Asian Journal of Water, Environment and Pollution, Vol. 15, No. 4 (2018), pp. 27–34.
DOI 10.3233/AJW-180054

Chemical and Ecological Characteristics of Lakes Located in the Muraviovka Park

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Received July 24, 2018; revised and accepted August 23, 2018

Abstract: The purpose of this research is to provide ecological and chemical characterization of lakes located in the Muraviovka Park, where more than 300 species of birds nest, rest and winter. High concentration of dissolved oxygen in the water of lakes that comes with as high biochemical oxygen demand (BOD_5) indicates that reservoirs experience eutrophication. Concentration of biogenic organic substances is caused to fluctuate by seasonal changes in water temperature. The fires make the hydro-chemical indicators of wetlands change. Lead concentration in the water is high because it enters the water, moving from the surface layers of soil when natural areas transform into cultivated lands. Macrophytes contain an excess concentration of lead and manganese. Heavy metal concentration in fish is below permissible limits. Despite significant differences in the biology of bird species, birds living in the Muraviovka Park have great amounts of iron, copper and zinc in their feathers. Feather lead concentration was also high. The ecological state of lakes located in the Muraviovka Park is necessary to investigate in order to undertake actions to regulate economic activities.

Key words: Lakes, heavy metals, macrophytes, eutrophication, bird habitat.

Introduction

The Muraviovka Park gave a new form of protection and management to natural and man-made populations and communities in order to use natural resources at the sustainable level. In 1995, the Park was included in the Ramsar Convention on Wetlands of International Importance. About 700 species of plants grow there. This is a place where more than 300 species of birds nest, rest and winter (birds from the IUCN Red List included). On the list of threatened species, one may find the red-crowned crane *Grus japonensis* (Müller, 1776), and the Oriental stork *Ciconia boyciana* (Swinhoe, 1873). The list of vulnerable species living in the park area includes the hooded crane *Grus monacha* (Temminck, 1835) and the Daurian white-naped crane *Grus vipio* (Pallas, 1811). Consequences of the Zeya and Bureya basin development that began in 1975 are evident in the Amur River floodplain: active use of land, biological and hydropower resources of the river and its valleys resulted in a destruction of some ecosystems. The Muraviovka Park is located in the southern part

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of the Zeya-Bureya Depression, which has undergone transformation induced by agriculture development. People grow grain crops and soybeans there.

Muraviovka Park area is a wet floodplain of the Amur River. This is a swamped area containing the prevalence of tussok sedge marshes and reed sedge swamps (Akhtyamov, 2002).

In fall, over three thousand cranes stop at the Muraviovka Park, next to rich food resources that remained after harvest (Smirenski, 2012). Agriculture intensification, cultivated land area change in different parts of crane habitat located within the Amur River floodplain, depletion and redistribution of water resources, and the crop composition change have both a negative and positive impact on the distribution and abundance of cranes. The reason behind this is that agriculture relies on huge amount of chemicals, but they cause food shortage and death from poisoning (Malovichko, 2011). Nesting habitats of the Amur River Basin are in decline across the territory of China (Su and Zou, 2012). Investigating the habitat of waterbirds is a relevant objective.

Chinese ecologists highlighted heavy metals accumulation in the habitat of red-crowned cranes living in the wetland ecosystems of northeastern China (Zuo, 2010; Tang, 2012; Zhang, 2012; Luo, 2013; Luo, 2014). However, similar studies were not conducted for wetlands of the Amur River basin in Russia.

The purpose of this research is to profile ecological and chemical characteristics of lakes located in the Muraviovka Park.

Methods

Water samples were taken from the lakes during the period of 2014-2016, according to the GOST 31861-2012 Water. General Requirements for Sampling. Measurements were taken using a digital spectrophotometer PD-303S (Apel, Japan). Mass concentration of microelements was determined by electrothermal atomic absorption spectrometry in water using a KVANT Z.ETA spectrometer.

Results and Discussion

Large lakes of the Muraviovka Park are the Kapustikha Lake, the Peschanoe Lake, etc. There are many small, mainly floodplain, lakes with a length of up to 1-2 km that are at different stages of overgrowing. Lakes located in the Muraviovka Park are highly coloured (86-245 Pt/Co units). Yellowness reaches its peak in fall. Water changes colour because of the type of soil—colour is linked to the level of total iron, manganese, organic substances in the water. In summer, when lakes gain in depth, water colour turns deeper—bottom sediments release more manganese and iron into the bottom layer due to a decrease in the oxygen level, so their contents become higher.

In summer, pH rose above normal in the Peschanoe Lake (8.9). Phytoplankton and aquatic plants take in carbon dioxide during photosynthesis and carbonate accumulation, thereby contributing to water alkalization. In other lakes, pH was within normal range (6.8-8.4). The pH value decreases with depth. It hits the lowest limit possible in fall. In summer, specific electrical conductivity of lakes was between 69 µs/cm (Dubovoye Lake) and 289 µs/cm (Kapustikha Lake), and increased with depth.

Water from the lakes is not so mineralized, for example, the total salt content in water from the Kapustikha Lake was 53.2-123 mg/dm^3 during the given period (for 2014-2016). Lake water is soft, for example, the total hardness of water from the Kapustikha Lake water was 3.85 mg-equ/L.

Summer concentration of ammonium nitrogen in the Kapustikha Lake, the Peschanoe Lake, and the Kamyshovoe Lake was below 0.1 mg $N\text{-}NH_4/dm^3$, so these lakes can be recognized as clean. Ammonium nitrogen is the highest in fall. High concentration of nitrite nitrogen in water from the Peschanoe and the First Meshki (0.04 mg $N\text{-}NO_2/dm^3$) lakes can be linked to nitrification, ammonia-N oxidation by nitrifying bacteria, and transformation to nitrites and nitrates. Amount of nitrogen compounds in water increases with depth. Summer level of nitrate nitrogen in water was small (0.003-0.07 mg $N\text{-}NO_3/dm^3$). Nitrate nitrogen level was significant (6.177 mg $N\text{-}NO_3/dm^3$) in spring 2013. Measurement was taken in an anonymous creek flowing from Muraviovka Park, and can show the consequence of fire that occurred in 2012.

With organic phosphorus, summer level of total phosphorus amounted to 0.03-0.21 mg/dm^3. High total phosphorus level makes the lakes of the Muraviovka Park eutrophic and hypertrophic in nature. Phosphate content in water from the Kapustikha Lake was high in spring 2013 (0.2-0.4 mg/dm^3), and it resulted from fire. Fires cause the hydro-chemical indicators of wetlands to change (Shesterkin, 2002). For example, sulphate and nitrate concentration gets higher mineralization process intensified (Ahtemyeva, 2014).

Total iron and manganese levels increase with depth in summer. In the bottom layer, their level is higher, since they flux from bottom sediments under anoxic circumstances.

Manganese is quite high in the lakes located in the Muraviovka Park (from 0.09 mg/dm^3 in the Kapustikha Lake to 0.74 mg/dm^3 in the Kamyshovoe Lake). Total iron and manganese in the lake water are high due to regional peculiarities. Summer gain in lake depth comes with the increase in the nutrient concentration in the bottom layer.

In summer, the lakes are saturated with oxygen (150% and higher). For lakes, vertical oxygen distribution is a common—top layer has high oxygen (10-12 mg O/L), but its level lowers down from top to bottom. High levels of dissolved oxygen and BOD_5 (9.1-14.1 mg O/dm^3) in lakes can indicate high biological productivity.

Lakes had high permanganate oxygen demand (OD) in summer 2014, indicating the allochthonous organic matter from flood that occurred in 2013, entering the water. In 2015 and 2016, OD was above the limit (8.4-10.8 mg O/dm^3).

There were times when lakes located in the Muraviovka Park had elevated lead content, for example, such a case emerged in summer 2015 (the First Meshki Lake – 7.9 μg/dm^3), in fall 2015 (the Kamyshovoe Lake –11 μg/dm^3, and the Peschanoe Lake – 7 μg/dm^3), and in spring and summer 2016 (the Kapustikha Lake – 11 μg/dm^3, and other lakes – 9 μg/dm^3. In summer and fall 2013, high concentrations of lead were found in water bodies located in the cultivated land. Some serious floods caused the heavy metals to move from the soil top and enter the water (Pakusina, 2015).

Cadmium concentration on the contrary did not exceed the maximum permitted level, and was below 0.16 μg/dm^3.

Zinc concentration in lakes located in the Muraviovka Park were up to 4.6 times above the limit for natural reasons.

Of all lakes located in the Muraviovka Park, the minimum copper content was found in the Dubovoye Lake, while the maximum copper content in the Peschanoe Lake. Some heavy metal contents in water of lakes located in the Muraviovka Park were within the range of maximum permissible limit (data for the period between 2014 and 2016): chromium content was below 2 μg/dm^3, nickel content – below 0.04 μg/dm^3, arsenic content – below 8.12 μg/dm^3 and cobalt content – below 1.2 μg/dm^3.

Zinc concentration in bottom sediments hit the maximum permitted in the Kapustikha Lake (78 mg/kg),

Table 1: Composite lake pollution index

Lake's name	*Permanganate oxygen demand, mg O/dm^3*	*Dissolved oxygen, mgO$_2$/dm^3*	*Oxygenation %*	*BOD$_5$, mg O$_2$/dm^3*
Dubovoye	8.4-11.4/9.9±1.5*	11.0-12.0/11.4±0.7	110-133/121±3	7.1-10.4/8.7±0.4
Kamyshovoe	7.2-17.3/12.6±1.2	10.1-16.8/14.2±1.9	119-170/138±16	8.1-4.1/9.7±2.0
Kapustikha	2.8-26.2/11.0±5.9	6.3-9.0/8.1±0.7	50-106/75±10	0.9-9.0/3.6±2.1
First Meshki	10.8-18.4/15.4±2.1	12.7-13.7/13.1±0.3	122-156/141±9	6.0-7.0/6.4±0.3
Peschanoe	4.5-9.6/8.3±1.8	12.7-13.4/12.7±0.4	128-154/142±5	6.5-9.1/8.5±0.7
MPL	Below 5	Above 6	Above 80	Below 2

*Min-max/average value

Table 2: Heavy metals in lakes located in the Muraviovka Park, μg/dm^3

Lake's name	*Cu*	*Zn*	*Pb*	*Cd*
Dubovoye	2.7-23/10.7±3.4	2014-4636/3093±707	1.5-2.2/1.7±0.2	0.05-0.16/0.1±0.01
Kamyshovoe	5.6-30.7/13.8±8	1062-3335/2089±208	1.6-11/4.7±1.5	0.02-0.04/0.03±0.01
Kapustikha	1.7-32/10.7±14	1731-3547/2645±83	1.7-9/4.1±2.1	0.03-0.1/0.075±0.01
First Meshki	2.7-23/10.7±3.4	705-3906/2166±698	1.7-7.9/3.9±1.9	0.05-0.06/0.05±0.00
Peschanoe	4.1-88/28.4±27	858-3794/1868±976	1.5-9.0/4.7±1.1	0.07-0.09/0.08±0.01
$MPL_{fishery\ water}$	1	10	6	5
$MPL_{utility\text{-}and\text{-}drinking}$	1000	1000	10	1

the Kamyshovoe Lake (66 mg/kg) and the Peschanoe Lake, while in other lakes it was below the MPL. Copper, lead and cadmium levels were also below the limit.

Fishes are a sensitive component of aquatic ecosystems – they react sensitively to changes in the state of environment (Moiseenko, 2002). Since fish are at higher trophic levels, they are usually the biotic metal accumulators. Research on the effect of some factors on the content and accumulation of heavy metals in fish fauna was carried out on the silver carp *Carassius gibelio* (Bloch, 1782) and a sleeper *Perccottus glenii* (Dybowski, 1877) caught on the Kapustikha Lake using a fishing rod.

Research on metal content in fish muscles and gonads is important since these parts are in human diet. Fish living in the Kapustikha Lake is to feed red-crowned cranes, which are grown and released into the Park.

In the Kapustikha Lake, metal content in fish is within the permitted range. Heavy metal concentrations in the muscle tissue of fish from the Kapustikha Lake follow the decreasing order Zn> Fe> Cu> Mn> Pb> Cd.

Metal accumulation depends on fish species, age, feeding habits, econiche occupied, metal properties and biochemical role, and environmental conditions (Chukhlebova, 2010; Kovekovdova, 2013).

Heavy metal accumulation by higher aquatic vegetation is the most important biological process in which small rivers and lakes go through natural purification. Aquatic plants enrich the lake water with oxygen via photosynthetic activity. Although helophyte plants photosynthesize outside the water column, their stems have cavities filled with air, so the water gets extra oxygen.

Copper, iron, manganese and zinc are microelements vital for plants; they are present in metalloenzymes to transport electrons. They also take part in important processes, such as photosynthesis, carbohydrate and protein metabolism, oxidation-reduction reactions and specific functions in defense mechanisms (Kabata-Pendias, 2001).

Aquatic vegetation is a priority food resource of waterbirds and their habitat. Birds eat floating lake and pond weeds, water milfoil, fresh shoots and rhizomes, and seeds of coastal-aquatic plants. Waterbirds hide in tangled coastal-aquatic plants to molt and nest. In the Muraviovka Park, lakes are overgrown with macrophytes, in which condition the pattern is either spotted, or bordered, or both.

The amount of heavy metals in higher aquatic plants depends on the state of the lake and the metal concentration in water and bottom sediments. Different kinds of hydrophytes accumulate different amounts of heavy metals. In decreasing order of content, heavy metals, distributed in the hydrophytes of lakes located in the Muraviovka Park, are sorted as Fe> Mn> Zn> Pb> Cu> Cd.

Cadmium level in plants is below 0.001 mg/kg. In macrophytes, the concentration of copper (5-30 mg/kg) and zinc (27-150 mg/kg) is normal.

Lead concentration in the *Trapa japonica* (First Meshki Lake) is also within normal range. The remaining higher aquatic plants, especially those in the Dubovoe and Kamyshovoe lakes, contain an elevated lead concentration (>30 mg/kg). Hydrophytes contain an elevated concentration of manganese.

Lead and cadmium are toxic to birds. Five times elevated concentration of lead in bird feathers inhibits

Table 3: Average heavy metal concentrations in bottom sediments of lakes, µg/kg

	Cu	*Zn*	*Pb*	*Cd*	*Mn*	*Fe*
Kapustikha	13.5±4.1	78.2±23.5	11.5±3.5	0.10±0.03	847±254	20737±6221
Dubovoye	4.7±1.4	32.9±9.9	26.1±7.8	0.12±0.03	57±17	3037±911
Kamyshovoe	9.1±2.7	66.1±19.8	9.2±2.8	0.11±0.03	980±294	15027±4508
First Meshki	5.2±1.5	28.4±8.5	8.4±2.4	0.11±0.03	125±37	4420±1326
Peschanoe	12.1±3.6	54.3±16.3	18.0±5.4	0.10±0.03	139±41	34425±10327
MPL	33-35	55-100	32	1-5	1500	

Table 4: Average heavy metal concentrations in muscle tissues of fish from the Kapustikha Lake (*n* = 10), mg/kg

	Mn	*Fe*	*Cu*	*Zn*	*Cd*	*Pb*
Carassius gibelio	0.67±0.13	0.69±0.14	0.57±0.11	17.01±3.40	<0.1	0.29±0.06
Perccottus glenii	0.31±0.06	0.90±0.18	0.58±0.12	36.04±7.21	<0.1	0.36±0.07

Table 5: Average heavy metal concentrations in macrophytes from lakes, mg/kg

Macrophytes	*Habitat*	*Cu*	*Zn*	*Pb*	*Mn*	*Fe*	*Cd*
I. Submerged hydrophytes							
Myriophyllum spicatum L.	Dubovoye Lake	21.5±2.2	77±8	43.4±4.3	2305±231	4344±434	<0.001
Potamogeton manchuriensis (A.Benn.) A.Benn.	Kamyshovoe Lake	16±**1.6**	35±**4**	24±**2.4**	656±**66**	3499±**350**	<0.001
Hydrilla verticillata (L. fil.) Royle	First Meshki Lake	5.5±**0.5**	27±**3**	28±**2.3**	1287±**128**	2595±**260**	<0.001
Potamogeton manchuriensis	Peschanoe Lake	18±**1.8**	12±[illegible]	24±**2.4**	356±**35**	745±**745**	<0.001
II. Rooted hydrophytes with floating leaves							
Sagittaria natans Pall.	Dubovoye Lake	11±**1.1**	23±2	11±1	114±**11**	1568±**157**	<0.001
Nuphar pumila (Timm) DC.	Peschanoe Lake	17±**1.7**	5±0,5	12±1	818±**82**	740±**74**	<0.001
Persicaria amphibia (L.) S.F. Gray (stems)	Peschanoe Lake	16±**1.6**	8±**0.8**	11±[illegible]	676±**68**	2055±**206**	<0.001
(roots)		13±**1.3**	20±**2**	9±**0.9**	1067±**107**	2597±**259**	<0.001
III. Free-floating hydrophytes							
Trapa sibirica Fler.	Dubovoye Lake	5±0.5	63±6.3	16.51,6±	64665±	1771177±	<0.001
Trapa japonica Fler.	First Meshki Lake	8±**0.8**	10±1.0	6±0,6	820±82	630±63	<0.001
Spirodela polyrhiza (L.) Schleid.	Kapustikha Lake	11.5±1.2	48±4.8	28.8±2.9	4095±409	4947±495	<0.001
IV. Hydrophytes growing along the edge of lakes and littoral shelves at 20 (40) cm depth							
Cyperus glomeratus L. (shoots)	Dubovoye Lake	9±**0.9**	25±**2.5**	11±**1.1**	171±**17**	104±**10**	<0.001
(seeds)		21±**2.1**	52±**5.2**	17±**1.7**	67±**7**	166±**17**	<0.001
Bolboschoenus yagara (Ohwi) A.E. Kozhevnikov (rhizome)	Peschanoe Lake	9±**0.9**	24±**2.4**	14±**1.4**	250±**25**	37910 **±3791**	<0.001
(shoots)		7±**0.7**	7±**0.7**	8±**0.8**	107±**11**	76±**7,6**	<0.001
(seeds)		9±**0.9**	7±**0.7**	11±**1.1**	92±**9**	8±**0,8**	<0.001
Scirpus orientalis Ohwi (rhizome)	Peschanoe Lake	13.6±1.4	87±8.7	61.3±6.1	172±17.2	15774 ±1577	<0.001
(shoots)		5.8±0.6	36±3.6	14.4±1.4	287±28.7	213±21	<0.001
(seeds)		11.7±1.2	55±5.5	0.2±0.02	56±5.6	173±17	<0.001

its growth and survival (Burger, 2009). Research papers on determining concentration of heavy metals in feathers of endangered birds are relevant now (Pain, 2005; Zuo, 2010; Zhang, 2012; Luo 2014). The focus is mostly on water birds and predators, but *Passeriformes* are successfully used to monitor the environment near metallurgical plants, mines, and technogenically polluted areas (Bel'skii, 2005; Eeva et al., 2009; Berglund, 2010). Heavy metal concentration is assessed in a variety of samples, for example in eggshell, blood, tissues, feces, and feathers. The age of birds is an important factor here for metal accumulation (Berglund, 2011).

We measured heavy metal concentrations in feathers of protected species, such as *Ciconia boyciana*, *Grus monachus* and *Grus vipio*. We also addressed feathers of the most common order of birds (*Passeriformes*): the azure-winged magpie *Cyanopica cyana* (Pallas, 1776), the yellow-throated bunting *Emberiza elegans* (Temminck, 1836), the willow tit *Poecile montanus* (von Baldenstein, 1827), and the Eurasian nuthatch *Sitta europaea* (Linnaeus, 1758). Poachers pose a threat to the population of *Phasianus colchicus* (order Galliformes) (Linnaeus, 1758).

Despite significant differences in the biology of bird species, birds living in the Muraviovka Park had great amounts of iron, copper and zinc in their feathers. Amounts of cobalt and cadmium were the least. Elements were distributed in such a way during the evolution of biosphere, following one's biological role and geochemical conditions. Lead concentration in bird feathers, especially in feathers belonging to *Phasianus colchicus* and *Poecile montanus*, was high from the habitat and feeding habits. Birds eat seeds of plants accumulating lead in toxic concentrations. Cadmium concentration in feathers of *Cyanopica cyanus* was also found toxic.

Conclusions

Ecological and chemical monitoring of lakes located in the Muraviovka Park allowed detecting the accumulation of heavy metals in the bird habitat. Heavy metals entered the lake water, moving from the surface layers of soil after the natural areas were disturbed and transformed into cultivated lands. The concentration of organic and nutrient compounds depended on seasonal changes in water temperature, and on the lake depth. In summer, water in the lakes was observed to become cooler with depth. Fires caused the phosphate and nitrate concentration in water to increase. High concentration of dissolved oxygen in the water of lakes that comes with as high biochemical oxygen demand (BOD_5) indicates that reservoirs experience eutrophication. In decreasing order of content, heavy metals in macrophytes are sorted as Fe> Mn> Zn> Pb> Cu> Cd.

Macrophytes contained an elevated concentration of lead and manganese. Heavy metal concentrations in the muscle tissue of fish from the Kapustikha Lake follow the decreasing order Zn> Fe> Cu> Mn> Pb> Cd. Lead concentration in feathers of birds living in the Muraviovka Park was found elevated. Ecological aspect is a key to the protection of wetlands as habitats of waterbirds, so solution to the ecological problem is a priority. By solution, we mean the protection of bird populations and their maintenance as part of the overall problem of aquatic ecosystem conservation.

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Table 6: Average heavy metal concentrations in feathers of birds, mg/kg

Name	*Cu*	*Fe*	*Ni*	*Zn*	*Co*	*Pb*	*Cd*
Ciconia boyciana	43.34	19.0	1.6	26.4	0.112	1.5	0.0396
Grus monachus	17.71	392.2	2.8	15.3	0.1558	1.6	0.0217
Grus vipio	48.10	528.0	2.4	85.1	0.096	2.4	0.0137
Phasianus colchicus	11.36	635.8	2.4	101.0	0.0225	4.9	0.0095
Cyanopica cyanus	3.70	80.9	1.6	6.7	0.0164	3.1	0.3953
Emberiza elegans	7.66	10.0	2.2	11.7	0.0691	3.4	0.0344
Poecile montanus	3.44	7.9	2.4	6.9	0.0686	3.7	0.0248
Sitta europaea	3.17	3.7	2.1	5.3	0.1112	3.6	0.0023

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