BIOAVAILABILITY OF PHOSPHORUS IN SUSPENDED SOLIDS FROM THE NEARSHORE ZONE OF LAKE ERIE

by

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ABSTRACT

The forms of phosphorus and iron have been determined in suspended solids collected from within and off the Grand River estuary, Lake Erie, in August and October of 1985. Concentrations of organic and inorganic carbon, aluminum and manganese were also measured. These chemical parameters were then used to evaluate the relative contribution of stream solids, shoreline erosion, and lake sediment resuspension to suspended solids in the studied area. Considerable spatial and temporal variation was found in the distribution of the measured parameters. Both, total and bioavailable P (BAP) in suspended solids were higher in the summer than in the fall, BAP accounting for about 34.5% of total P in August and about 17.5% in October. The BAP distribution is consistent with the distribution of ferric ion, whereas apatite-P follows the distribution of aluminum and ferrous ion in chlorite and other clay minerals. The concentration of BAP is generally higher in the near-surface solids and increases with increasing distance from the river mouth. The seasonal and spatial trend in BAP and organic carbon concentrations reveal, that a large proportion of particulate P is of biogenic origin.

RÉSUME

Les espèces de phosphore et de fer ont été déterminées dans les matières en suspension recueillies dans l'estuaire de la Grande Rivière et près de celui-ci, au lac Erié, en août et en octobre 1985.

On a également mesuré les concentrations de carbone organique et inorganique, d'aluminium et de manganèse. Ces paramètres chimiques ont été utilisés pour évaluer la contribution relative des matières solides de l'écoulement, de l'érosion du rivage et de la remise en suspension des sédiments du lac aux matières solides en suspension de la zone à l'étude. On a observé des variations spatiales et temporelles considérables dans la distribution des paramètres mésurés. Les valeurs du phosphore total et biodisponible (PBD) dans les matières solides en suspension étaient plus élevées en été qu'en automne, le PBD comptant pour environ 34,5 % du P total en août et pour environ 18,7 % en octobre. Les distributions du PBD ne correspondaient pas à la distribution des ions ferriques, alors que le P à l'état d'apatite correspondait à la distribution des ions aluminium et ferreux dans la chlorite et d'autres minerais de type argile. La concentration de PBD est généralement plus élevée dans les matières solides près de la surface et augmente en fonction de la distance de l'embouchure de la rivière. Les tendances saisonnières et spatiales des concentrations de PBD et de carbone organique indiquent qu'une grande proportion de matières particulaires est d'origine biogénique.

MANAGEMENT PERSPECTIVE

Phosphorus control programs instituted in the early 70's have resulted in significant improvement in the water quality in offshore Lake Erie. Nearshore areas close to large rivers however, on ocassions still show high densities of algae.

The objective of this report is to evaluate the bioavailability of particulate phosphorus in the estuary of the Grand River, Ontario. The Grand River is a major source of phosphorus to Lake Erie, accounting for about one third of the total Canadian phosphorus input. In 1985 the annual phosphorus loading from the Grand River was estimated to be 731 metric tons (D.M. Dolan). Particulate phosphorus accounts for more than 70 % of the total P load (Water quality data, OME). The data presented here suggest that particulate P in the immediate vicinity of the Grand River mouth is less bioavailable than the particulate P further offshore, which is mainly incorporated in algal tissue and organic debris. This information has important implications for understanding of particulate P dynamics in the nearshore zone which in turn is of great importance in instituting phosphorus control programs.

PERSPECTIVE - GESTION

Les programmes de déphosphatation mis sur pied au début des années 70 ont entraîné une amélioration significative de la qualité de l'eau au large du lac Érié. Toutefois, on observe encore parfois de fortes densités d'algues dans les zones près du rivage voisines des grandes rivières.

L'objectif du présent rapport est d'évaluer 13 bic disponibilité du phosphore particulaire dans l'estuaire de la Grande Rivière, en Ontario. Cette rivière est une source importante de phosphore déversé dans le lac Érié; elle compte pour environ un tiers de l'apport total canadien en phosphore. En 1985, la charge de phosphore provenant de la Grande Rivière a été évaluée à 731 tonnes métriques (D.M. Dolan). Le phosphore particulaire compte pour plus de 70 % de la charge totale de P (données de la qualité de l'eau, MOE). Les données présentées dans le présent article suggèrent que le P particulaire dans le voisinage immédiat de l'embouchure de la Grande Rivière est moins biodisponible que le P particulaire qu'on retrouve plus au large, qui est principalement incorporé aux tissus alguaires et aux débris organiques. Cette information a d'importantes implications pour la compréhension des caractéristiques dynamiques du P particulaire dans la zone près du rivage, qui est elle-même très importante pour l'établissement des programmes de déphosphatation.

INTRODUCTION

Suspended solids represent an important fraction of the total solids load to the aquatic environment. Their importance stems from their ability to transport nutrients and contaminants (Nriagu et al. 1981, Oliver and Charlton 1984) within the aquatic system. Canadian tributaries contribute 1.36 million metric tons of total solids annually to Lake Erie (Ongley 1976). The Grand River, Ontario, is the principal source, accounting for 65.8% of the total Canadian load. Recognizing the importance of the tributary particulate P load to the overall water quality in Lake Erie and the distinct character of the nearshore zone (Gregor and Rast 1979), we have focussed our attention on the characterization and fate of particulate P in the Grand River estuary.

The objectives of the present study are: (1)to evaluate the bioavailability of particle bound phosphorus in the vicinity of the Grand River discharge into Lake Erie; (2)to evaluate the relative contributions of stream solids, shoreline erosion and bottom sediment resuspension to the total amount of particulate P in this area; and (3)to determine the role of Fe in P availability. We used spatial and temporal differences in concentrations of various forms of P, Fe and other chemical parameters (total and organic C, Al and Mn) as indicators of processes in the studied area.

MATERIALS AND METHODS

Sample Collection and Preparation

A transect extending from the mouth of the Grand River was sampled on two occasions (Fig.1). Suspended sediment samples were collected from four lake stations in August 1985 and from seven lake stations in October 1985, using a continuous-flow Westphalia separator. The October sampling included, in addition to the lake stations, three stations on the Grand River (Fig. 1). The lake stations were about 2 km apart. At most stations about 600 L of water was pumped from 2 m below the surface and from 2 m above the sediment-water interface. The collected solids were frozen immediately and freeze-dried later in the laboratory.

Temperature profiles showed that the water column was strongly stratified in August, while in October, the onset of unstratified period was evident, especially at three nearshore stations. The quantity of material collected by centrifugation, with the exception of stations LE-1 and LE-2 was less than 1 g. The near-surface material appeared to be more fluffy than the near-bottom material.

Characterization of Particulate Phosphorus and Other Chemical Parameters

Biologically available P in the suspended particulate solids was estimated using the procedure of Williams et al. (1980), employing Ø.1N NaOH/1.Ø N NaCl extracting reagent. The strong correlation between P estimated by this procedure and bioavailable P (BAP) estimated by bioassay (Golterman et al. 1969; Dorich et al. 1980, Williams et al. 1980, De Pinto et al. 1981, Young et al. 1985) makes this form of P a reasonably good surrogate measure of bioavailable P (Young et al. 1985). Concentrations of total P, organic P, non-apatite inorganic P (NAI-P) and apatite-P were measured according to Williams et al. (1976a) and Mayer and Williams (1981). Inorganic and organic carbon were determined with a Leco induction furnace, organic carbon being measured after removal of the carbonate carbon with sulfurous acid (Kemp 1971). Total concentrations of Fe, Al, and Mn were determined by acid dissolution and subsequent atomic absorption spectrometry (McKeague 1978).

Mossbauer Spectroscopy

The principal iron compounds were determined by Mossbauer spectroscopy. Mossbauer spectra were recorded at room temperature, using a Co^{57}/Fe^{57} source, an electromechanical velocity transducer and a 512 channel multichannel analyzer. Spectra were computed using the program of Stone (1967). Lorentzian line shapes were assumed and area ratios and half widths within a quadrupole doublet were constrained equal

(Manning et al.1983). Chi-squared values and visual examination were used for goodness of fit. The isomer shifts are reported relative to the Fe-metal foil.

RESULTS AND DISCUSSION

Characteristics of Particulate Nutrient Chemistry

A strong positive correlation is observed between the BAP and NAI-P (r=0.99) and between the BAP and total P concentration (Fig. 2). The BAP concentrations in August range between 864 and 1510 mg/kg and account for about 34.5% of total particulate P in August samples (Table 1), whereas in October the concentrations of BAP range only between 277 mg/kg and 722 mg/kg. On average, the BAP in October accounts only for about 17.5% of the total P, which is about 50% of the summer value. The mean summer value of total particulate P and BAP are 3377 mg/kg and 1165 mg/kg, respectively. The mean values of the same parameters in the fall are 2324 mg/kg and 414 mg/kg, respectively. The near-surface samples tend to have consistently higher values of BAP, NAI-P and total P concentration than the near-bottom samples. The differences are more pronounced for BAP and NAI-P than for the total P concentrations, due to the increased apatite-P values in the near-bottom samples (Table 1). Resuspension of bottom sediments contributes most likely to the higher apatite-P values measured in suspended solids from just above the water-sediment interface. Bloesch (1982) estimated that more than 80% of the

material collected by sediment traps placed 2 to 3 m above the bottom in eastern Lake Erie was resuspended surficial sediment.

The concentration of BAP in the suspended solids increases gradually with increasing distance from shore (Figs. 3 and 4). The BAP concentration at the mouth of the river (station LE-1) was slightly higher than that of the last station on the Grand River (GR-3), indicating possible input of phosphorus from the fertilizer plant, which is located upstream of the Grand River delta (station LE-1). Although the plant is presently not operational it once was a major source of P. Waste ponds may be the source of P from this unused fertilizer facility (S. Painter, pers. comm.). The seasonal and spatial trends in total particulate P, apatite P and BAP values suggest that a significant proportion of BAP is of biogenic origin. Indeed, as much as 440 mg/kg of BAP could be generated from the algal material alone, assuming that org.matter = $2 \times C_{ORG}$ and that about 12% of total P is extracted from algae by NaOH/NaCl extractant. Our laboratory experiments (Mayer, 1985) show that about 12% of total P was extracted from laboratory cultured algae Chlorella, containing 9.1 mg/g of phosphorus. The organic carbon data (Table 1), which exhibit similar trends to those of BAP, support this conclusion.

The total and organic carbon values of solids (Table 1) from all the lake stations except station LE-1 are much higher than those of surficial sediments (C_T 1.8-4.85% and C_{ORG} Ø.43-1.78%) from the same stations. The values compare favorably with those of Mudroch (1984) from a nearby location and

with the values of Eadie et al. (1984) obtained on the sediment trap material from Lake Michigan. Concentrations of total and organic C in particulates from station LE-1 (Table 1) are similar to the carbon values of tributary solids from the last river station (GR-3). The organic carbon is negatively correlated (r=-0.88) with apatite. This is to be expected if primary production is the main source of organic carbon and apatite P is of abiotic (detrital) origin.

The apatite-P concentrations of solids from the first lake station (LE-1) and the last river station (GR-3) are very similar. The values decrease rapidly with the distance from the river mouth (Figs. 4 and 5), indicating the loss of solids through sedimentation. The loss is more apparent in surficial samples than in the bottom samples, where the resuspension of benthic sediment masks the loss. The August apatite-P concentration of the surface particles from the thermally well stratified water column drops by 53% within 4 km and 70% within 6 km, which represents a drop of about 12% of apatite-P per distance of one km. Considering the fact that apatite P is likely to be associated with rapidly settling detrital particles its transport from nearshore areas towards the basin will be Thus, only that portion of particulate phosphorus limited. associated with particles of low settling velocity, mainly the BAP, will probably enter the lake wide processes. The organic C/P ratios of surface samples are slightly higher than those of bottom samples, averaging 86 in summer and 95 in fall. Our C:P values are higher than the average ratio for plankton 42:1 (Redfield et al. 1963) and comparable to the value of 79:1 for

trap material from Lake Michigan (Eadie et al.1984). Our values are however, significantly lower than the 131, reported for trap material from similar depth of stratified Lake Erie (Gachter and Bloesch, 1985). This deviation from the "ideal" Redfield ratio is systematic in most freshwater lakes (Gachter and Bloesch 1985) and is caused by considerable P regeneration within the water column.

Spectral Interpretations

Chlorite and amorphous hydrated ferric oxides are ubiquitous in the soils and sediments. We used Mossbauer spectroscopy to quantify the proportion of iron in these compounds in suspended solids. A typical Mossbauer spectrum is shown in Fig. 6. All spectra are qualitatively similar and can be fitted on the basis of two doublets (Manning and Jones, 1982, Manning et al. 1983). The outer doublet corresponds to ferrous ions located in octahedral positions in the chlorite and clay lattice. Chlorite was also confirmed by X-ray diffraction. The average computed values of isomer shift, quadrupole splitting and line width corresponding to chlorite (outer) doublet are 1.13, 2.60 and Ø.39 mm/s, respectively. All values are reproducible to \pm 0.02 mm/s. The inner doublet corresponds mainly to Fe³⁺ in amorphous hydrated oxides. The average corresponding Mossbauer parameters for the inner doublet are 0.35 mm/s, 0.58 mm/s and $\emptyset.57 \text{ mm/s}$, which are consistent with ferric ions in an oxide ion environment (Coey et al 1974). All the values for the inner doublet are reproducible to ± 0.02 mm/s. The excellent computed

spectral fits show that the two doublets account for more than 95% of total Fe. Fe³⁺:Fe²⁺ ratios were obtained from the ratios of areas beneath the respective doublets. Concentrations of ferrous and ferric ions were calculated using these ratios and total iron concentrations (Table 2).

Iron-Phosphorus Interaction

The close relationship between iron and phosphorus in lacustrine sediments has been well documented. Some of the recent studies of suspended particulate matter (Mudroch 1984) however, found no or little correlation between the total particulate phosphorus and iron. As already discussed, chlorite and amorphous hydrated ferric oxides account for most of the iron in suspended solids and surficial sediments. The importance of the latter compounds stems from their ability to remove and retain the phosphate ions from solution by adsorption and/or precipitation. The iron present in the lattice of chlorite mineral is inert and probably plays a minor role in phosphorus cycling. Furthermore, chlorite undergoes little diagenetic change in the aquatic environment and can be regarded therefore as a conservative parameter. The Fe^{2+} in chlorite correlates closely (r=0.93 for n=23) with Al, which is bound mainly in clay minerals (Kemp & Thomas, 1976; Kemp et al. 1976; Manning and Jones 1982) and can be considered a conservative element.

The apatite=P concentration closely follows the concentration of both conservative parameters Al and Fe^{2+} . The linear regression analysis yields a correlation coefficient (r) of 0.90 and 0.92, respectively, confirming the association of this form of P with the particles of detrital origin.

Although, the relation between the particulate BAP and Fe is not easily defined, the BAP and Fe³⁺/Fe²⁺ ratios show a curvilinear dependence (Fig. 7), suggesting an association between the BAP and Fe³⁺ from hydrated Fe oxides. Assuming that the particles are of the same origin the Fe^{3+}/Fe^{2+} ratio of suspended solids would be more or less constant. The increasing Fe³⁺/Fe²⁺ ratio suggests, in addition to lesser resuspension, an increased input of autochtonous material containing freshly precipitated Fe³⁺ from the water column. The Fe³⁺/Fe²⁺ ratio would increase more in the summer, when pH increases due to the photosynthetic activity, thus creating more favorable conditions for Fe³⁺ precipitation and subsequent P adsorption and/or coprecipitation. The corresponding increase in the particulate BAP at this time of the year is however much greater than would be anticipated from the increase in Fe³⁺/Fe²⁺ ratio. The high BAP values in the upper portion of the graph (Fig. 7) represent the summer conditions, when the productivity was high and a large portion of P would be incorporated in the algal tissue and organic debris, rather than inorganicaly bound to reactive Fe oxides. The BAP, associated predominantly with particulates of biogenic origin, is regenerated rapidly in the water column, which is also evident from seasonal differences in this parameter

Influence of Grand River and Lake Hydraulic Regime on the Particle Chemistry and P-bioavailability

Other elements such as Mn and Al also provide important information on the origin of suspended solids. Mn is often strongly correlated with P in the sediments (Bortleson and Lee 1974, Delfino et al. 1969, Williams et al. 1976), although it is generally believed that the concentration of P in the sediments is controlled by Fe rather than by Mn (Bortleson an Lee 1974, Williams et al. 1971, Williams et al 1976). The correlation between P and Mn is probably indirect and attributable mainly to the strong correlation between Fe and Mn, which is based on the frequent association of Fe and Mn in secondary mineral species (Bortleson an Lee 1974, Williams et al. 1971, Williams et al Thus, the spatial distribution of both elements should 1976). reflect the terrigenous influence. Indeed, total concentrations of both Fe and Mn (Table 2) decline with the increasing distance from the river mouth, indicating the loss of the allochtonous material through the processes of sedimentation and possibly through dilution by autochtonous organic material. Iron and manganese concentrations are also consistently higher in the near-bottom samples than those in near-surface samples, probably due to the input from resuspended benthic sediment.

The spatial distributions of Al, apatite-P and Fe²⁺ (Figs. 4, 5 and 8a, b) clearly show the effect of the nearshore processes. The loss of terrigenous material in the near-surface samples, as indicated by decreased Fe^{2+} , Al and apatite P concentrations, is very pronounced for both sampling events. The fall concentration

of Al and Fe²⁺ in near-bottom suspended solids from most nearshore stations exceeded the concentrations of the total particulate Al and Fe²⁺ from chlorite at station LE-1, at the mouth of the river, suggesting a significant input of resuspended benthic sediments. The vertical distribution of both conservative elements (Fig. 8a,b) at this time of year indicates a well-mixed water column at stations LE-2, and LE-3. The chemical characteristics of particles, pointing to internal input are consistent with the temperature profiles, which indicate a complete disappearance of the thermal stratification at these stations. The temperature profiles at the remaining stations show very weak remnants of the thermocline. Concurrently, the effect of mixing on the chemical characteristics of near-surface particles decreased with the increasing depth and distance from the shore. The concentrations of apatite-P, Al and Fe²⁺ (Figs. 5, and 8a, b) in near-bottom particles, originating presumably from the benthic nepheloid layer (Chambers and Eadie 1981, Sandilands and Mudroch 1983, Bell et al.1980) decreased drastically about 10 km from the shore. At about the same distance the relative contribution of Fe³⁺ to total Fe increased from 45 to 54 % (Fig. 9b), a proportion similar to that measured in the near-surface solids. In the summer samples, the relative contribution of Fe³⁺ to total Fe averaged about 59 %, with the values slightly higher for the near-surface solids than those of near-bottom solids (Fig. 9b). In the fall the relative contribution of Fe²⁺ from chlorite to Fe is generaly higher (Fig. 9b) in the near-bottom samples. The input of resuspended

material is more pronounced at stations LE-4, LE-5, where the surface and bottom waters did not mix completely. Interestingly, at station LE-3 the proportion of Fe^{3+} and Fe^{2+} is about the same in the solids collected from the two depths (Fig. 9b). This is the only station where the proportion of Fe^{2+} from chlorite in the near-surface solids is higher than Fe^{3+} and the values of several measured parameters (org. C, apatite-P, Fe, Al) were equal for both sampling depths.

At the nearshore stations, it is difficult to discern whether the apatite-P is from the tributary solids or from the shoreline erosion. However, based on the chemical characteristics of the particulates it can be concluded that the influence of the Grand River and the shoreline erosion processes is confined to a distance of about 4 km from shore. This distance is somewhat greater than that estimated by Painter and McCabe (1987) (2 km) from a <u>Cladophora</u> distribution study. A study of Nichols et al. (1983) found the influence of the Grand River plume on Lake Erie phytoplankton to be confined to an area within 5-10 km of the river mouth. Our results appear to indicate more inshore-offshore differences, whereas the results of Painter and McCabe and Nichols et al.indicate the effect of the river plume along the northeastern shore of Lake Erie, reflecting inshore lateral variability.

The low NAI-P concentrations (123-297 mg/kg) and the low organic C concentrations $(\emptyset.43-1.78 \text{ s})$ of the surficial sediments in the investigated area (unpublished data) are consistent with a movement of P associated with fine particles further offshore to low energy deposition areas.

In summary, our two sampling episodes revealed substantial seasonal and spatial variation in the concentration of particulate BAP in the vicinity of the Grand River discharge into The higher total P, BAP and organic carbon Lake Erie. concentrations in summer suspended solids suggest that a significant proportion of BAP is biogenic. Whereas concentrations of apatite-P decrease with increasing distance from shore (Table 1) due to the loss of tributary solids and particles from shoreline erosion, concentrations of BAP, NAI-P and org.P increase dramatically in the August sampling and to lesser extent in October sampling (except for station LE-1). The influence of the Grand River on the forms and concentrations of particulate P is of lesser importance, particularly at the time of mixing (October). The zone of influence is limited to a distance of less than 4km.

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- 1. Location of the sampling sites.
- 2. Relationship between bioavailable and total P.
- 3. Bioavailable P in suspended solids from Lake Erie. October 1985.
- 4. Concentrations of organic C, bioavailable and apatite P in suspended solids from Lake Erie. August 1985.
- 5. Apatite P and organic C concentrations in suspended solids from Lake Erie. October 1985.
- 6. Room temperature Mossbauer adsorption spectrum of near-bottom suspended solids from station LE-2.
- 7. Relation between bioavailable P and Fe^{2+}/Fe^{3+} ratios.
- 8. Concentrations of Fe²⁺, Fe³⁺ and Al in suspended solids from Lake Erie; (a) August 1985; (b) October 1985.
- 9. Contribution of Fe²⁺, Fe³⁺ to total Fe in suspended solids from Lake Erie. (a) August 1985; (b) October 1985.



Fig 1







station





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PERCENT ABSORPTION

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Fig 6



Fig 7



Fig. 80



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	SAMPLING DEPTH	BIOAVAILABLE P	NAI-P	APATITE-P	ORGANIC P	TOTAL	TOTAL	ORG.
STATION	D	mg kg ⁻¹	ž	X				
			AU	GUST 1985				
LE-1	4	864	952	377	1100	2415	8.25	5.59
LE-2	2	1104	1146	267	1992	3561	15.50	13.72
	13	994	1026	274	1657	3034	13.58	11.40
LE-3	2	1093	1162	174	1956	3459	20 70	10.10
	14	1335	1322	209	1864	3392	19.10	17.05
	•	1510						
LC-4	2	1510	1545	113	2053	3970	22.94	20.90
·	4 1	1437	1230	298	2051	3818	20.55	18.55
			001	COBER 1985				
LE-1	4	722	1024	345	1488	2912	10.06	7.22
LE-2	2	293	493	288	1237	2068	13.49	11.30
	12	277	468	350	941	1701	9.84	7.68
LE-3	2	369	538	260	1506	2291	15.39	12.92
	13	349	Ŝ02	243	1513	2247	15.58	13.09
LE-4	2	425	523	128	1891	2655	20.64	18,51
	20	382	493	305	1047	1854	11.26	9.35
LE-5	2	480	572	120	1992	2792	22-96	20.27
	21	281	408	298	1088	1835	12.12	9.49
LE-6	2	474	621	96	1685	2513	24,19	20.04
	23	344	472	186	1343	1983	17.12	14.03
LE-7	2	653	742	97	2165	3335	23, 91	20.68
	25	331	452	146	1370	2022	16.47	13.77
SR-1	2.	317	428	363	679	1460	6.98	3.88
;R-2	2	367	483	363	684	1492	7.82	3.65
SR-3	2	580	566	339	1050	1926	9.78	6.24

TABLE 1 PHOSPHORUS AND CARBON CONCENTRATIONS IN SUSPENDED SOLIDS FROM LAKE ERIE AND GRAND RIVER

The organic P was determined by difference between the total P and the orthophosphate in combined extract, used for total P determination (Mayer & Williams, 1981).

Fe AN	D FE T IN SUSP	ended sol	.105 FROM LA	ake erie af	ND GRAND I	RIVER	
STATION	SAMPLING DEPTH	FeT	Fe ³⁺	Fe ²⁺	AlT	Mn	
	(m)	%	Z	8	7	%	
		▲UG	UST 1985				
LE-1	4	3.52	2.085	1.43	5.40	0.179	
LE-2	2 13	2.71 2.87	1.61 1.67	1.10 1.20	4.37 5.11	0.145 0.144	
LE-3	2 14	1.55 2.24	0.93 1.29	0.62 0.96	3.02 3.93	0.128 0.107	
LE-4	2 21	1.02 1.61	0.62	0.40 0.69	1.86	0.045 0.125	
		0 СТО	BER 1985				
LE-1	4	3.24	1.86	1.38	4.51	0.147	
LE-2	2 12	2.49 2.86	1.32 1.49	1.17 1.37	4.36 5.25	0.092 0.089	
LE-3	2 13	2.01 2.00	0.99 0.98	1.02	3.58 3.58	0.067 0.068	
LE-4	2 20	0.99 2.86	0.50 1.33	0.49 1.53	1.71 5.10	0.056 0.119	
LE-5	2 21	0.90 2.62	0.48 1.18	0.41 1.44	1.63 3.04	0.053 0.113	
LE-6	2 23	0.76 1.14	0.41 0.62	0.34 0.52	1.31 2.14	0.052 0.069	
LE-7	2 25	0.80 1.17	0.44 0.62	0.36 0.55	1.51 2.20	0.051 0.083	
GR-1	2	3.45	1.91	1.54	5.5	0.125	
GR∸2	2	3.49	1.97	1.52	5.84	0.129	
JR-3	2	3.29	1.87	1.42	5.40	0.124	

TABLE 2

CONCENTRATIONS (wt. 2) OF TOTAL IRON, MANGANESE, ALUMINUM, AMORPHOUS