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Determining surface water and bed sediment quality of Lake Kopa

Kopa Gölü'nün yüzey suyu ve yatak sediment kalitesinin belirlenmesi

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Abstract

In this research, the results of a hydro-chemical study of Lake Kopa in Kazakhstan are described, in the context of the regional geography and aggravating ecological problems of the lake. Besides analyzing the concentrations of all major ions, heavy-metal ions and other pollutants, their vertical and horizontal distribution were also assessed. Moreover, water pollution indices (WPI) were calculated for individual ions, classes of pollutants, and total pollution, revealing serious overload of human-induced pollution within the lake's ecosystem. Concentrations of major ions and WPI were monitored over 2009-2013 period, revealing a distinct seasonal pattern and a multi-year periodicity in respect to the measured parameters. In addition, studying ion exchange between lake water and bottom sediment showed complex non-equilibrium processes besides leaching out Ca2+ and its exchange for Na+.

Özet

Bu araştırmada, Kazakistan'ın Kopa Gölü'nde yapılan hidro-kimyasal çalışmanın sonuçları gölün bölgesel coğrafyası ve ciddileşen ekolojik sorunları bağlamında anlatılmıştır. Tüm majör iyonların, ağır-metal iyonlarının ve diğer kirleticilerin yoğunluklarının analiz edilmesi yanında, bunların dikey ve düşey dağılımları da irdelenmiştir. Bununla beraber, su kalitesi indisleri (water quality indices-WPI) kullanılarak her bir iyon, kirlilik sınıfları ve toplam kirlilik üzerinde yapılan hesaplamalar, göl ekosisteminde insan-kaynaklı ciddi bir fazla yük kirliliği olduğu ortaya çıkarmıştır. Majör iyonların konsantrasyonları ve su kalitesi indisleri (WPI) 2009-2013 periyotu boyunca izlenmiş ve ölçülen parametreler için belirgin bir mevsimsel desen ile çok yıllık periyodiklik olduğu açığa çıkmıştır. Ayrıca, göl suyu ve yatak sedimenti arasındaki iyon alış-verişinin araştırılması, Ca+2'un yıkanması ve Na+ ile değişimi yanında karmaşık dengesizlik süreçleri de göstermiştir.

INTRODUCTION

Studies of the quality of natural waters are urgently needed for both ecological science and practical water security (Romanova et al, 2013). Environmental systems, including lakes can respond to various man-made pressures in widely different ways, displaying different degrees of robustness and abilities to recover. Ultimately, the entire evolution of a system can be irreversibly directed along a different path. Hence it is crucial to monitor, in real time, the hydro-ecological effects of human impact on water basins and to reveal their mechanisms timely. This can be achieved principally by surveying the entire ecosystem in its integrity and the feedback between natural and economic factors.

The subject of the present study is the hydrochemical processes in Lake Kopa in Kazakhstan, with their hydroecological and socio-economic implications. The problems of the lake attracted attention rather recently, due to pending use of the lake as a source of drinking water for nearby settlements. They were mainly discussed in mass media; there being no comprehensive scientific research of the hydrochemical regime and water quality since 1993. In fact, it is increasingly doubtful whether Lake Kopa can be maintained in its current state for the requirements of developing economy. Dropping of the water level, rising salinity and pollution cause environmental degradation and endanger the lake's use as a water supply source, regarding both quantity and quality of water. For a long time the lake is under direct human impact. Nowadays these ecologic problems are of already region-wide (Kalashnikov 2004; Mustaphina 2005; Khusainov 2005; Shaukharbayeva 2008; Mukhamedzhanov 2008). The aim of our study is to identify hydro-ecological effects of human impact on Lake Kopa, with the practical purpose of developing science-based recommendations and measures to remedy the lake's ecological problems under conditions of fluctuating water level. To achieve this, it was necessary (i) to explore the present hydrochemical regime of Lake Kopa and single out the main factors influencing it, (ii) to evaluate the water quality status by chemical analysis and calculate the pollution index, (iii) to measure oil contamination of water, (iv) to explore the feedback between the lake-bed sediment and the polutants in lake water, and (v) to determine the dynamics of the lake surface area over several years, using the data from Earth Remote Sensing (ERS) and Geo-Information Systems (GIS). Some preliminary results have been published elsewhere (Romanova and Kazangapova 2013).

Figure 1 Lake Kopa, view from the south-western shore. Crosses indicate the places where water samples were taken

MATERIALS AND METHODS

In 2009-2010 we undertook 6 field expeditions and carried out 6 hydrochemical surveys of the lake area, taking *ca.* 100 samples of lake water for chemical analysis, at three different locations (Fig. 1). The daily variation of the water chemical composition was monitored by taking samples every 2 hours for 48 hours. To reveal the vertical distribution (stratification) of admixtures, the water samples were taken both from the surface layer (up to 0.5 m depth) and from the bottom layer (within 0.5 m from the bottom), using a Molchanov bathometer GR-18. The bottom sediment were sampled using a Petersen grab or DCh-0,025 sampler. To ensure statistical reliability (Charykov 1984), we explored first the variations of the bottom sediment composition by taking 30 samples at equal distances, covering the entire area of the lake, within the upper 30 cm layer of the bottom where the highest variability can be expected. Each sample was analyzed for absorbed bases, HCO_3^-, CO_3^{2-}, dry residue content and pH of the aqueous extract. Of these, HCO_3^- showed the highest variability, which was therefore used to calculate the number of repeated measurements required to determine this ion with 0.001% (per soil weight) precision at 95% significance. This number varying from 9 to 16 at different points, the final sampling was carried out with 16 repetitions at random points over the lake area. The samples taken at the same depth at different points, were thoroughly mixed.

The sediment was analyzed according to Arinushkina (1961). Air-dried samples were ground and sifted through 1 mm sieves and stirred for 3 min with bidistilled degassed water in 1:5 ratio (adjusting the sample weight for remaining moisture), which was filtered. Exchangeable bases were determined using gypsum extract. The description of sediments are based on the classification of Bazilevich et al. (1985). Labile forms of heavy metals in sediments were determined according to Rin'kis (1983) and their gross content by quantitative spectral analysis.

In accordance with the Methodical Recommendations (2010), the pH and unstable admixtures (HCO_3^-, CO_3^{2-}, NO_2^-, NH_4^+, oxidability, O_2, CO_2) were determined immediately after the sampling, other admixtures in the laboratory on the samples stabilized by suitable reagents. The admixtures were analyzed by standard hydrochemical methods recommended by Pashkov et al (1997), Romanova (2007), and Unified Methods (1987). Chlorides were defined by volumetric argentometric method, sulfates by gravimetric method, hydrocarbonates and carbonates by volumetric acidimetric method, calcium by titration with Trilon B solution in the presence of Murexid indicator, magnesium and total hardness by titration of the sample with Trilon B solution in the presence of black chromogen indicator, sodium and potassium by the method of flame photometry, oil products by gravimetric method (GOST, 2011), pH values and oxygen content in water by electrometric method. The content of heavy metals was measured by ICPCHEM/ICPSETUP method (sensitivity up to 10^{-8} - 10^{-9} mg/l). Every sample of water was analyzed at least in triple; variation of the results shows statistically meaningful dispersion comparable with usual instrumental errors. For the later period (2011-2013), the concentrations of admixtures in lake water (in breach of permissible levels), were taken from the Environmental Information Bulletins of Kazakhstan, which used similar standard approach.

The quality of surface waters was quantified using the Water Pollution Index (WPI), the approach developed by the group of Kazakhstani environmental scientists headed by academician M. Zh. Burlibayev and adopted by the Ministry of the Environment of Kazakhstan in March 2003 (Burlibayev 2007). The method is used by organizations reporting directly to the Water Resources Committee of Kazakhstan, as well as many scientific-industrial bodies and higher education institutions. In this method, all pollutants are classified into six groups, viz.

- major ions: Ca^{2+}, Mg^{2+}, $Na^{+}+K^{+}$ (sum), SO_4^{2-} , Cl^{-}, etc.;
- biogenic species: NH_4^{+}, NO_2^{-}, NO_3^{-}, P (total), phosphates, Si, etc.;
- heavy metals: Cu, Zn, Pb, Cd, Cr^{3+}, Cr^{6+}, Mn, Hg, Hg^{2+}, Ni, Co, Sn, Bi, Mo, Fe^{2+}, Fe^{3+} , etc.;
- toxic agents: CN^{-}, SCN^{-}, F, H_2S, As, nitrobenzene, etc.;
- organic matter: oil products, gums, carbohydrates, fats, phenols, synthetic surfactants, etc.;
- chloroorganic pesticides: DDT, DDD, DDE, HCCH, sevin, yalan, dicofol, hexachloro-benzene, etc.

The WPI is calculated separately for each (*j*-th) group by Eq. 1,

$$WPI_j = (\sum_{i=1}^{n} C_i / MPC_i) / n \qquad (1)$$

where C_i is the actual concentration of an *i*-th pollutant in the *j*-th group and MPC_i is its maximum permissible concentration (both in mg/l), *n* is the number of pollutants of the *j*-th group, present in the water sample. Note that for an individual admixture, WPI is simply the ratio of its concentration to MPC. Water quality can be described by seven WPI bands (Table 1).

Satellite images are obtained from Google Earth Professional, as high-resolution photographs by Digital Globe Co. from the Ikonos, WorldView-1 and Quick Bird satellites, and were processed using ENVI 4.8 software package. The lake surface area was measured using ESRI (USA) and ArcGIS 10.1 software.

Table 1 WPI bands as criteria of surface water quality

Water quality level (WQL)	Water quality description	WPI
1	Highly pure	≤ 0.3
2	Pure	0.31 – 1.0
3	Moderately impure	1.01 – 2.5
4	Impure	2.51 – 4.0
5	Polluted	4.01 – 6.0
6	Highly polluted	6.01 – 10.0
7	Extremely polluted	> 10.0

GEOGRAPHICAL SETTING

Geographical conditions of the region.

Kopa (Fig. 1) is a typical continental lake of the arid zone (see Lavrenko, 1964; Statistical Data, 2009). Kazakhstan is the least watered country in Central Asia; most of its 48,000 lakes (all but 270 of which are less than 10 km^2 in area) are closed lakes (endorheic basins), i.e. have no regular outflow of water. Due to natural climatic trends and economic activity, freshwater lakes tend to salinate, periodically dry up, or even completely disappear, as shown by Vesyolov (2000), Malkovskii et al (2007), and Ryabtsev (2008). Lake Kopa lies near the foot of the Kokshetau Elevation in the Akmola Province, in north-central Kazakhstan, which has the highest concentration of natural water bodies in the country. The south-eastern shore of the lake is occupied by the town of Kokshetau (population 150,000).

Geographical conditions of Lake Kopa

Lake Kopa is 5.3 km long and 3.6 km wide, with the average surface area of 13.95 km^2, which (according to our survey of satellite photographs) is practically unaltered since 2004 (Fig. 2) and close to the 1992 estimate of the Ecological Department of the Akmola

Province (13.6 km^2). However, the depth and water volume of the lake progressively decreases due to silting-up, as the satellite images clearly show (Fig. 2). The bottom is smooth, miry, covered by a layer of clay and loam mud or sand with mud of 0.5 to 2.8 m depth, up to 6 m (in the northern part). The average depth is approximately 2 m while the maximum depth can be up to 3.1 m. Due to shallowing of the lake and the resulting stronger solar irradiation and warming of the water, increasing pollution by sewage and agricultural fertilizers washed into the lake, the water vegetation is encroaching intensely upon the open water area and already covers approximately 50% the lake, whereas previously it was confined to a reed bed of 0.3-1.0 km width and a rush bed of 300 m average width along the western and northern shores (Kalashnikov 2004).

The lake is fed by two rivers, the Chaglinka (by far the larger) and the Kylshakty. The spring flood of the rivers is usually violent and lasts for 20-40 days. By mid-June and spring-autumn, stable and low-water conditions, respectively, are established, which last until ice forms in winter. The water level can rise by 1.0-1.5 m from intense rains which, however, are rare (once in 5-10 years). Spring ice-flow is a rare phenomenon, which does not occur every year. In exceptionally high-water years ice-drifting is intense and is accompanied by massive ice-jams at meanders. In winter (late December to early January) the river freezes down to the bottom, apart from some pools and the vicinity of underground springs. The Chaglinka flows out of the lake on the northern side. In dry years the lake intercepts all the water from the upper river, hence in summer the lower Chaglinka dries up into isolated pools. In wet and medium years, the lake overflows into the river, maintaining a continuous flow throughout the summer. The water mineralization of the upper Chaglinka during spring flood ranges from 20 to 60 mg/l and hardness from 1.5 to 6.0 mg-mole (i.e. soft to moderately hard). The ionic composition is characterized by prevalence of HCO_3^- (40-22 mol.%) and Ca^{2+} (30-21 mol. %) ions, more rarely Na^+ (28-21 mol. %); drinking quality of the water is good. On the river there are several earthen dams. The water is used for drinking, watering of cattle and for basin ('liman') irrigation (Batalov, 1999; Ryabtsev, 2008).

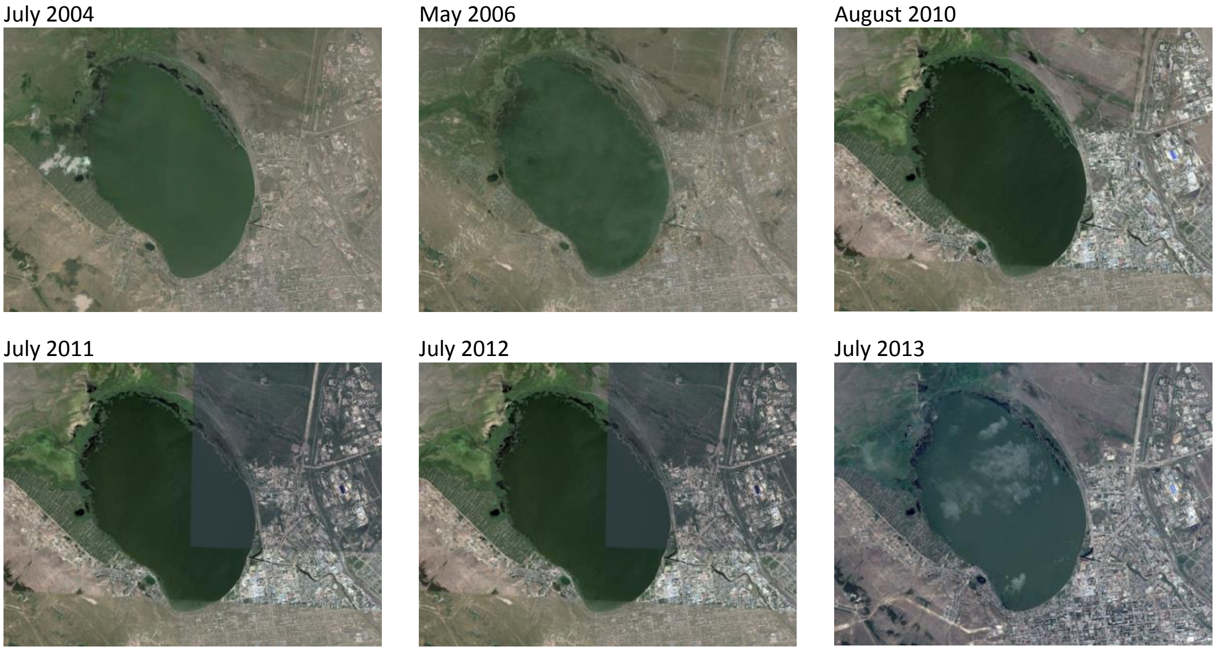

Figure 2 Satellite images of Lake Kopa and vicinity. The corners correspond to the coordinates: (1) 53°20′36″ N, 69°17′31″ E; (2) 53°20′20″ N, 69°26′01″ E; (3) 53°16′44″ N, 69°25′04″ E; (4) 53°16′54″ N, 69°17′47″ E.

Silting-up of the lake is intense. During a spring flood, ca. 20,000 m^3 p.a. (Khusainov, 2005) of silt and topsoil are washed down by tributaries and from the catchment area. Sedimentation critically reduces of the depth of the lake. In summer, this facilitates warming of the lake water and hence higher water losses by evaporation, as well as overgrowing of the lake with aquatic plants, whereas in winter (in low-water years) this allows the lake to freeze practically to the bottom. A survey of 2009, revealed the depth of silt layers from 0.5 to 2.2 m, with the total silt volume of up to 22 million m^3 (Department of Ecology 2011).

The unregulated tapping of lake water by businesses causes significant drop of the lake's water level in summer and its further evolution into a marsh. The only practical remedy appears to be a complete removal of silt deposits, which is still on the planning stage.

Hydrobiological processes in Lake Kopa.

In Lake Kopa, the zoobenthos is presented by larvae of dragonfly, diving beetle, and mollusks, with an average biomass of 26.1 g/m^2 (Serikova 2001). Zooplankton (daphnids, amphipods, rotifers) especially flourishes in spring. The species composition and biomass volume of zooplankton changes in a multi-year cycle. Zooplankton volumes were adversely affected by shrinking of the open lake surface and worsening hydrological and hydrochemical conditions.

The ichthyofauna includes perch, roach, ide, pike, zander, bream (an introduced foreign species, now well-acclimatised) and crucian. A regular annual fishery in the lake started in 1964, the catch consisting mainly of bream (80%). Abiotic conditions for fish habitation, water pollution and low oxygen levels hinder fish reproduction. Steady decline of aboriginal fish is explained by the prevalence of bream. The water level lowering year on year, suffocation of fish in the lake occurs annually, usually for perch, bream, ide and ruff. In 2001, a catastrophic fish suffocation occurred, involving perch, roach, ide, pike, zander, bream, and crucian (Serikova 2001).

The abundance of decomposing plant remains in the lake lowers oxygen concentration and thus depresses ichthyofauna, while high concentration of decomposition products (methane, suspended solids) adversely affect the sanitary and recreational quality of the lake.

RESULTS AND DISCUSSION

The observed organoleptic properties of the lake water are presented in Table 2. We found that the turbidity of the lake is higher in spring than in summer because of the turbidity index averaging 4.05 and 4.75 mg/l, respectively. The difference is due to the runoff caused by melting snow, bringing with it various insoluble and colloid particles of organic and inorganic pollutants from urban areas. Besides, the lake's main tributary, the Chaglinka River, is turbid (4.38-19.45 mg/l) throughout the year. Thus the concentration of suspended solids in the lake (26.20 – 31.10 mg/l) is well above the standard of 0.75 mg/l. Water transparency (in various years) ranged from 2.0 to 5.0 cm. Water smell is about 2-5 points, cf. the standard of 0 points. Water color varied from 165 to 325^0, cf. the standard of 35^0.

Table 2. Organoleptic properties of water in different parts of Lake Kopa.

Characteristics	Norm	Northern part	Southern part	Eastern part
Suspended solids mg/l	0.75	26.20	31.10	27.50
Floating solids present	no	yes	yes	yes
Transparency, cm	> 10	5.0	2.0	3.5
Smell, point	0	3 (obvious)	5 (strong)	2 (faint)
Colour, degree	35	165	245	325

The concentration of dissolved oxygen varied from 1.79 to 12.22 mg/l, averaging 7.01 mg/l over 2009-2013, which satisfies the standards for fishing purposes. Low oxygen levels are usually observed in spring. The biochemical oxygen demand over 5 days (BOD$_5$) varies in the range between 0.83 and 4.46 mg/l, with annual averages of 1.32 to 4.00 mg/l (see Figures 3 - 6). Lake water has weakly basic reaction with pH ranging between 7.48 and 9.27, with the all-season average of 8.39.

It is known that the presence of the major ions (HCO_3^-, CO_3^{2-}, SO_4^{2-}, Cl^-, Ca^{2+}, Na^+, K^+) in water defines the level and character of water mineralization. After the spring-flood filling of the lake, water mineralization increased from 0.61 to 1.44 g/l and its hardness decreased from 12.94 to

1.85 mmol/l eqv. With the average hardness of 8.25 mmol/l eqv, the lake water qualifies as medium-hard. The ionic content of water at present is characterized by strong prevalence of Na^+ (12.0 mmol/l eqv) and SO_4^{2-} (4.76 mmol/l eqv) ions. According to the Alyokin classification (Alyokin, 1970), Lake Kopa water belongs to the sulphate class, sodium group, type II, water index S^{Na}_{II}. Type II waters are mixed, as their composition relates to sediments from which various salts are leached.

Water chemical composition indices vary significantly over the lake basin in horizontal direction, as shown in Table 3. The alkali ions and sulphate concentrations are fairly constant across the lake, but those of carbonate, chloride, calcium and magnesium ions show very large variations. On the other hand, we did not observe vertical stratification of mineralization and major ions distribution, which can be explained by shallowness of the basin, aridity of the area, intense wind-driven mixing of water masses, and intense solar irradiation. Similar situation has been found in other lakes of Kazakhstan (Romanova 2008), in contrast to lakes of humid regions.

Table 3. Major ion concentrations (mg/l) and pH in different parts of Lake Kopa

Place of sampling	pH	$HCO_3^- + CO_3^{2-}$	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	Salts, total
1	7.42	209.8	1.8	230.5	122.4	46.3	276.1	9.5	896.5
2	9.40	72.6	52.2	227.0	20.5	10.6	275.1	9.6	613.2
3	8.36	298.9	90.3	229.8	106.5	90.8	275.7	9.7	1071.8
average	8.39	193.8	48.1	229.1	83.2	49.2	275.6	9.6	888.6

Note: 1-off the town beach (recreational area); 2-off Chapaev Street (urban area), 3-off the old airfield (brownfield site)

We have traced, for the first time, seasonal variations of the WPI on major ions (Figure 3) in a multi-year sequence, using the hydrochemical data for 2009-2013 and the improved calculation methods (Mal'kovskii et al, 2008). Over the studied period, WPI in winter varied from 1.65 to 2.65, which corresponds to the water quality level (WQL) 3 to 4, i.e. moderately impure to impure. In spring, WPI is at the lowest, 0.61 to 1.68 (WQL 2 to 3, i.e. pure to moderately impure), rising to 1.13–2.35 in summer (WQL 3 entirely) and to 1.44 – 3.74 in autumn (WQL 3 to 4). The annual average WPI increased from 1.44 in 2009 before stabilizing at 2.0-2.1 in the following years, hence the mean WQL is 3, or moderately impure. The all-season average WPI is 1.16 (WQL 3) for the whole of the lake; however, this parameter varies substantially across the lake, from 0.89 to 1.59, in line with general increase of water mineralization.

In a similar way, we analyzed seasonal dynamics of concentrations of individual pollutants over 2010-2013 (Figs. 4-7), which we found often significantly exceeding the maximum permissible concentration (MPC) limits for fishing water bodies. This applies especially to sulphates (268.5-406.3 mg/l, MPC=100 mg/l), magnesium ions (61.3-83.6 mg/l, MPC=40 mg/l), copper (3.4-4.8 µg/l, MPC=1.0 µg/l), chloride ions (238.5-457.6 mg/l, MPC= 300,0 mg/l) and manganese (0.039-0.076 mg/l, MPC=0.01 mg/l). Therefore, WPI>>1 (see Eq. 1). The oil products concentration was monitored throughout 2009, giving the maximum WPI=4.6 in the spring.

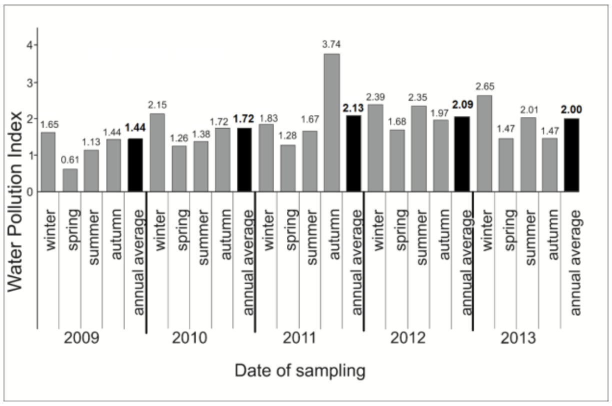

Figure 3 Seasonal WPI changes in Lake Kopa between 2009 and 2013.

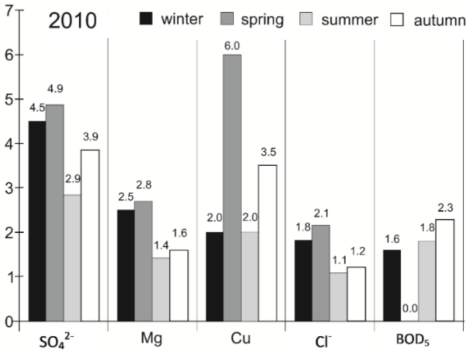

Figure 4 Seasonal changes of WPI, by groups of pollutants, in Lake Kopa water in 2010.

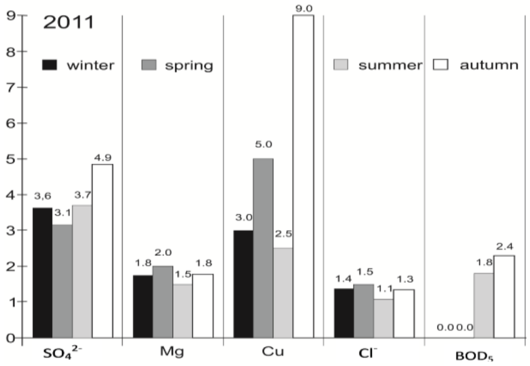

Figure 5 Seasonal changes of WPI, by groups of pollutants, in Lake Kopa water in 2011.

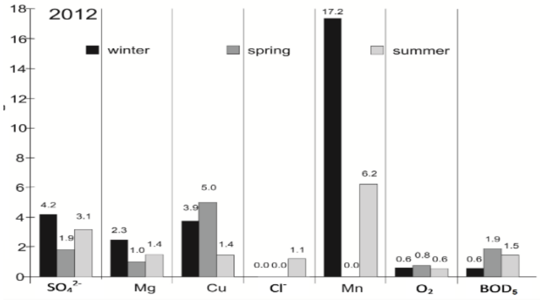

Figure 6 Seasonal changes of WPI, by groups of pollutants, in Lake Kopa water in 2012.

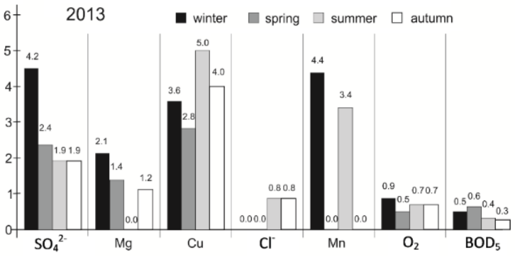

Figure 7 Seasonal changes of WPI, by groups of pollutants, in Lake Kopa water in 2013

Table 4 Metal concentrations in Lake Kopa water, µg/l

Sampling date	Pb	Co	Cd	Cu	Mn	Zn	Ni	Sr	Ag	Mo	Cr	Be
23.10. 2013	2.1	1.1	20.0	0.4	31.1	0.7	0.9	142	350	3.0	12.0	2.1
	2.3	1.3	10.0	0.5	31.0	40.0	1.2	71	345	3.1	11.8	2.0
	2.5	1.4	10.2	0.4	31.2	14.0	0.9	86	352	3.2	12.2	2.2
average	2.3	1.3	13.4	0.4	31.1	18.2	1.0	99.6	349	3.1	12.0	2.1
03.12. 2013	5.0	1.3	1.2	0.6	20.7	0.7	0.7	142	347	3.4	12.5	2.4
	2.5	1.0	1.5	0.4	20.6	14.6	0.9	140	335	3.1	12.4	2.4
	2.5	1.6	0.9	0.5	19.8	2.2	0.6	136	300	3.5	11.7	2.6
average	3.3	1.3	1.2	0.5	20.4	5.8	0.7	139	327	3.3	12.2	2.5
MPC	100	10	5	1	10	10	10	7000	50	500	500	0.2

Concentrations of heavy metals in the lake were analyzed in the autumn and winter of 2013 (Table 3). We found the absolute concentrations to decrease in the succession Sr > Ag > Mn > Zn > Cd > Cr > Mo > Pb > Be > Co > Ni > Cu in autumn and Sr > Ag > Mn > Cr > Zn > Pb ≈ Mo > Be > Co > Cd > Ni > Cu in winter. While concentrations of most metals were within normal limits (Methodical Recommendations, 1988), the MPC were exceeded in autumn for Zn, Cd, Mn, Ag and Be (WPI=1.8, 2.7, 3.1, 7.0 and 10.5, respectively), and in winter for Mn, Ag and Be (WPI=2.4, 6.5, 12.5). The main sources of this pollution are the industrial enterprises located within the catchment area, viz. the Altyntau PLC (gold-containing ore enrichment), Heating Network PLC and the diary-processing factory, whose wastewaters receive incomplete treatment and are often contaminated with mineral and organic substances, as well as rainstorm drains of the town of Kokshetau and overflowing septic tanks of private households.

Bed-silts as a defining factor of hydrochemical regime and water quality of Lake Kopa

We have studied the composition of the lake bed sediments, as well as the exchange of mineral and organic components between the sediments and lake water. The sediments in Lake Kopa, which are mostly silts of siltstone and clayey character saturated with organic matter (ca. 15 wt % of organic carbon), show weak to moderate salination of sulfate (with soda)/magnesium/sodium type and can be classified as solonchak (salt-marsh) or carbonate type, the carbonates content varying from 1.2 to 24.7%. Besides, exchange reactions between reduction products of mineral salts and end-products of organic matter decomposition, can yield hydrocarbonate salts, gypsum and other compounds. Exchange reaction between alkali metals sulfates and carbon dioxide, yielding soda, are also possible and obviously detrimental to the quality of lake water. These complex and diverse hydrochemical processes, including metamorphization, are overlaid by recurrent physical and hydrodynamic processes (concentration, dilution, intense mixing, floating, etc.), which further complicate their understanding. Besides, metamorphization processes in the water/silt system depend on kinetic factors, and hence on the duration of contact between solid and liquid phases, supply of inorganic and organic components in the silt, the ratio between the reacting surface of the sediments and the water volume, etc. The peculiar water balance (section 3.1) ensures that vast amounts of solids brought in by the rivers are trapped in the lake. Furthermore, due tofrequent dust-storms Lake Kopa receives large amount of solids, mostly clay and colloidal particles, by aeolian way (Information Bulletins, 2009). These solids must be taken into account considering the metamorphization of the chemical composition of the lake water.

To clarify these questions, we carried out an experiment on chemical dynamics in a water/sediment system. Simultaneously taken samples of lake water (mineralization 1.130 g/l, the Alyokin index S_{II}^{Na} , pH 7.05) and bottom sediment (moderate salinity, of sulphate-soda/calcium/sodium chemical type) of 5:1 mass ratio were kept in static contact for 15 days; the interaction was monitored by chemical analysis of both phases at certain intervals. In spite of their common source, the two phases were not in the state of equilibrium from the start, but showed ion exchanges of considerable complexity (see Table 5). The initial stage (6 to 24 h) was characterized by vigorous leaching of readily soluble salts from the sediment, with rapidly rising mineralization of water but practically no change of pH and Alyokin index. Most prominent was the enrichment of water phase with Ca^{2+}, in agreement with simultaneously observed depletion of it in the sediment. An obvious explanation would be a direct Ca^{2+}/Na^{+} ion exchange between water and sediment, but although the concentration of Na^{+} in water did decrease, this happened in a non-equivalent proportion, with a considerable time-lag after the surge of Ca^{2+}, and in a non-monotonic manner. The Ca^{2+}/SO_4^{2-} ratio (0.23–0.27) was consistently below unity, which proves water metamorphization related to ion exchange. Table 6 shows the changes of ion concentrations and exchange capacity of the sediment (monitored simultaneously with those in water) which qualitatively agree with the above reasoning, the sediment being enriched with Na^{+} and depleted of Ca^{2+}, although only a small fraction of Ca^{2+} is actually replaced. Table 7 lists the analysis of muriatic extracts from the sediment, taken before and after the experiment, which shows altered proportions of various oxides.

other factors, that the exchange between sediment and (bulk) water is mediated by the aquatic solutions within sediment's pores. Secondly, same ions in the sediment may be present in more or less readily extractable forms. The gradual depletion of SO_4^{2-} ions in the water phase during the experiment, may be due to biochemical reduction (Shishkina, 1974), which can be represented in a simplified scheme as:

$$2\,SO_4^{2-} + C_{org.} + H_2O \rightarrow 2S + CO_3^{2-} + 2HCO_3^{-}$$

Table 5. Changes of total mineralization and relative concentrations (initial=1) of major ions in the lake water, during contact with bottom sediments

Contact duration	Ca^{2+}	Mg^{2+}	$Na^{+}+K^{+}$	HCO_3^{-}	CO_3^{2-}	SO_4^{2-}	Cl^{-}	Mineralisation total, mg/l
0	1	1	1	1	1	1	1	1130
2 h	1.8	2.2	0.8	2.6	0.2	1.6	1.5	1273
6 h	1.8	2.6	1.1	3.0	0.2	1.4	1.9	1314
1 day	1.8	2.8	0.4	3.0	0.2	0.9	1.9	1275
5 days	1.8	2.8	0.6	3.0	0.6	0.7	1.9	1282
10 days	1.8	2.9	0.9	3.0	0.6	0.1	1.9	1237
15 days	1.6	3.0	0.8	3.0	0.6	0.4	1.9	1259

Table 6. Concentrations of exchangeable cations and cation exchange capacity (CEC) in bottom sediments of Lake Kopa (in mEq/100g) based on water/sediment contact duration.

Contact duration	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CEC
0 (initial)	7.7	5.6	0.21	0.14	10.4
2 hours	7.6	5.8	0.29	0.15	10.2
6 hours	7.4	5.8	0.32	0.14	9.4
1 day	7.3	6.0	0.30	0.14	8.0
5 days	7.1	6.3	0.38	0.15	7.6
10 days	7.2	6.3	0.56	0.08	7.5
15 days	7.0	6.2	0.62	0.16	7.6

Table 7. Selected oxide contents (mass %) in the muriatic extract from the bottom sediment, before and after exposure to lake water

	SiO_2	R_2O_3	CaO	MgO	K_2O	Na_2O	Al_2O_3	Fe_2O_3	balance
Initial	0.48	18.5	9.8	3.4	0.2	0.41	4.5	3.2	59.51
Final	0.48	17.7	8.2	2.9	0.19	0.36	3.2	2.4	64.57

It is well known that chemistry of bottom sediments is one of great complexity (Nikanorov and Stradomskaya 2006). In the present case, one should consider, among

This creates favorable conditions for precipitation of $CaCO_3$ and $MgCO_3$, further facilitated by CO_2 emanating from organic matter fermentation. Thus, exchangeable calcium partly deposits as $CaCO_3$, and most part of it concentrates in the liquid phase. Stoichiometrically, the observed loss of 1.5 mEq/l of SO_4^{2-} ions corresponds to 75 mg/l of $CaCO_3$ in lake water.

CONCLUSIONS

We obtained the first comprehensive information about composition and quality of water in lake Kopa since 1993. Due to cumulative effect of pollution and decreasing water volume (silting-up), concentrations of sulfates, magnesium ions, chloride ions, copper, manganese and oil products, and occasionally cadmium and beryllium all exceed safe levels manifold, revealing an unfolding hydro-ecological crisis. Water mineralization shows a persistent and growing (due to decreasing depth) horizontal gradient, but no vertical stratification, in stark contrast to lakes of humid regions. Water pollution shows regular seasonal variations in a multi-year sequence (2009-2013). Bottom sediments of the lake affect chemical composition and quality of the water. Metamorphization processes in the water-silt system ultimately lead to the formation of calcium carbonate in the lake water and its deposition into the silt.

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