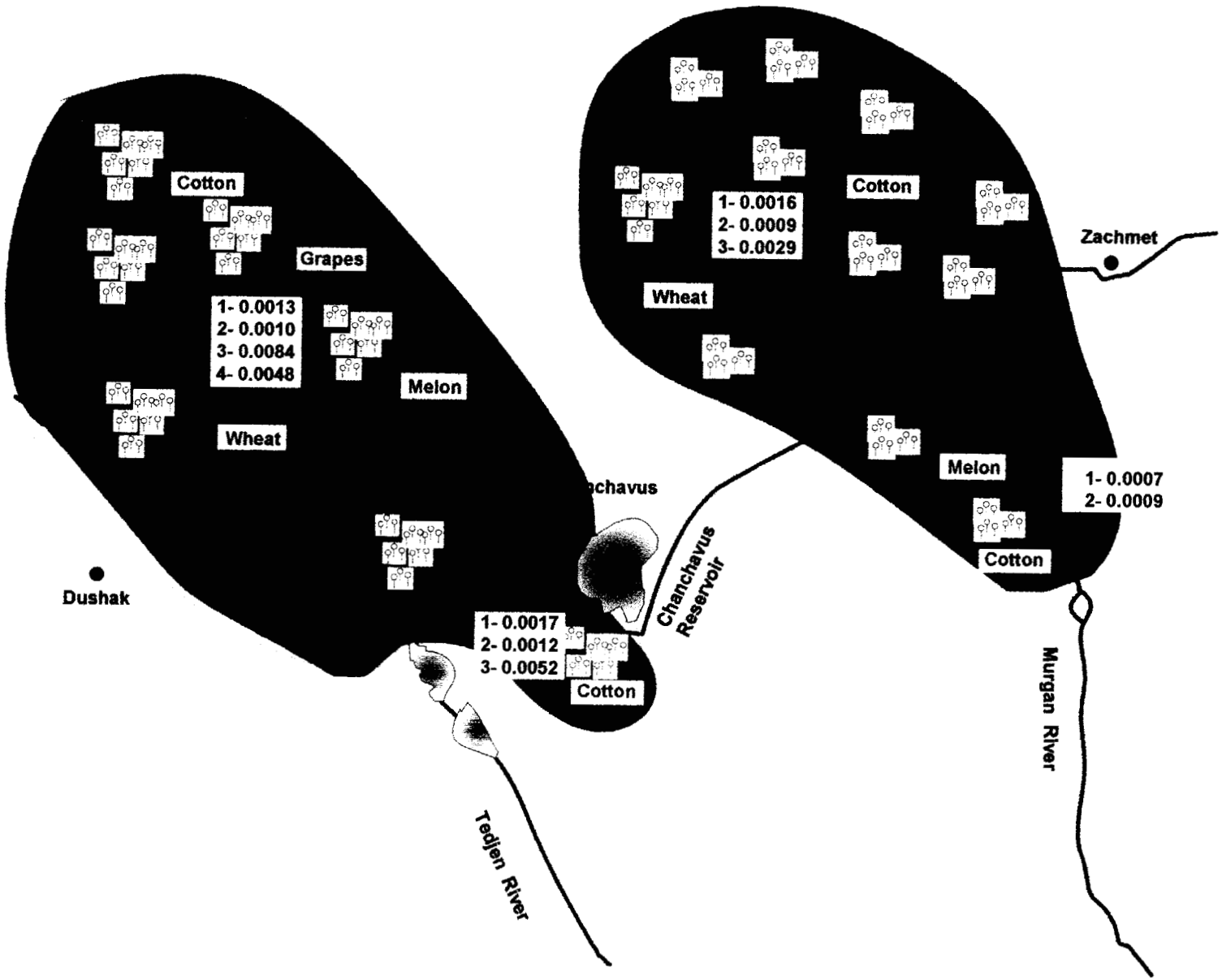

Cotton
Grapes
1- 0.0013
2- 0.0010
3- 0.0084
4- 0.0048
Melon
Wheat
Dushak
1- 0.0017
2- 0.0012
3- 0.0052
Cotton
Chanchavus Reservoir
Tedjen River
1- 0.0016
2- 0.0009
3- 0.0029
Cotton
Wheat
Zachmet
Melon
1- 0.0007
2- 0.0009
Cotton
Murgan River

FIG. 2B

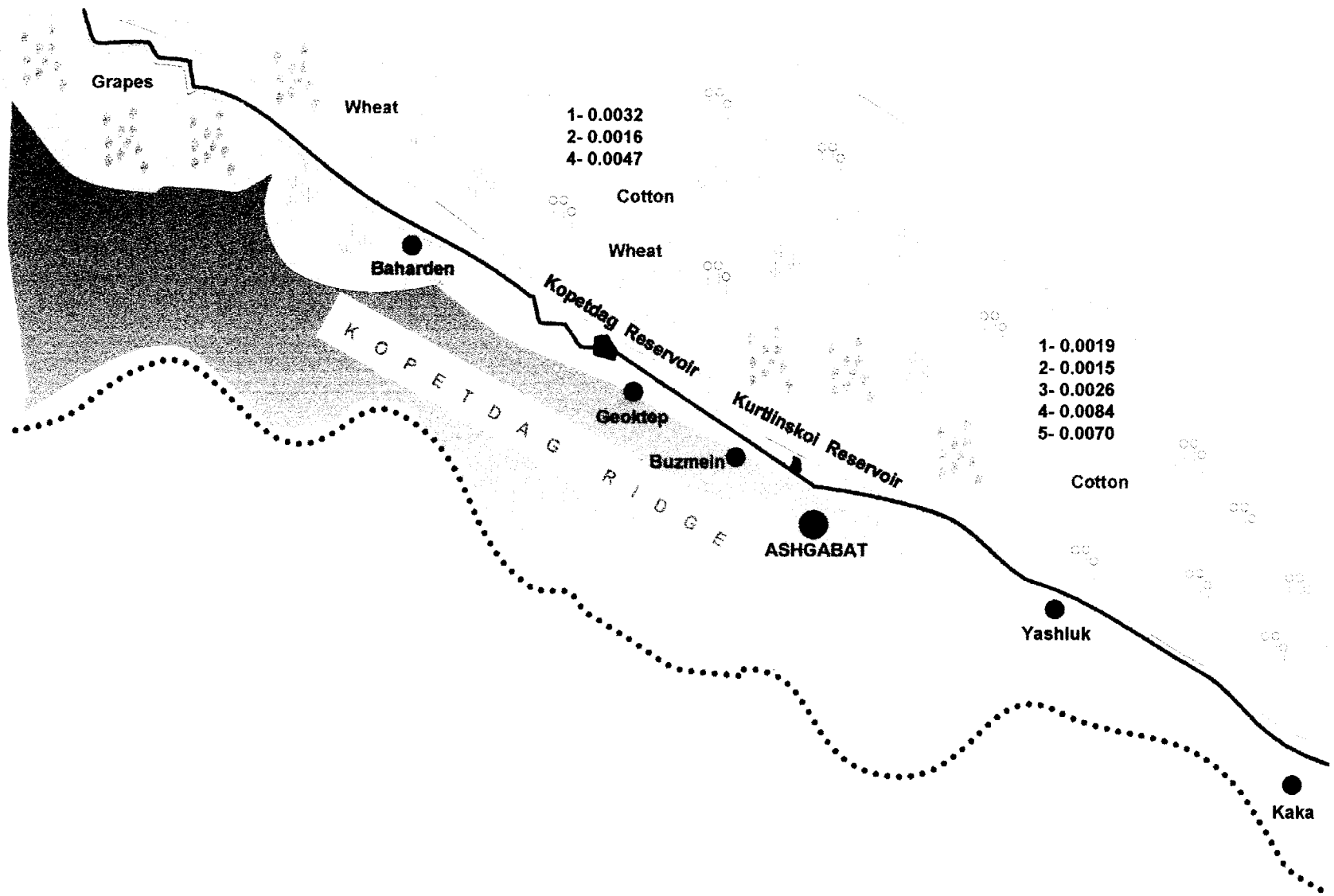

Grapes
Wheat
1- 0.0032
2- 0.0016
4- 0.0047
Cotton
Wheat
Baharden
Kopetdag Reservoir
Kurdinskoi Reservoir
K O P E T D A G R I D G E
Geoktep
Buzmein
ASHGABAT
1- 0.0019
2- 0.0015
3- 0.0026
4- 0.0084
5- 0.0070
Cotton
Yashluk
Kaka

FIG. 2C

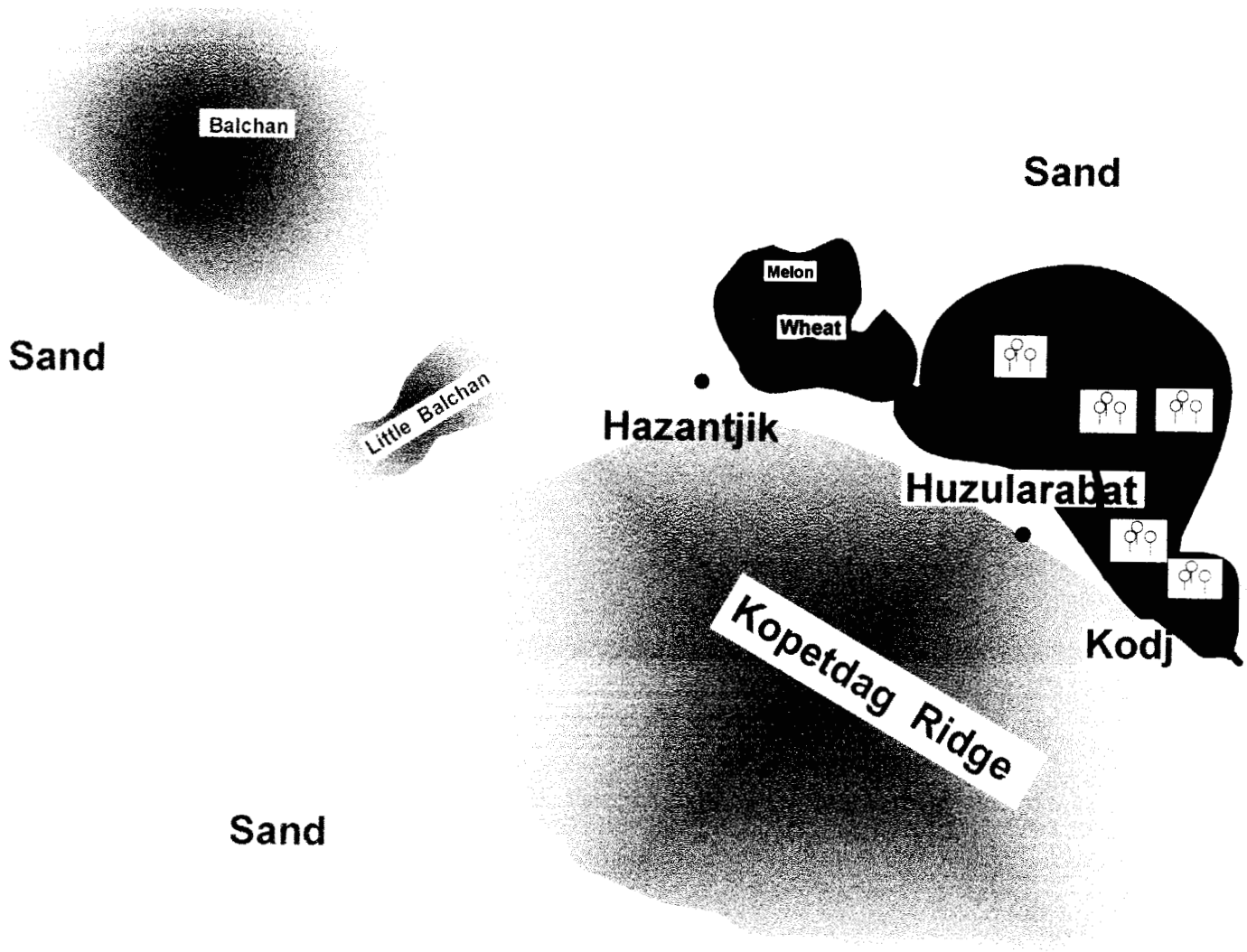

Balchan
Sand
Little Balchan
Melon
Wheat
Sand
Hazantjik
Huzularabat
Kodj
Kopetdag Ridge
Sand

FIG. 2D

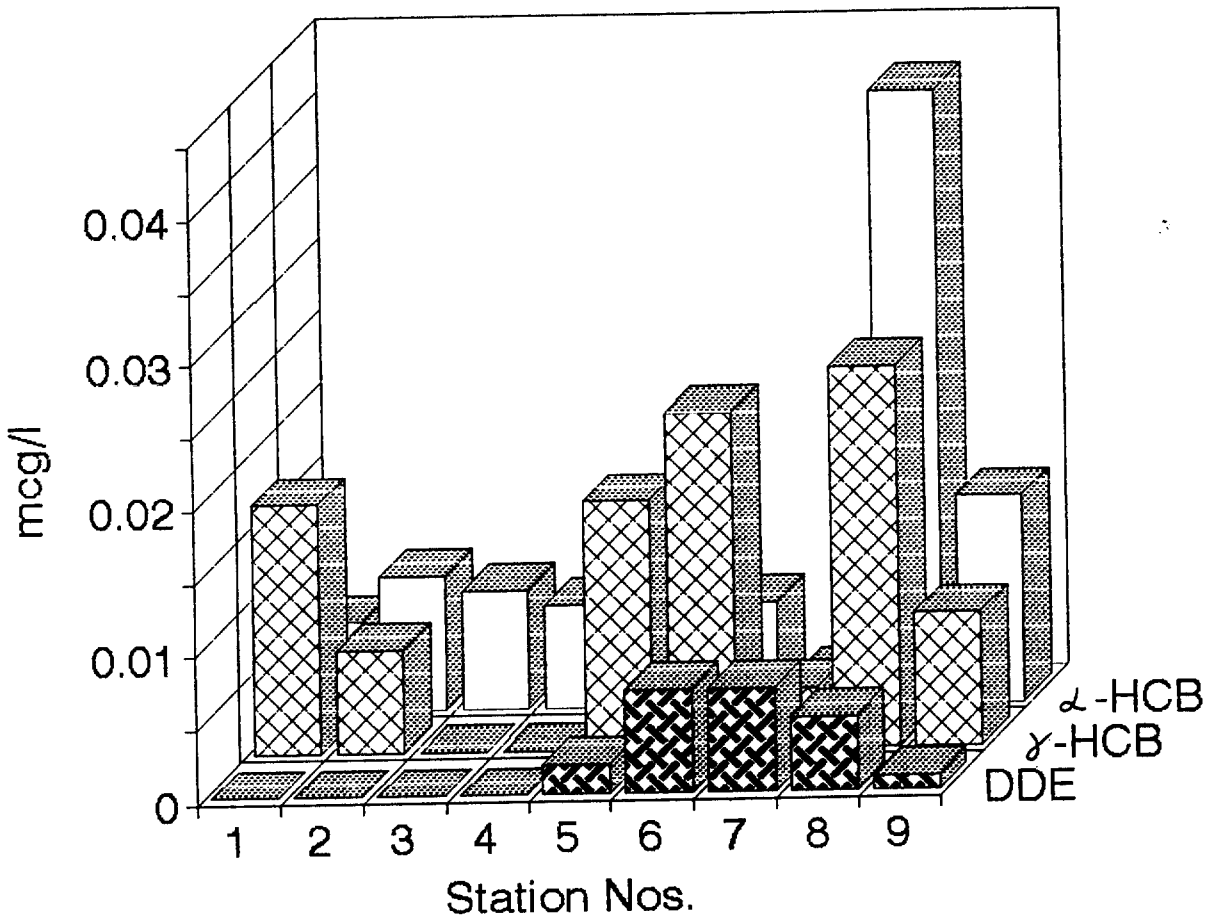
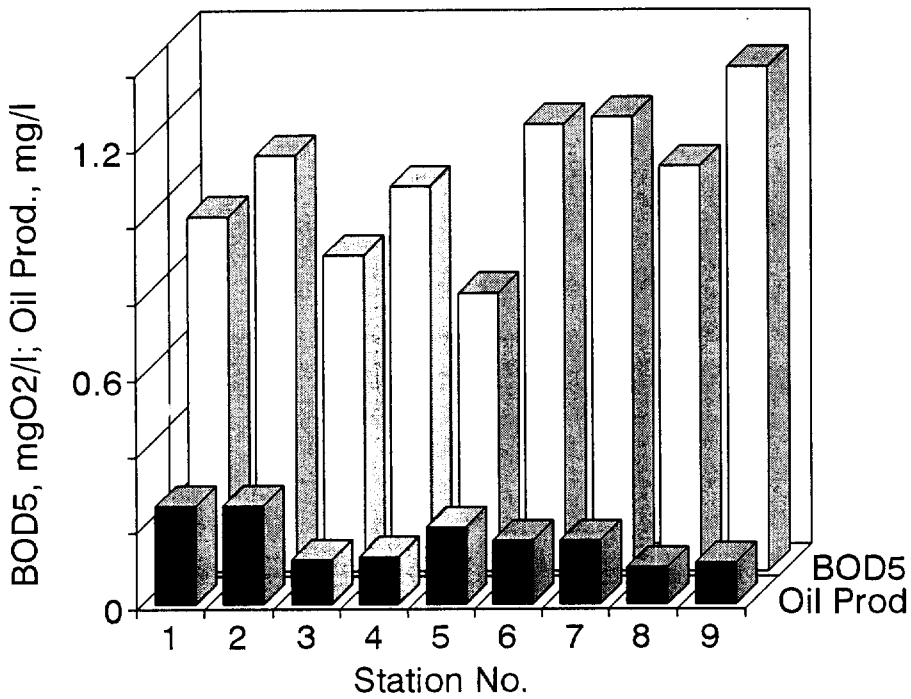


FIG. 3


BOD5, mgO2/l; Oil Prod., mg/l
1.2
0.6
0
1 2 3 4 5 6 7 8 9
Station No.
BOD5
Oil Prod

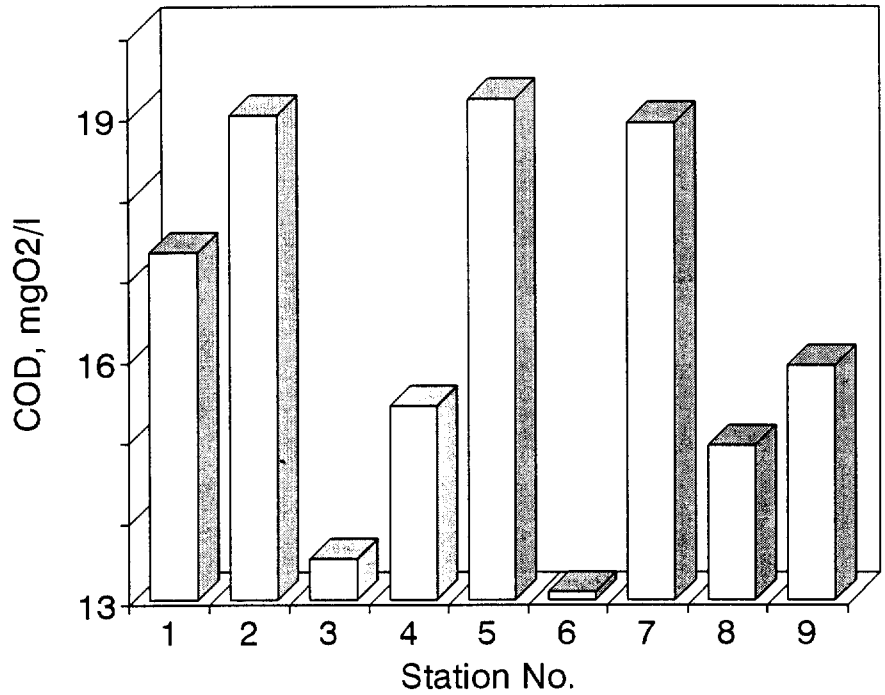

COD, mgO2/l
19
16
13
1 2 3 4 5 6 7 8 9
Station No.

FIG. 4