EFFECTS OF OIL DRILLING ACTIVITIES ON Ba CONCENTRATIONS IN SUPERFICIAL SEDIMENTS FROM THE BLACK SEA ROMANIAN SHELF*

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Abstract: Graphical and mathematical analyses of analytical data for $CaCO_3$, Fe_2O_3, MnO and Ba concentrations in sediments from Black Sea continental shelf have identified a 30% increase of Ba mean concentration in superficial sediments attributable to oil exploratory and productive wells drillings. A 35000 km^2 surface is affected by drilling mud discharges. The normal Ba mean concentration in this zone has increased with ≈ 90%.

Key words: Black Sea, continental shelf, oil exploration, drilling mud, sediments, Ba concentration

Both Romanians and Ukrainians have intensively drilled exploratory wells for oil and gases on the Black Sea north-western continental shelf.

The Romanian oil explorations on the Black Sea continental shelf have begun in 1977 when the drilling platform "Gloria" became operational. They increased steadily over the years until 1987, when the same "Gloria" became the first Romanian oil extraction platform, and maintained at a high level until 1992. After this year the oil explorations decreased gradually, at the present most of the platforms on the Black Sea Romanian shelf being used solely for extraction. Such extensive activities have undoubtedly greatly affected the benthic environment.

Although barium is not a toxic element for the marine environment (the 96-hour LC_{50} of barite is >100000 μg/g – UNEP, 1986), its extensive use as an weighting agent in drilling muds makes it a sensitive tracer for drilling discharges and determined its selection for the assessment of the extent of influences exerted by oil exploration activities on the sea bottom in the Romanian sector of the Black Sea. Ba concentrations, together with some other components including those exerting the main controls on trace elements concentrations in sediments (Fe_2O_3, $CaCO_3$, MnO and since 1994 – TOC) were systematically investigated since 1991 as part of the GEOECOMAR geoecological monitoring programme of the Black Sea Romanian shelf.

The usual sampling pattern utilised during the period 1991-1994 consisted in three transects with a rough W to E orientation:

– south of St. Gheorghe – from 12.5 to 71 m water depth,

– E Constantza – from 20 to 50 m depth,

– E Mangalia – from 19.5 to 66 m depth.

and a submeridional transect, approximately following the shore line at water depths varying between 34.5 and 54.5 m.

In 1991, 41 sampling stations were performed along these transects. They were kept as a basis for the next years but the total number of sampling stations was increased to 63 in 1992 and kept at this value for the next years.

Sediment samples were extracted from each station with a Van Veen box-grab; two subsamples were usually taken from each primary sediment sample, one from the superficial layer (0-1 cm – Level I) and one from 10-12 cm depth in sediment (Level II). At the central laboratory the subsamples were grounded, sieved until the entire quantity of material passed through a 0.063 mm mesh sieve and analysed by wavelength dispersive X ray fluorescence spectrometry on a VRA 30 sequential spectrometer. Calibration and quality control were done using a series of SRM's kindly supplied by US Geological Survey, NIST – USA, National Research Council of Canada and MEL – Monaco.

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Analyses for calcium carbonate and total organic carbon were done by volumetric methods (Black, 1965; Gaudette et al., 1974).

Although the number of stations performed each year differed the obtained results were directly comparable and led to some interesting conclusion regarding Ba distribution in superficial sediments.

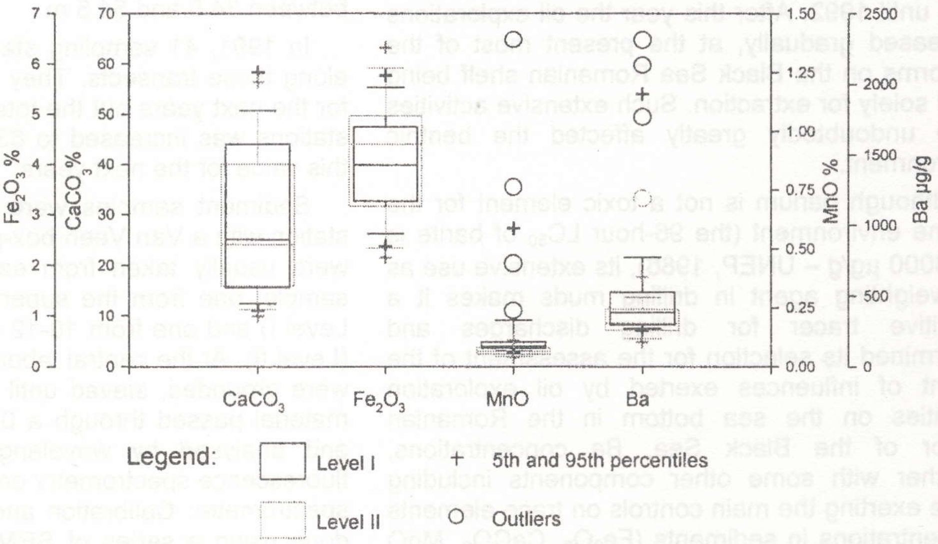
A graphical analysis of the 1991 data (Fig. 1) indicated almost identical distributions in the two sampling levels for $CaCO_3$ and Fe_2O_3, with numerous similarities (see also Table 1). The skewness (b_1) and kurtosis (b_2) values (Table I) allow the acceptance of all component distributions as gaussian and no outliers were signalled for both components, in either level. At the same time a *t* approximate test (Möller, 1979) demonstrates the statistically significant identity of the sampling level mean concentrations for both components. The only greater differences are a slightly higher concentration for $CaCO_3$ upper quartile in Level I and a greater median concentration for Fe_2O_3 in Level II.

values in Level I, the upper quartile concentrations of component distributions in Level II being close to the median concentrations in Level I. The presence of outliers concentrations is characteristic for Level I, although one Ba outlier and one Ba suspected outlier appear in Level II also (Fig. 1).

Because of the presence of outliers both component distributions in Level I and Ba distribution in Level II cannot be accepted either as gaussian (normal) or lognormal. The *t* approximate test indicate a statistically significant difference between the mean component concentrations in the two levels (Table I).

These differences between sampling levels become even more evident after eliminating outliers and recalculating the statistical parameters. Although Ba distribution in Level II may now be accepted as gaussian, analogous to those of major components in both levels, both MnO and Ba distributions in Level I remain different and may be accepted only as lognormal. The component mean concentrations in Level I are approximately 31% higher than those in Level II

Figure 1. Box plots of $CaCO_3$, Fe_2O_3, MnO and Ba concentrations



All the similarities recorded between the distributions of the two major components demonstrate, as expected, the constancy of the sedimentary regime over the relatively short time interval represented by 10 centimetres of sediment.

On the contrary, the distributions of MnO and Ba in the sampling levels differ significantly. They are displaced towards much higher concentration

and the statistical difference between level mean concentrations increases.

Such important variance, especially after eliminating outliers, can not be explained by the previously demonstrated constancy of the sedimentary regimen and some other processes must be involved in controlling the MnO and Ba concentrations in the superficial layer of sediment.

The explanation for MnO behaviour is simple. The post depositional mobilisation of manganese in reducing conditions, its upward migration and enrichment in oxidising sediments, sometimes as manganese nodules and micronodules, are well known and documented (Lynn and Bonatti, 1965; Manheim, 1965; Bonatti *et al.*, 1971; and others). The Black Sea shelf sediments, with high organic carbon contents and an oxidising layer usually 1 to 2 cm thick offer ideal conditions for these processes, the manganese enrichment taking place preferentially at the sediment-water interface.

The Ba problem is not so readily explainable. The close proximity of the signalled anomalous Ba concentrations (outliers) to oil exploratory drilling locations immediately suggests the drilling mud discharges as a possible source for the excess Ba in superficial sediments. However, before attributing the excess Ba to this source some other enriching possibilities must be examined.

Table 1. Statistical parameters of $CaCO_3$, Fe_2O_3, MnO and Ba distributions in sediments from the Black sea Romanian shelf ($CaCO_3$, Fe_2O_3 and MnO concentrations in %; Ba concentration in μ/g)

Level	Parameter	$CaCO_3$	Fe_2O_3	MnO	Ba	MnO corrected	Ba corrected
Level I 0–1 cm	n	41	41	41	41	37	38
	X_{min}	10.67	1.90	0.053	253	0.053	253
	X_{max}	64.40	5.79	1.389	2302	0.168	773
	$\overline{X}$	29.666	3.994	0.1494	530.68	0.0890	409.47
	s	15.4605	1.0247	0.2323	463.45	0.0227	148.51
	M_d	25.13	3.99	0.086	380	0.084	369
	$C_v\%$	52.12	25.66	155.52	87.33	25.5	36.27
	b_1	0.560	0.031	4.340	2.867	1.319	1.045
	b_2	2.098	2.211	22.086	10.408	5.589	3.169
Level II 10–12 cm	n	39	39	39	39	No outliers were detected for MnO in Level II	37
	X_{min}	9.71	1.98	0.034	170		170
	X_{max}	61.26	6.40	0.112	1178		524
	$\overline{X}$	27.621	4.210	0.0675	344.72		312.03
	s	14.7801	1.2199	0.0216	175.74		91.00
	M_d	24.08	4.41	0.064	307		295
	C_v	53.51	28.98	31.99	50.98		29.16
	b_1	0.720	-0.083	0.592	3.025		0.539
	b_2	2.431	2.207	2.379	14.408		2.743
	$t_{v, calc}$	0.605	0.855	2.247	2.395	4.225	3.436
	$t_{v, theor}$ ($\alpha/2=0.025$)	1.990	1.993	2.020	2.007	1.993	1.999

The most probable alternative is the associated MnO enrichment of the superficial layer, especially so since its relative value is extremely close to that of Ba enrichment. Manganese hydrous oxides have a high affinity for Ba. Calvert (1976) signalled Ba concentrations varying between 2500 and 3000 μg/g, in manganese nodules and crusts from various shallow marine environments. Similar concentrations – 3000-3600 μg/g – were recorded for manganese nodules from Black Sea shelf (Secrieru, unpublished data). Taking into account that Black Sea manganese nodules contain 20 - 25% MnO (Secrieru, unpublished data) and considering all Ba from nodules retained by manganese hydrous oxides, the MnO mean absolute enrichment of the superficial layer for uncorrected data (0.082%) can account for a mean Ba enrichment of 15 μg/g at the most, which is very far from the almost 100 μg/g absolute enrichment recorded for corrected Ba concentrations. Even the highest MnO concentrations locally recorded in superficial sediments belonging to the *Modiolus* mud type (≈1.5% MnO), where the presence of adequate surfaces (*Modiolus* shells) favours manganese reprecipitation as crusts or nodules can not account for a Ba enrichment greater than 250 μg/g, a value extremely far from values up to 2000 μg/g excess Ba met in the vicinity of drilling locations. Besides, although manganese enriched sediments are also enriched in Ba, such manganese enrichments do not coincide with the highest Ba concentrations.

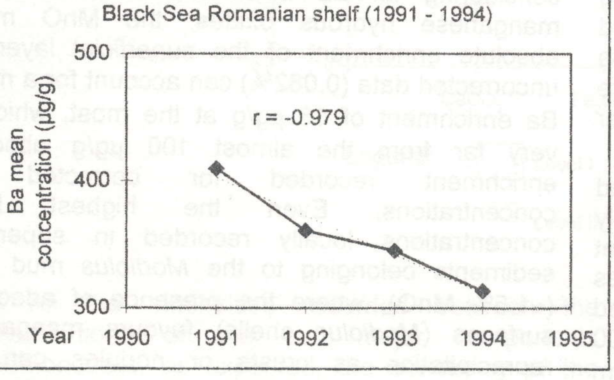
These considerations completely eliminate the possible relationship between manganese and Ba enrichments of the superficial sediments, the only remaining source of excess Ba remaining the discharges of drilling mud in the marine environment. The presence of two anomalous Ba concentrations in the deeper sediment layer (Level II) is explained by the earlier beginning of oil exploration activities compared with the beginning of the monitoring programme and is in concordance with the local sedimentary rates (0.5 - 1 cm/year) (PECO/EROS-2000, 1997).

Similar results were obtained for the 1992 - 1994 period (relative enrichments of 21% – 1992; 32% – 1993; 35% – 1994). Excepting the 1992 value, the others are close enough to conclude that the drilling activities on the Black Sea shelf are responsible for a relative Ba enrichment of the superficial layer of sediment of at least 30%, excluding the obviously anomalous values from calculations.

The analytical variability, the extremely high sedimentary variability characteristic to Black Sea shelf and the inherent errors in ensuring a high reproducibility to the positioning of the ship in sampling stations induced some variation of results. Nevertheless, a small but significant decrease of Ba mean concentration (no outliers included) in Level I was detected (Fig. 2).

Although no previous data concerning Ba concentrations were available, the coincidence of the decrease with the beginning of drilling activities decline suggests as cause of the process the quantitative decrease of drilling mud discharge and its progressive dilution with uncontaminated sedimentary material.

Figure 2. Time variation of Ba mean concentrations in superficial sediments from Black Sea Romanian shelf (1991 - 1994)



In 1995 a general survey of the Black Sea continental shelf was performed in the framework of the EROS 2000 programme. The sampling pattern, totally different from the one used in GEOECOMAR monitoring programme, consisted in 30 sediment sampling station (one of them in the deep sea zone) covering the entire north-western shelf, from Varna to Sevastopol. The use of a Reineck box corer (60x30x30 cm) allowed a mean sampling depth of 30 cm and up to 50 cm in soft sediments, thus ensuring sampling of certainly uncontaminated sediments. Sediments subsamples were acquired at 10 cm interval beginning from sediment-water interface.

The complex sampling programme allowed a more detailed analysis of sediment Ba concentrations based on the Ba – Fe_2O_3 relationship. Usually, in normal, uncontaminated sediments, because of their common terrigenous origin, Ba concentrations are closely related to those of Fe_2O_3. The mathematical analysis of all analytical data for Ba and Fe_2O_3 for the sediment samples from EROS 2000 programme showed initially a complete lack of correlation between the two components ($r = -0.049$).

However, the graphical analysis of the same data (scatter diagram Fe_2O_3 – Ba, Fig. 3) disclosed the existence of two types of Ba concentrations:

1 – a group visibly related to the Fe_2O_3 concentrations (Ba I);

2 – a group with no apparent relation with Fe_2O_3 concentrations.

To avoid possible interferences due to manganese enrichments in sediments from *Modiolus* mud unit and from deep sea Unit II sediments (Degens and Ross, 1974) characterised by high Ba concentrations (≈ 1300 µg/g; Secrieru, unpublished data), the analytical data for samples having manganese concentrations MnO>0.17% and total organic carbon TOC>3% were filtered out from the diagram.

The first group (Ba I) of Ba concentrations is linearly related to Fe_2O_3 by the relation:

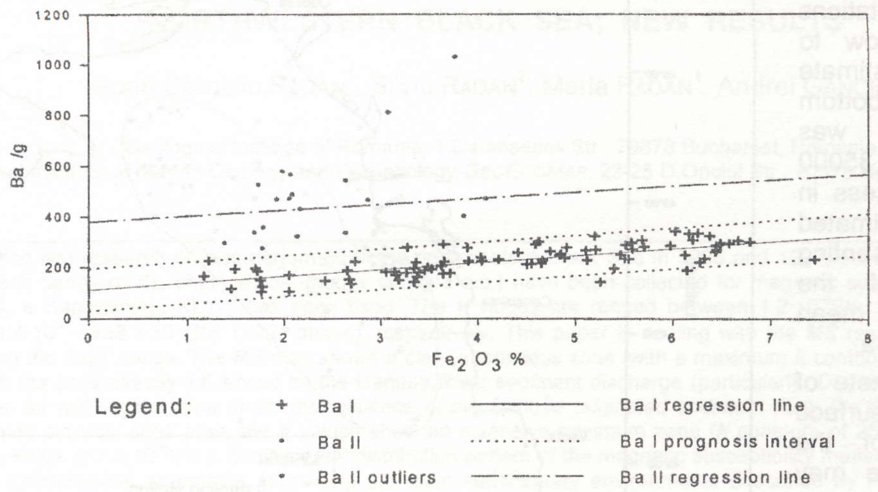
$$\text{Ba I}(\mu g/g) = 27.269\ Fe_2O_3(\%) + 112.145$$

with a correlation coefficient $r_{87} = 0.735$, which is highly significant for the number of data.

The slope of the regression line (27.269) represents the Ba contribution to the sediment total Ba content, in µg/g, associated with each percent of Fe_2O_3 and was assumed to represent particulate Ba of terrigenous origin, reaching the bottom by gravitational sedimentary mechanisms. The intercept of the line represents the mean quantity of Ba in sediments independent of their Fe_2O_3 content and probably corresponds to Ba introduced in the marine environment in dissolved form and transported to the sediment by some other mechanism, presumably controlled by biological factors Turekian, 1968). The sediments belonging to this group were considered as normal, uncontaminated, with component

Figure 3. Scatter diagram of Fe_2O_3 and Ba concentrations

(filters: TOC<3%; MnO<0.17%)



concentrations determined by the relative mixing proportions of terrigenous and marine carbonated materials.

The second group of Ba concentrations (Ba II) consists of 19 data points, two of them clearly outliers, all situated outside the prognosis interval for Fe_2O_3 – Ba I relation. The correlation coefficient calculated for the entire set of data points was r_{19} = 0.491, still statistically significant at a confidence level α = 0.05 although much lower than the previous one. This is an example of how misleading can be the presence of outliers for such calculations. Their elimination led to a correlation coefficient r_{17} = 0.181, with no statistical significance. Although without statistic significance, the relation relating Ba II and Fe_2O_3 concentrations:

$$\text{Ba II } (\mu g/g) = 23.269\ Fe_2O_3\ (\%) + 379.270$$

is interesting. The slope of the regression line is almost identical to that for Ba I (see Fig. 3) and was assumed to correspond to the same particulate, terrigenous Ba. On the contrary, the intercept of this line is 3.4 times greater than in the case of Ba I. If we assume a Ba quantity originating from dissolved barium similar to that of Ba I group (112 μg/g) than 260 μg/g of the Ba mean content of sediments has a different origin. This quantity was considered as being abnormal and of anthropic origin activities.

All sediment samples with abnormal Ba concentrations come from 9 stations grouping together in an elongated zone, with a rough NE – SW orientation (Fig. 4). The zone covers more than 35000 km², from approximately 45°45'N to 43°19' N and from 29° E to 32°10' E and is literally covered with drilling wells locations (more than 60), allowing the attribution of excess Ba to drilling activities. Romanian well locations are massed in the southern half of the zone the northern half being covered with Ukrainian locations. Very few well locations known to the authors remain outside this zone, probably because of stations number and density.

The abnormal concentrations usually affect the first 10 cm of sediment albeit in a few places they exceed 20 cm depth. The contamination depth and depth profile of Ba concentration are definitely a function of the beginning date of drilling activity, its dynamic and local sedimentary rate and offer another favourable argument for attributing the abnormal barium to these activities.

An estimate of mean Ba enrichment due to drilling activities can be made using the Fe_2O_3 – Ba I relation and taking into account the mean Fe_2O_3 concentration of contaminated samples. According to these the normal mean Ba concentrations for the 19 contaminated samples, for a 95% confidence interval is 177±80 μg/g Ba. Even considering the highest limit of this concentration the excess Ba for the abnormal zone is 230 μg/g, similar to that obtained from the intercepts of the regression lines and roughly doubling the estimated normal Ba mean concentration of these sediments.

In conclusion, the drillings of oil exploratory and productive wells have undoubtedly affected a great surface of the Black Sea continental shelf bottom. A relative increase of ≈ 30% was estimated for Ba mean concentration in superficial sediments compared with the corresponding concentration of sediments from 10-12 cm depth under the water – sediment interface.

Although the sampling stations density is too low to allow a precise estimate of the affected bottom surface, this was appreciated at 35000 km^2. The Ba excess in this zone was estimated at 230 µg/g representing almost 90% of the estimated normal mean concentration of Ba.

A better estimate of the affected surface extent and of the affectation degree may be obtained by increasing the density of sampling station.

The ecological, especially biological consequences of these influences remain to be assessed.

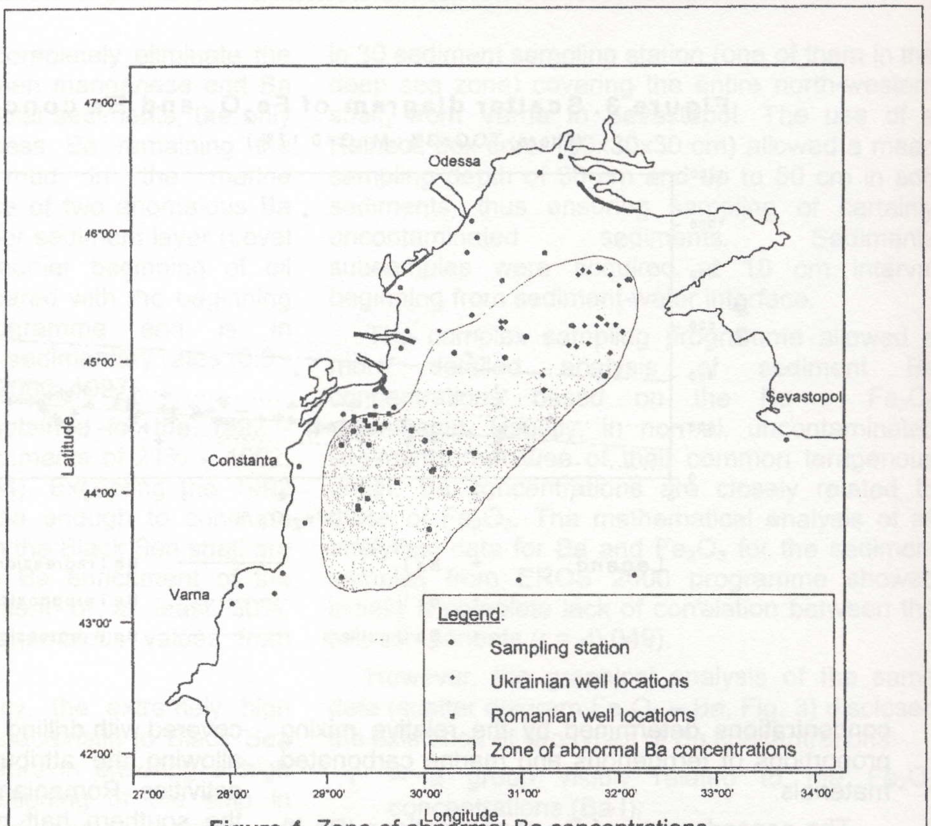


Figure 4. Zone of abnormal Ba concentrations
(Well locations after Enterprise Oil Exploration Ltd, 1996)

REFERENCES

BLACK, C.A., 1965, Methods of soil analysis, Am. Soc. Agronomy, Mono 9, Madison, Wisconsin, 1572 p.

BONATTI, E., FISHER, D.E., JOENSUU, D., RIDELL, H.S., 1971, Posdepositional mobility of some transition elements, phosphorus, uranium and thorium in deep sea sediments, Geochimica Cosmochimica Acta, 35, 180-201.

Enterprise Oil Exploration Ltd., 1996, Map of Black Sea Region – Tectonic elements and datapoint locations.

GAUDETTE, H.E., FLIGHT, W.R., TONER, L., FOLGER, D.W., 1974, An inexpensive titration method for the determination of organic carbon in recent sediments. Jour. Sed. Petrology, 44, 249 - 253.

HIRST, D.M., 1974, Geochemistry of sediments from eleven Black Sea cores – In: The Black Sea – geology, chemistry and biology – DEGENS, E.T. and ROSS, D.A., Eds., A.A.P.G. Memoir, 20, 430 - 455.

LYNN, D., BONATTI, E., 1965, Mobility of manganese in diagenesis of dep-sea sediments. Marine Geology, 3, 457-474.

MANHEIM, F., 1965, Ferromanganese accumulations in the shallow marine environment. Narragansett Marine Laboratory Publ. 3-1965, University of Rhode Island, 217-276.

MÖLLER, F. 1979, Manual of methods in aquatic environment research. Part 5: Statistical tests – FAO Fish. Tech. Pap., 182, 131 p.

PECO/EROS-2000, 1997, Pilot Phase – Final Executive Report, part B – IBSS, Sevastopol, Ukraine.

ROSS, D.A., DEGENS, E.T., 1974, Recent sediments of Black Sea – In: The Black Sea – geology, chemistry and biology – DEGENS, E.T. and ROSS, D.A., Eds. A.A.P.G. Memoir, 20, 183-199.

TUREKIAN, K.K., 1968, Dep-sea deposition of barium, cobalt and silver – Geochimica Cosmochimica Acta, 32, 603-612.

UNEP – 1986, The impact of Water-based Drilling mud dicharges on the environment. An overview – Moscow, 50 p.