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Depth Water of Lake Baikal: A Natural Reference of Fresh Water

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Abstract

This paper shows that the depth water of Lake Baikal is useful as a reference material in intra- and interlaboratory quality control of chemical analysis for low-mineralized natural waters. The results of numerous determinations of major ion contents in Baikal water, as well as pH and electrical conductance values, are considered. Our data on the concentrations of the main ions in the reference material based on the depth Baikal water and the results of intercalibration with this reference material obtained from 14 hydrochemical laboratories are presented.

INTRODUCTION

In hydrochemical analysis of natural waters, the correctness and reproducibility of results may be essential to cost-effective management concerned with sustainable development. The error of analysis can lead to an overrated degree of natural water pollution and to a struggle against non-existing "man-made sources", or to an underestimated degree of real changes. In both cases, the society incurs considerable material losses.

In order to ensure correct analysis, hydrochemical laboratories should undergo intercalibration at regular intervals. The general procedure of intercalibration starts with sending out to different laboratories the same artificially prepared solution containing known "true" concentrations of components. Calibration of techniques against the artificially prepared "standards" (called "reference materials" in the world literature) has some methodological drawbacks: neglect of the matrix effect, difficulties in preparing large amounts of reference materials and storing them for at least 10 years as required for permanent supply to many hydrochemical laboratories, and possible difference between every new lot and the first one. That is why artificial reference specimens of sea water are expensive (about $ 600 for 200 ml). Natural reference fresh waters, as far as we know, are not available in the world market.

Creation of a natural standard of fresh water with constant amounts of both cations and anions is hindered by the fact that the composition of rain waters, as well as river and lake waters and many subterranean waters, is not stable, and even the main characteristics show seasonal and more frequent fluctuations. In Canada, *e. g.*, "certified reference materials" are produced (http://www.imb.nrc.ca/crmp/encat_e.pdf), but they cannot be considered to be natural water since they are acidified. The constancy of composition of this material is dubious, because it is prepared from river water, and the composition of river waters is subject to strong seasonal and annual fluctuations.

The present publication describes the creation of a natural reference material based on the depth water of Lake Baikal, proves that the main ion content of this material is constant, and demonstrates its utility for intercalibration of hydrochemical laboratories. According to expert estimations [1], about 200 million hydrochemical analyses were carried out in the USSR. Creation of a reliable reference material for analysis of fresh waters has a great practical importance.

CHARACTERISTICS OF BAIKAL WATER

Lake Baikal is world's largest reservoir of fresh water; it contains about 20 % of the land fresh water, *i. e.*, of water from all world's lakes and rivers. The water volume of Baikal amounts to 23 000 km^3. The lake is well stirred, as indicated by the continuous presence of oxygen in concentrations of 14 to 9 mg/l at all its depths down to the maximal depth (1637 m). The concentrations of biogenic elements – nitrogen, phosphorus, silicon – in the surface and near-bottom waters of Baikal are subject to seasonal fluctuations because of their consumption and regeneration by the biota in the upper layers of water and because of the unique mechanism of renewal of the near-bottom waters of the lake. In the "core" of Baikal, at depths of 300 m from the surface to 100 m over the bottom, the concentrations of the biogenic elements change but little both with respect to depth and to seasons [2–5].

Lake Baikal is a very inertial system; its complete replacement by the waters of the tributaries takes about 400 years. The Angara river carries away 60 km^3 annually, and approximately as much water is supplied to the lake by its tributaries, the main of which, the Selenga river, brings 30 km^3 per year. Evaporation from the lake surface makes up only a small part of the water balance (about 5 % [6]). The age of "core zone" waters, *i. e.*, the average time required for surface waters to penetrate to a depth within the range of 300 m from the surface – 100 m from the bottom is equal to about one decade; benthic waters are somewhat younger [2]. These circumstances are responsible for the constancy of the main ion content of the core waters of Baikal which is unique compared to the waters of small fresh water lakes.

It is noteworthy that we are not speaking of constancy on the geological time scale, but, rather, we refer to the life span of several human generations (100–200 years). Studies of dated precipitations of Baikal showed that the state of its ecosystem changed considerably 10–15 thousand years ago, after the global

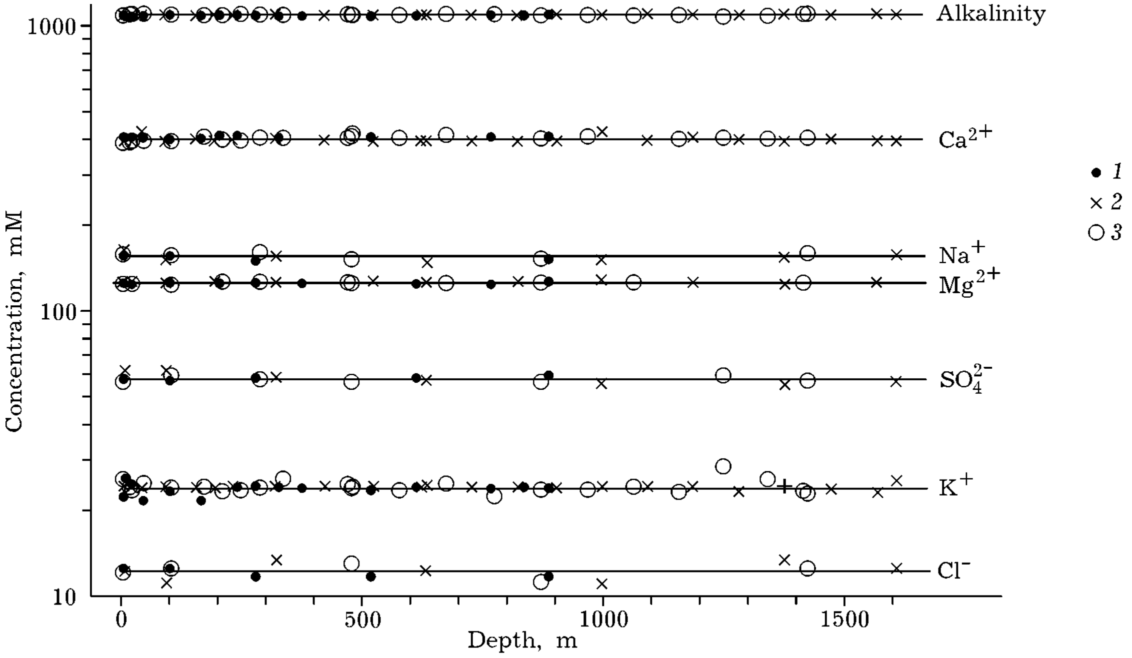

Fig. 1. Results of analysis of Baikal water obtained in [11]: *1–3* – northern, middle and southern hollows, respectively.

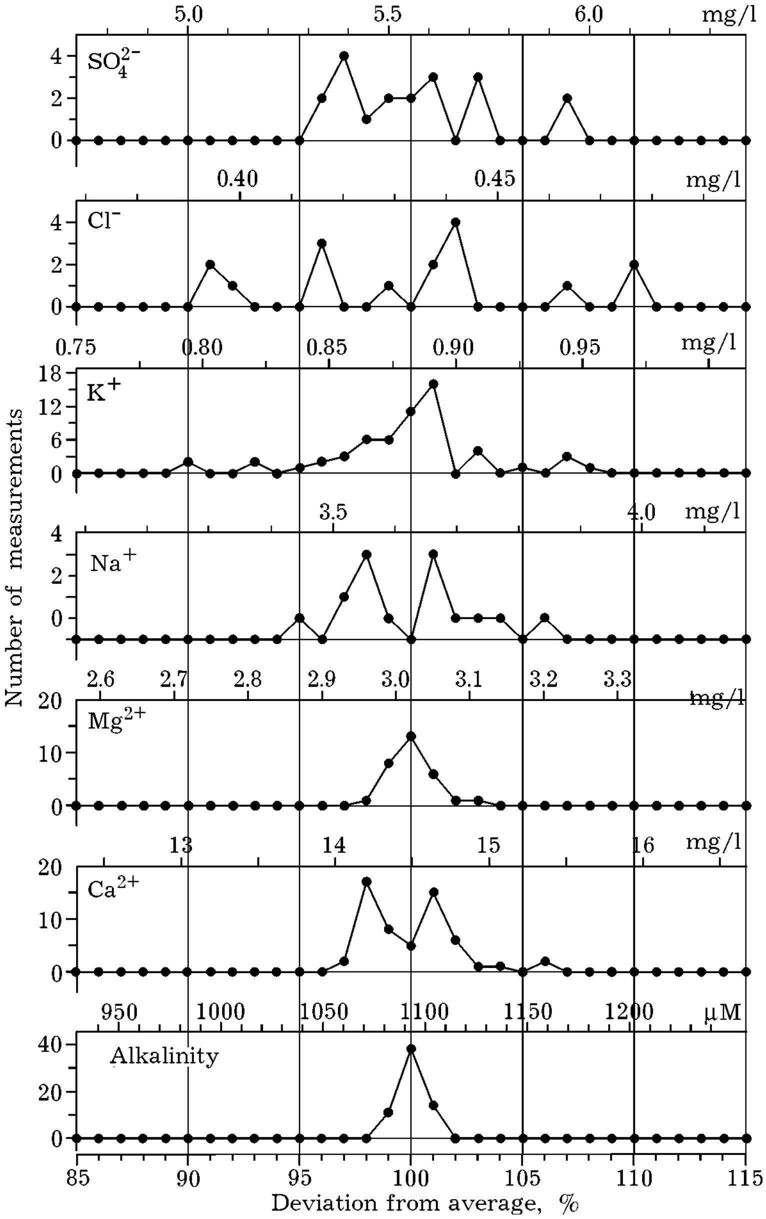

Fig. 2. Hydrochemical characteristics of Baikal water according to [11]. Y axis – the number of values within the stated range; X axis: top – the concentrations found, bottom – percent of the average provided that the average is 100 % for each characteristic.

warming at the end of Pleistocene. For example, at the maximum of the global glaciation, 18 000 years ago, diatomic algae were absent in open Baikal [7–9]. However, in the last centuries no considerable changes in the Baikal ecosystem occurred. This is evidenced by the constancy of assortment of leading diatom species. Diatoms are one of the most sensitive quality indicators for natural waters. Their species composition varies radically (some species disappear, while others appear) when the lakes become acidified with sulphur oxides from remote man-made sources, with excess fertilizers from water catchment areas due to development of even primitive agriculture. There are so many examples of such lakes on the territory of European and North American countries that it has even become possible to calculate so-called transfer functions – dependence of the species compositions of diatoms on the acidity and trophicity, permitting reconstruction of the history of chemical changes in the lakes by determining the valves of diatomic algae buried in the lacustrine sediments.

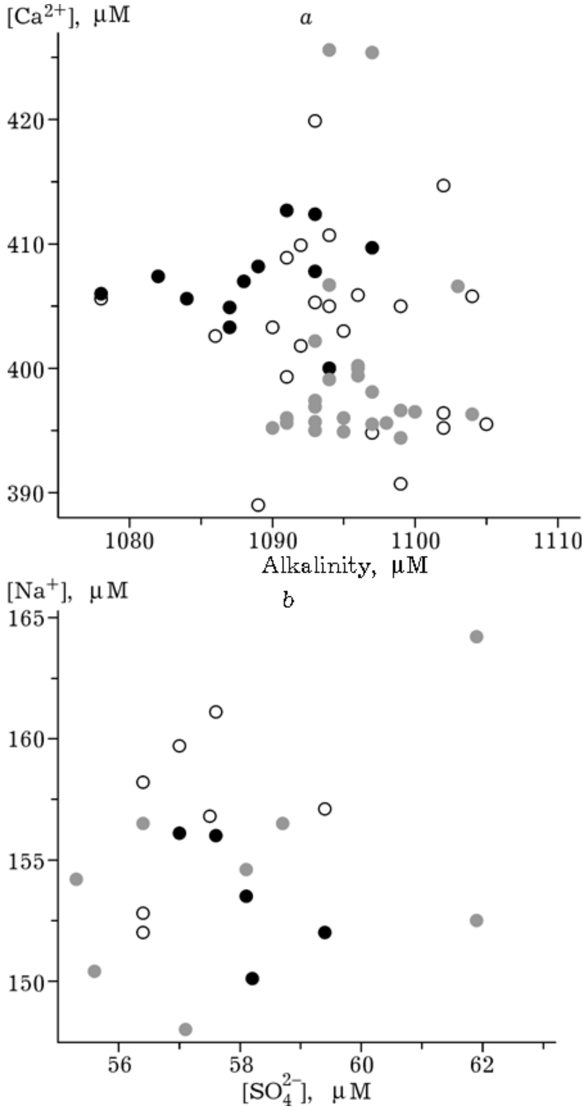

Fig. 3. Absence of correlation between the calcium ion contents and alkalinity (*a*) and between the concentrations of the sodium and sulphate ions (*b*) according to [11].

A thorough diatom analysis of dated sediments of Baikal has demonstrated that during the industrial revolution that took place throughout the 20th century and led to boom economic development of Siberia, the qualitative composition of diatoms in Baikal did not change at all, and neither did the ratio of numbers of various species [10].

Man-induced contamination of Baikal is taking place, and it must be controlled. However, the simple calculations presented in monograph [9] show that anthropogenic sources could never change the main ion contents of Baikal water appreciably. Thus *e. g.*, in order to get a statistically significant change in the concentration of any of the main ions, it would be necessary to discharge into Baikal tens of million tons of a respective salt. The waters of the Selenga bring annually “only” 0.2 million tons of sulphate, while the Angara discharges 0.3 million tons. No man-made source is capable of supplying million tons of sulphate to Baikal within a short period of time. For example, the Baikal Pulp and Paper Mill discharges about 0.01 million tons of sulphate, and this is the main source of industrial pollution [9].

DATA OF PREVIOUS HYDROCHEMICAL STUDIES

In the 1990s, Baikal became the object of wide-scale international cooperation. For studies of the composition of its waters, contemporaneous methods were applied. The results of one of the most thorough studies were published by Falkner *et al.* [11]. Some of them are discussed below.

Figure 1 presents the results of alkalinity and concentration measurements for the main ions in Baikal water samples taken at all depths at stations situated in the central parts of three hollows of the lake. The chemical analysis failed to reveal any statistically significant differences between these samples or any trends with respect to the depth or to the longitudinal cut of the lake.

Figure 2 shows the frequency distributions of data occurrence. One can see that the minimal statistical dispersion is characteristic for alkalinity data – the whole range of their values is within the interval (100 ± 1) %. The statistical dispersion of the rest of characteristics is much larger. The distribution of deviations from the average for some features does not obey the Gauss function and can witness the presence of systematic analysis errors. The maximal dispersion (up to 10 %) is characteristic of chlorides, sulphates and potassium ions whose concentrations in the Baikal water are low.

BALANCE OF CATIONS AND ANIONS

Estimating the metrological quality of the body of data studied, one has to keep in mind that the real concentrations of the main ions

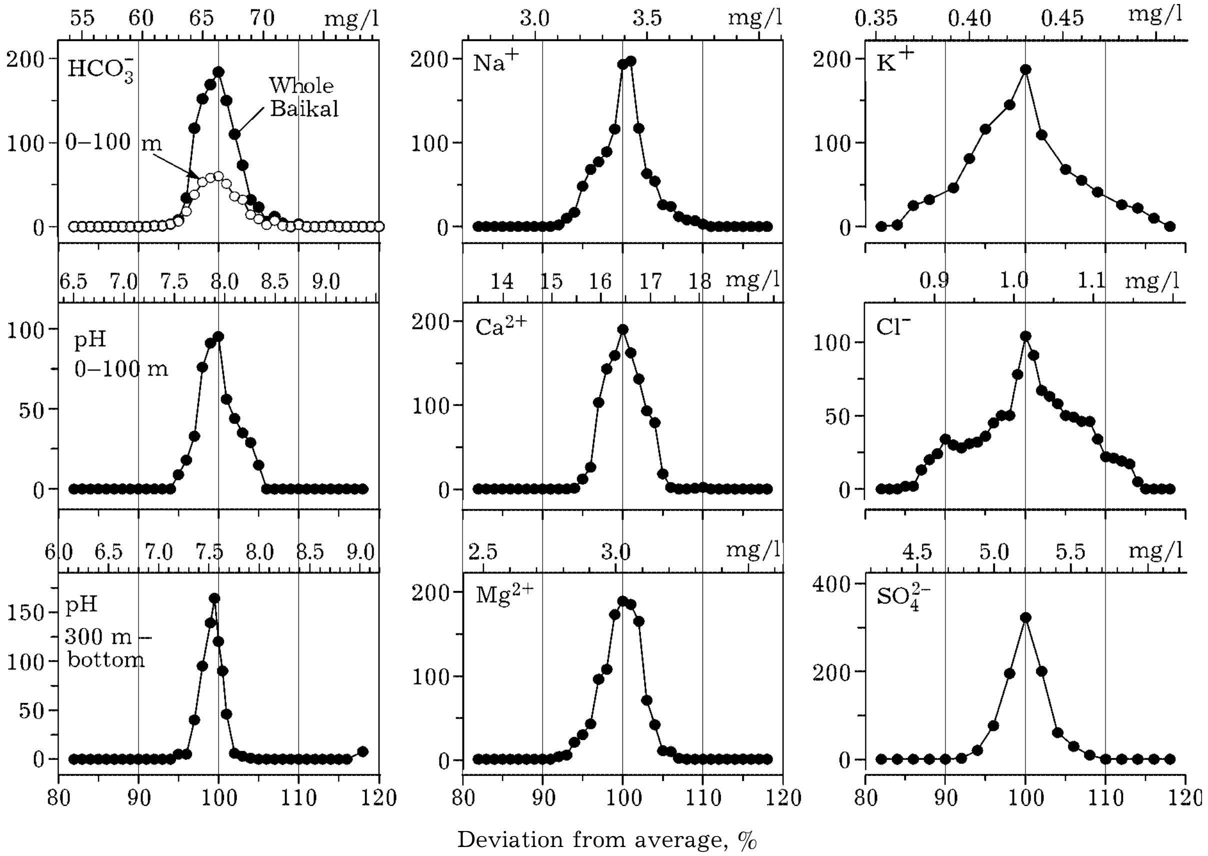

Fig. 4. Distribution of the hydrochemical characteristics of Baikal water at different depths in three hollows. Y axis – the number of values from the stated range; X axis: top – concentrations, bottom – concentrations (in %) of the average provided that the average is 100 % for each characteristic.

are interdependent. The sum of the mole equivalents of cations in solution must equal that of anions because if there is a disbalance, the solution would acquire an electric charge. Regretfully, many hydrochemical laboratories do not think it important to calculate the cation-anion balance from their data, although this is the simplest method of preventing gross errors of personnel. The ion balance in [11] coincides to an accuracy of about 1 %.

If one admits that fluctuation of hydrochemical data is not the result of measurement errors, but is a real reflection of salt impurities, then the fluctuations of concentration for definite anions should correlate with those for certain cations. However, no such correlations have been found by Falkner *et al.* [11]. This is illustrated by Fig. 3, showing a correlation between the potassium (main cation) concentration and alkalinity (measure of content for the main anion – bicarbonate) and also a correlation between the concentrations of the sulphate and sodium ions. The latter would have taken place if the fluctuations of the concentrations found had reflected the anthropogenic contamination of Baikal with sodium sulphate. Therefore, the most natural conclusion lies in the fact that within the limits of ±1 % there are no real fluctuations of cation and anion concentrations in Baikal waters, and that the dispersion of these values beyond the limits of 1 % is just a measurement error.

LAST YEARS FIELD DATA

A similar conclusion may be made on the basis of the results obtained by the members of the Limnological Institute, SB RAS, in studies of Baikal at many stations in three hollows, at all depths (Fig. 4).

For alkalinity and Na^+, Ca^{2+}, Mg^{2+} and SO_4^{2-} concentrations, dispersion is mainly limited to ±5 %. The statistical error of measurement of K^+ and Cl^-, whose concentrations are very low, is considerably larger.

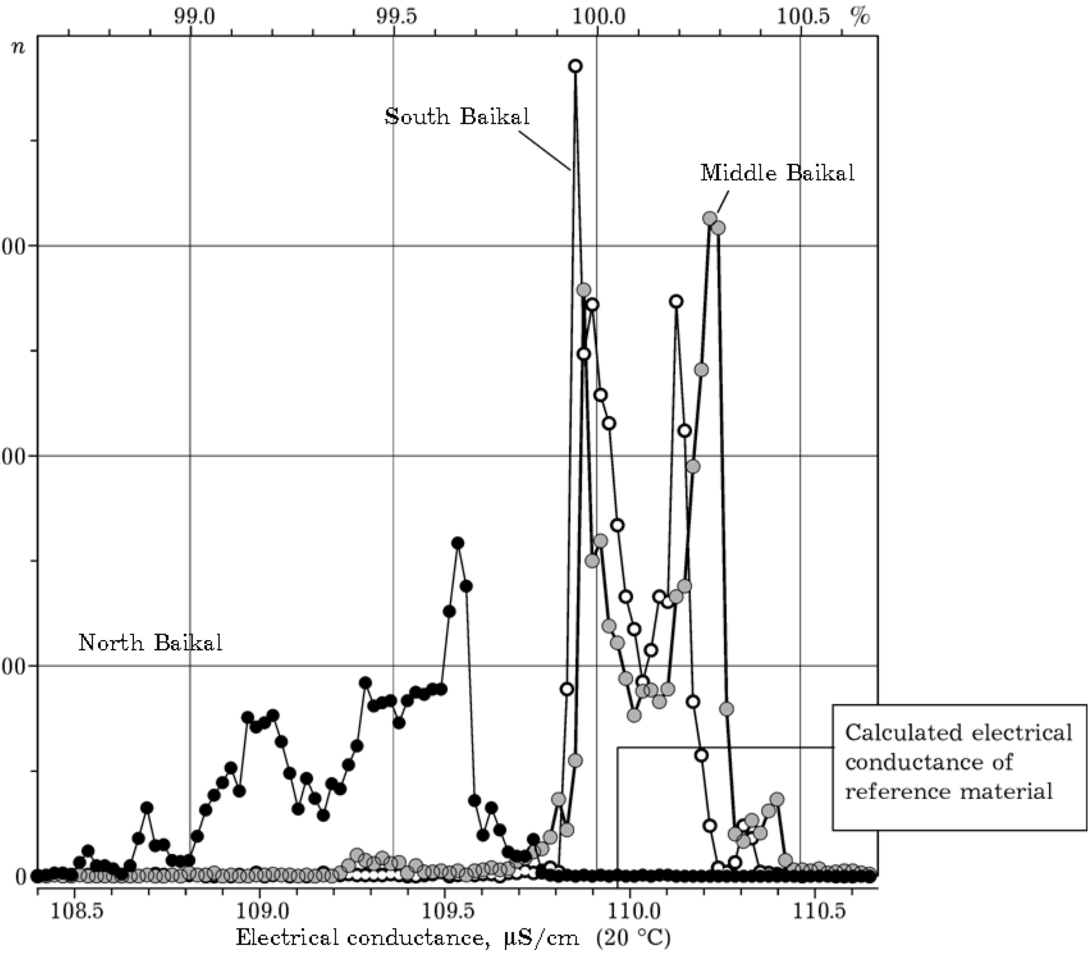

Fig. 5. Distribution of electrical conductance of Baikal water brought to 25 °C and atmospheric pressure (data of [5]) with an assumption that the average conductance equals the theoretical value obtained from ion concentrations, 109.9 μS/cm (*n* is the number of measurements that gave the values in the ranges indicated on the horizontal axis).

The difference between pH of the upper layer of the Baikal water (0–100 m, average value 7.95) and that of the depth water (300 m – bottom, average value 7.65) is 0.3. In our opinion, this may be accounted for, firstly, by the amount of carbon dioxide spent on photosynthesis, and secondly, by slow exchange of depth waters with those of the surface, which takes about 10 years [2]. Indeed, when pH increases by 0.3 units, 1.5 mg/l of carbon dioxide is spent on photosynthesis in the Baikal water. The difference between the total concentration of the solute inorganic carbon in the surface and depth waters amounts to 2.5 % and could not be detected by alkalinity measurements by means of titration with an indicator: the error of this method is too high, 5–7 % (see Fig. 4). As for the bicarbonate assay technique using HPLC (high-performance liquid chromatography) [12] widely employed for characterizing the pilot lot of reference material (see below), it is actually applied to all forms of the solute inorganic carbon, but not to the given anion. This technique could ensure the required accuracy; however, when using it, one has to take care to prevent a change in the concentration of the solute inorganic carbon after sampling (before analysis), which can take place due to the contact between the sample and the atmosphere, or due to the oxidation of the dissolved organic matter by bacteria.

SALT CONTENT MEASURED WITH AN OCEANOLOGICAL CTD PROBE

Distribution of the electrical conductance (EC) of water from three hollows of Baikal is

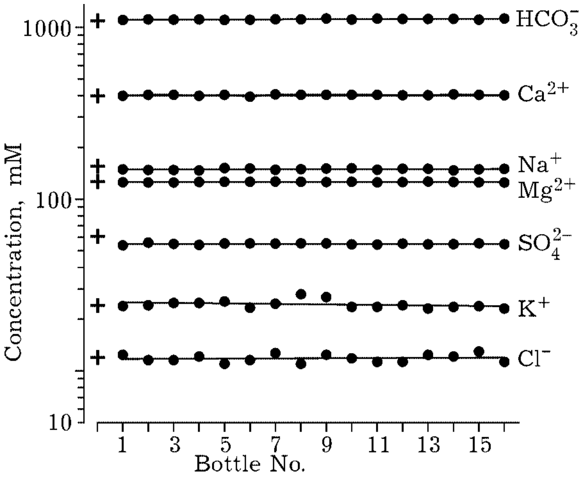

Fig. 6. Results of analysis for 16 samples of reference material – depth water of Lake Baikal (the method is described in the Experimental Section). Crosses indicate average values for the whole Baikal.

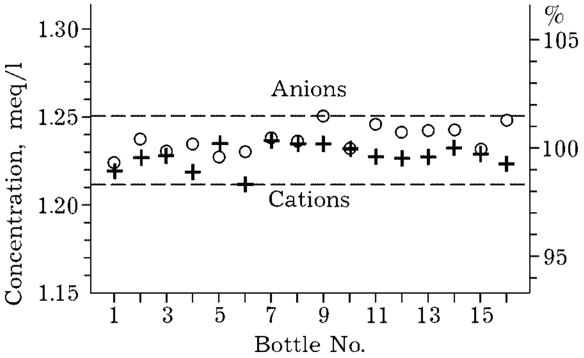

Fig. 7. Anion and cation concentrations found for specimens from the pilot lot of reference material.

demonstrated in Fig. 5. One can see that the EC of water from the northern part of Baikal is significantly lower than the EC for the middle and southern parts. There are significant differences in EC also for waters of each hollow. These are real differences associated with differences in the salinity of waters and affecting the density and movement of Baikal water masses [2–5]; however, their discussion is not the subject of the present work. In South Baikal water (see Fig. 5), the range of values is (100 ± 0.2) %.

A natural hypothesis following from the EC data seems to be that the ion concentrations in the depth waters of South Baikal are also constant within the limits of ±0.2 %. This hypothesis cannot be considered to be strictly proved, but it can be disproved only with the help of very accurate methods of direct assay for each main ion. As for the conventional hydrochemical methods, the depth water of South Baikal can be considered to be a *natural reference material* of an unknown but constant composition which will not change within the next decades. This is not a new idea; in 1983 it was proposed that the hydrochemical laboratories engaged in Baikal studies should be intercalibrated in joint expeditions using the same samples collected from the lake [1]. However, this

TABLE 1

Characteristics of reference material and data of [11] for South Baikal

Characteristic	Reference material*		Falkner *et al.* [11]	
HCO_3^-	(68.50 ± 0.47) mg/l	(1.116 ± 0.0077) meq/l	(66.79 ± 0.41) mg/l	(1.095 ± 0. 0065) meq/l
Cl^-	(0.420 ± 0.022) mg/l	(0.0118 ± 0.00062) meq/l	(0.447 ± 0.035) mg/l	(0.0126 ± 0.001) meq/l
SO_4^{2-}	(5.27 ± 0.05) mg/l	(0.1097 ± 0.00101) meq/l	(5.52 ± 0.03) mg/l	(0.115 ± 0.003) meq/l
Na^+	(3.44 ± 0.035) mg/l	(0.149 ± 0.0015) meq/l	(3.61 ± 0.06) mg/l	(0.157 ± 0.003) meq/l
K^+	(0.95 ± 0.05) mg/l	(0.0244 ± 0.0014) meq/l	(0.94 ± 0.05) mg/l	(0.024 ± 0.0012) meq/l
Ca^{2+}	(16.14 ± 0.13) mg/l	(0.806 ± 0.0063) meq/l	(16.10 ± 0.03) mg/l	(0.806 ± 0.0015) meq/l
Mg^{2+}	(3.03 ± 0.13) mg/l	(0.248 ± 0.0011) meq/l	(3.01 ± 0.04) mg/l	(0.2512 ± 0.002) meq/l
S_c	0.0977 g/kg		0. 0964 g/kg	
Concentration:				
anions		(1.224 ± 0.008) meq/l		(1.223 ± 0.010) meq/l
cations		(1.228 ± 0.007) meq/l		(1.238 ± 0.008) meq/l

*pH 7.62 ± 0.05, EC (25 °C) = (120.6 ± 0.26) μS/cm.

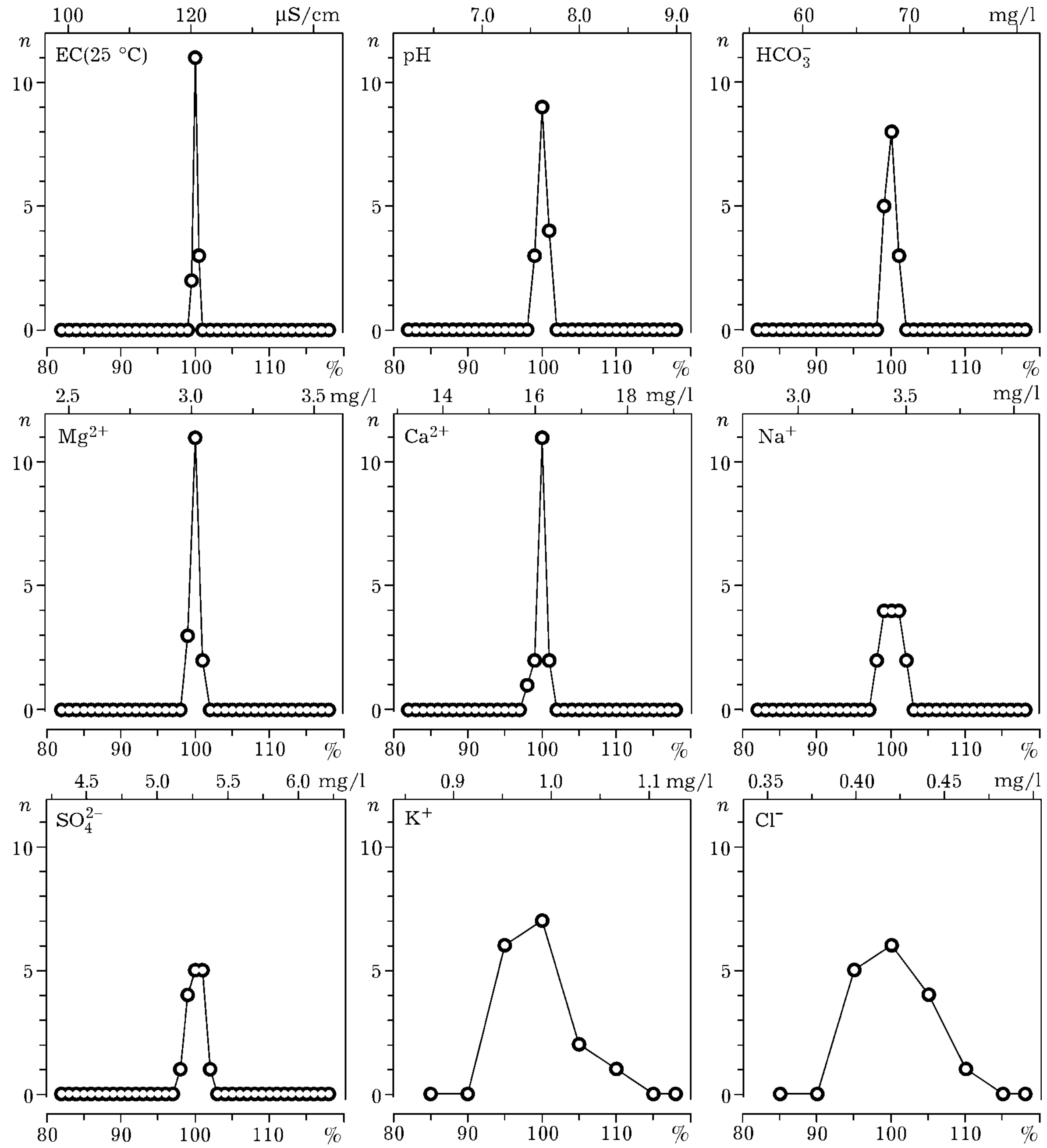

Fig. 8. Results of analysis for 16 samples of reference material. Y axis – the number of results corresponding to the values indicated in the plots; X axis: top – the found values, bottom – concentrations (in %) of the average provided that the average is 100 % for each characteristic.

cannot be practised for laboratories unable to take part in Baikal expeditions and for those using equipment that cannot be installed on board. In order to use Baikal water as a natural reference material, it is necessary to develop methods for sampling, filtering, weighing, and sterilizing large amounts of water to ensure the constancy of its composition during storage. These technologies are described in the patent [13] and in publications [14, 15] (the latter were published without a notice to executor analysts and contain some inaccuracies).

PILOT LOT OF REFERENCE MATERIAL

Drinking depth water of Baikal is produced according to the technology patented by the Limnological Institute [13]. By this technology

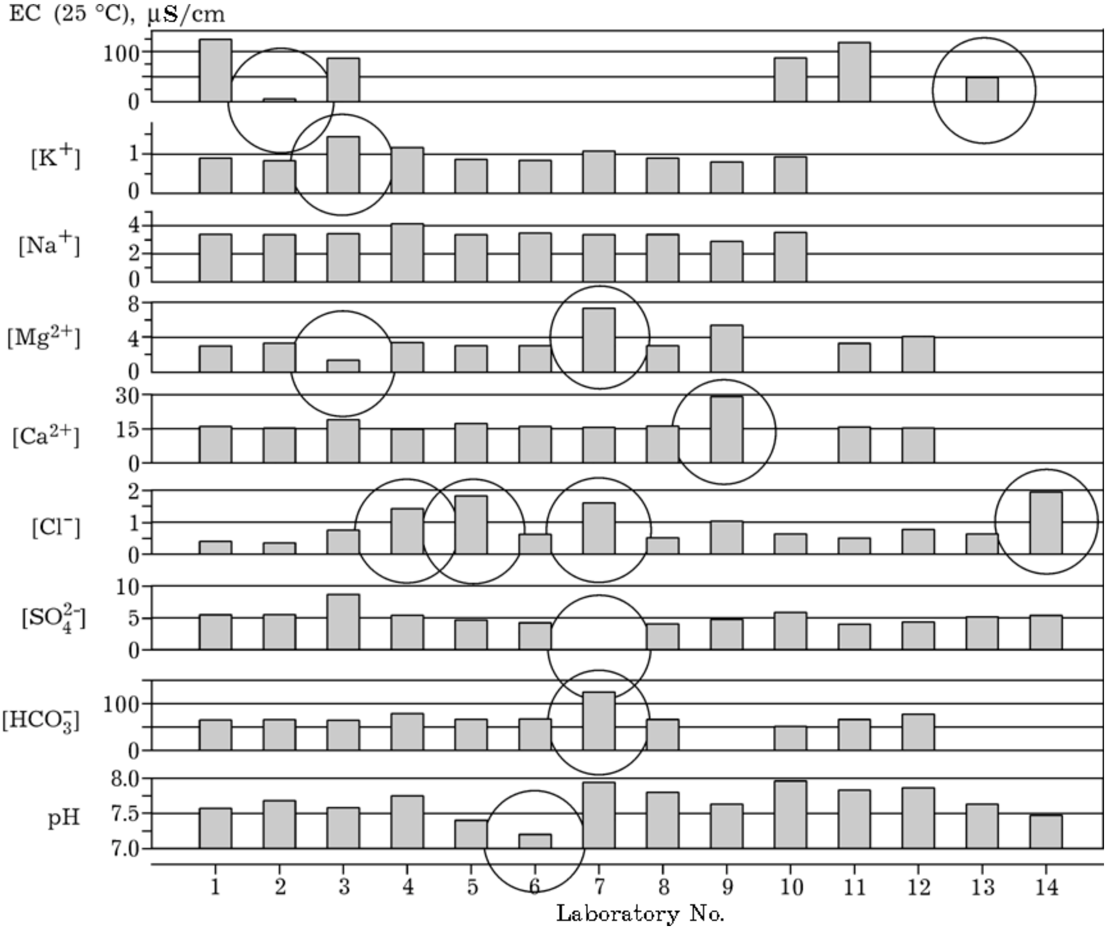

Fig. 9. Results of intercalibration of hydrochemical laboratories with respect to the reference material. Y axis − ion concentrations, mg/l; circles mark gross errors.

described in detail in [14], a pilot lot of depth water of South Baikal was produced as a reference material. The water was collected in July 2001, and the lot included 2000 bottles stored at room temperature. Microbiological analysis of water from randomly selected lot bottles showed that living microorganisms (the total microbial number, coli index, thermotolerant Escherichia coli) were absent 48 h and 16 months after the lot had been prepared. The results of our analysis of randomly chosen specimens from the pilot lot are shown in Figs. 6−8 and in Table 1.

The characteristics of the reference material hardly need any comments. As one would expect, the least dispersion was characteristic of conductance and pH data, and the greatest scatter of data is observed for the concentrations of ion minorities. The sum of cation and anion concentrations for each specimen converged within the limits of ±1.5 % (see Fig. 7). Data on the reference material have no systematic deviation from the data of Falkner *et al.* [11], except the sulphate concentration which was 4.5 % lower according to our data. The conductivity of the reference material calculated from our data on ion concentrations (as described in [5]) was 109.96 µS/cm for 20 °C. For Baikal water, the same quantity was calculated [5] from the data of Falkner *et al.* [11], and it was reported to be 109.91 µS/cm.

INTERCALIBRATION

Samples from the pilot lot of reference material were sent out to several hydrochemical laboratories with accompanying letters inviting them to participate in intercalibration and asking them to estimate the amounts of the main ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, HCO_3^{-}, Cl^{-}), pH and conductance (three bottles sent to each laboratory). The letters indi-

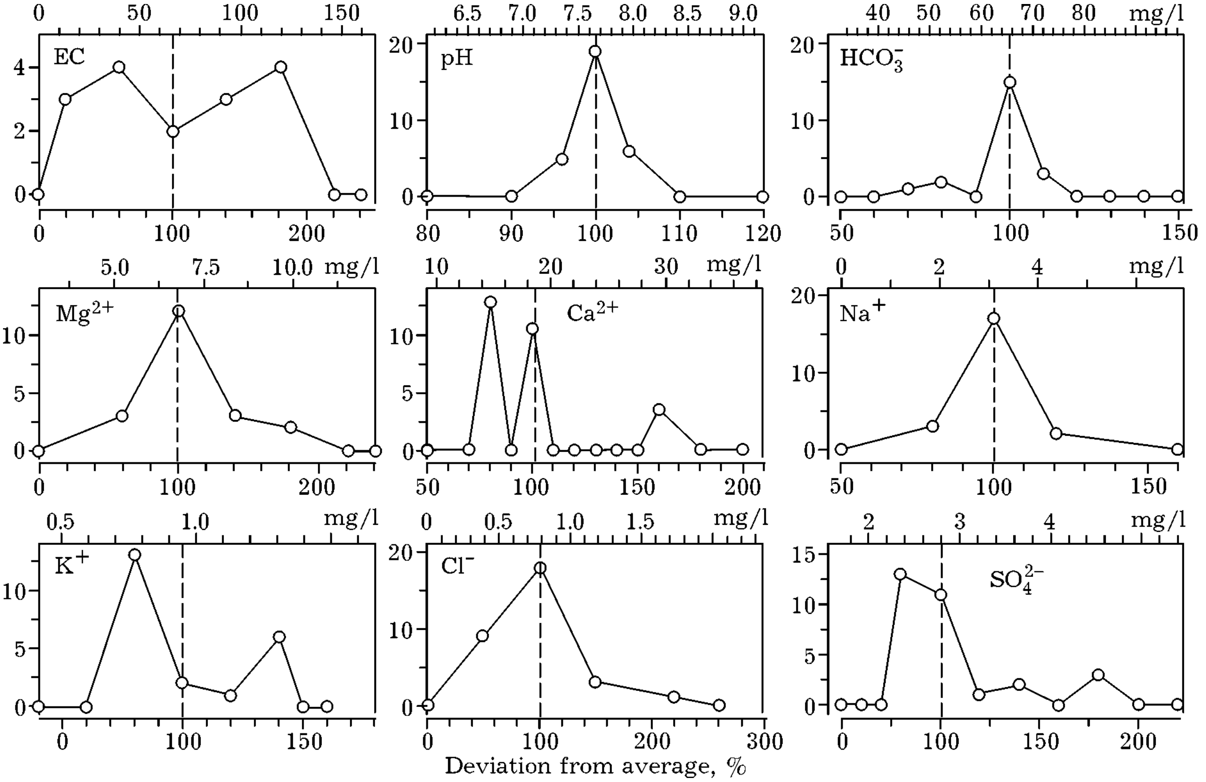

Fig. 10. Statistical analysis of intercalibration data. X axis: top – concentrations found, bottom – concentrations (in %) of the average provided that the average is 100 % for each characteristic (vertical dash line); Y axis – values from the stated ranges.

cated that the object of intercalibration was Baikal water. All the laboratories presented their results on official forms, and many sent copies of their State accreditation certificates and references to State standard documents approving the analytical methods. The work was mostly paid at common prices. Each participant laboratory was assigned a number; ours was No. 1. When the experiment was over, every participant laboratory received an anonymous (not naming other laboratories) summary report of data obtained by other participants.

The results of intercalibration are shown in Figs. 9 and 10. One can see that the situation in the system of hydrochemical laboratories was not satisfactory. Many of them committed gross errors. Analysis of the normative documentation demonstrated that the laboratories sometimes had no right to present particular indices; all they had to do was to indicate that the index was below the detection threshold. One of these indices was the content of the chloride anion, which in many cases was assayed by the mercurometric technique [16] whose detection threshold is 2 mg/l. All the laboratories that used this method were to indicate the result as "<2 mg/l" but not to give the particular value below this limit. Some laboratories were not alerted by the disbalance between anions and cations nor by the absolutely unrealistic values of conductivity. Figure 10 shows the results of the statistical treatment of intercalibration data. One can notice large deviations from the normal distribution law. This fact, together with the above mentioned ones, witnesses either personnel's errors or to considerable systematic errors of the methods.

EXPERIMENTAL

Water samples from Lake Baikal were collected by the members of the Institute using Nansen deep water bottles at 20 stations (6–7 stations in each hollow) during different seasons of 1995–2001. Sampling was made from the standard horizons: 0, 25, 50, 100, 200, 300, 400 and deeper, every 100–200 m to the bottom. Water samples for estimating anion and cation concentrations were stored in polypropylene containers placed in a refrigerator.

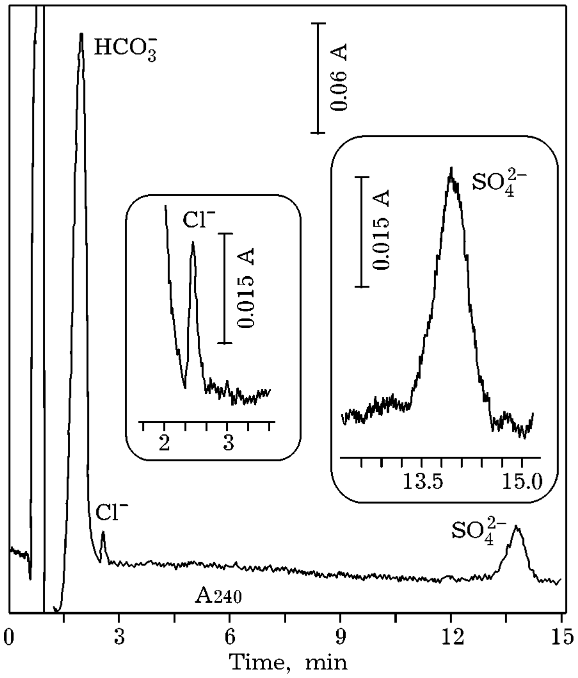

Fig. 11. Chromatogram of Baikal water.

pH measurements

Field measurements of pH were carried out on board immediately after sample collection, using the potentiometric method on a pH81 Yokogawa (Japan) field device with a combined electrode and a thermocompensator [12].

For pH measurements of the standard samples of Baikal depth water at Institute laboratories, we used a stationary Horiba F-21 (Japan) pH meter, also with a combined electrode. The sample temperature was brought to 25 °C in a water bath. For the given instruments, the error of the method was ±0.02 units.

Electrical conductance estimations for Baikal waters

To study the mechanisms of stirring for depth waters of Baikal, high-precision immersion oceanological probes have been used since 1988 for continuous parallel measurements of electrical conductance, temperature and pressure (depth) on the vertical sections. The CTD probes are well certified metrologically and have a very high sensitivity: they easily record changes in electrical conductance within several hundredths percent. The conductivity function is corrected [5] for changes in pressure using the average conductance estimated from the ion composition of Baikal water (data of Falkner *et al.* [11]). Profiles of this type were obtained using an SBE-25 Sea Bird Electronics probe during one expedition of 2001 at 44 stations distributed all over Baikal and were depth averaged with a pitch of 2 m.

Electrical conductance of reference material was measured at the Institute laboratory on a Horiba DS-12 (Japan) device with an error of ±0.02 μS/cm [16]. The sample temperature during measurement was brought to 25 °C using a water bath. Non-observance of this condition (which takes place quite often) can lead to great errors, despite the presence of a temperature compensator built in the instrument.

Determination of main anions

Determination of bicarbonate, sulphate and chloride ions was carried out by the HPLC method with indirect UV detection. The anions are separated on a column with an inverted phase dynamically modified with octadecyltrimethylammonium bromide. Analysis was carried out according to [12] . The sample volume was 30 μl. An example of chromatogram is shown in Fig. 11. The solutions of the Kanto Chemical Co. (Japan) were used as standards. The measurement error was 5–10 % for different anions.

In reference material specimens, bicarbonates were determined by HPLC; during field measurements, analysis was performed immediately after sampling by direct titration with HCl in the presence of methyl orange [17].

Determination of basic cations

The Ca^{2+} and Mg^{2+} contents in the Baikal water and in reference specimens were determined by the atomic absorption method [18]. In this method, resonance light absorption by free calcium and magnesium atoms is measured. Light is transmitted through the atomic vapor of the sample formed in air-acetylene flame, and its resonance absorption is determined. Calcium was detected at a wavelength of 422.7 nm, and magnesium at 285.2 nm. Full cathode lamps were used. The K^+ and Na^+ concentrations were estimated by the flame emission method [18] in which absolute emission intensity of potassium and sodium is measured at resonance bands of 589.0 (Na) and 766.5 (K) during excitation in acetylene – air flame. The solution atomization rate was 6–8 ml/min for all elements. Prior to estimation of a sample, the water was acidified with concentrated HNO_3 (ultrapure grade) taken in amounts of 20 μl per 20 ml of the sample. The graduation solutions prepared from the reference samples of Kanto Chemical Co. (Japan) were also acidified. The measurement error was 3–5 % for basic cations.

CONCLUSION

The above presented data convince us that using the depth water of South Baikal as reference material is very helpful in improving intralaboratory control both in Russia and worldwide.

Acknowledgements

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