

## Experimental geocology

### Karaseva O.N., Lakshtanov L.Z., Khanin D.A., Proskuryakova A.S. Influence of pH and organic ligands on dissolution kinetics of natural silicates\*

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**Abstract.** Natural silicates are potential sources of divalent cations, which are necessary for the mineralization of CO<sub>2</sub> in carbonate minerals. In order to study the dissolution kinetics of serpentine and talc in neutral and acidic solutions (HCl, citric and oxalic acids), experiments were performed in a flow-through reactor at 25 °C. It was found that under neutral conditions, the dissolution rate of silicate minerals is minimal, it increases with a decrease of pH and in the presence of organic ligands. Dissolution of silicate samples demonstrate two stages: a fast one with the predominant leaching of magnesium cations into the solution, and a slow stoichiometric stage. Initial incongruent stage may be the most promising for the development of carbonation technologies, since the minimum removal of the network-forming elements Si and Al prevents the undesirable formation of secondary minerals (for example, clays), which exclude divalent cations from the carbonation process and greatly reduce the permeability of rocks.

**Keywords:** mineral carbonation, serpentine, talc, dissolution, organic ligands, kinetics

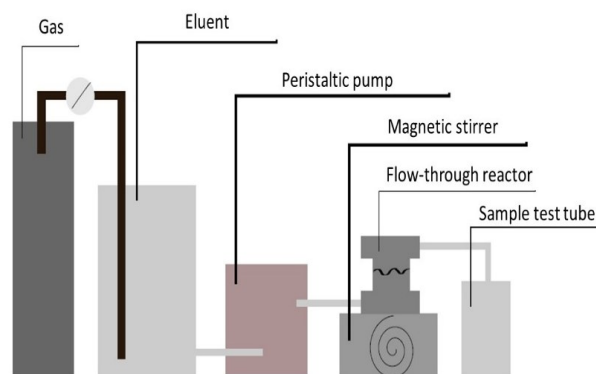
**Introduction.** A promising alternative to sequestering carbon dioxide into geological structures (oil and gas reservoirs, exhausted coal layers, salt mines) is mineral carbonation when CO<sub>2</sub> can be converted into stable solid carbonates by chemical reaction with rocks consisting mainly of magnesium and calcium silicates. CO<sub>2</sub> mineral sequestration has been successfully applied in the underground storage of carbon dioxide in basalt rocks (Gislason et al., 2014), and is also being actively implemented in mining enterprises, where a large amount of by-product is formed as dumps and tailings containing basic and ultramafic rocks (Kandji et al., 2017, Eloneva et al., 2008). However, unlike "fresh" basalts, which are at a sufficient depth in the depths of the earth, weathered rocks react with carbon dioxide much more slowly and, therefore, reduce the mineralization of CO<sub>2</sub> into stable carbonate minerals.

The most effective methods proposed for enhancing carbonation are leaching/dissolution of silicates in solutions and subsequent conversion of magnesium to carbonates (Huijgen and Comans, 2005). Thereby, various additives are attracting much attention: mineral (Teir et al., 2007) and organic acids (Park et al., 2003; Park and Fan, 2004), salts and alkaline solutions (Maroto-Valer et al., 2005; Jarvis et al., 2009).

Most studies have reported that organic ligands can significantly affect the dissolution kinetics of minerals, but the dissolution mechanisms are still a subject of discussion. Under some conditions, all elements are released into solution stoichiometrically (Brady and Walther, 1992), while under others, divalent cations are leached, whereas silica and aluminum predominantly remaining in the mineral lattice (Stumm et al., 1980).

In this work we have studied the effect of pH and organic ligands (citrate and oxalate) on the dissolution of silicates in an open system at 25 °C. Talc and serpentine were chosen as model minerals as perspective CO<sub>2</sub> mineralizers.

**Experiments.** The study of the dissolution kinetics of minerals in various solutions was performed in a flow-through reactor at 250 (Fig. 1). In the experiments, samples of talc were used, represented by a fine-grained aggregate from the Shabrovsky field (Central Urals) and serpentine from granite pegmatites of the Ministerskaya Kopi (Middle Urals), according to X-ray diffraction analysis, the bulk is lizardite. The specific surfaces of talc and serpentine were 6.2 and 71 m<sup>2</sup>/g, respectively. Solutions of 0.1 and 1.0 mM hydrochloric acid, 1.0 mM citric and oxalic acids were used in the experiments. All acid solutions were made to ionic strength I = 0.02 by adding NaCl. Eluents were supplied using a peristaltic pump at a rate of 0.72–0.75 ml/min. During the experiment, pH and concentration of silica and magnesium in the solution were monitored. The constancy of the pH values and the concentrations of Si and Mg in the filtrate testified to the achievement of a steady-state and the establishment of constant rates of mineral dissolution. The duration of the experiments was 4 - 7 days. Magnesium concentrations were determined by AAS. Silica concentrations were determined using the molybdate blue colorimetric method.

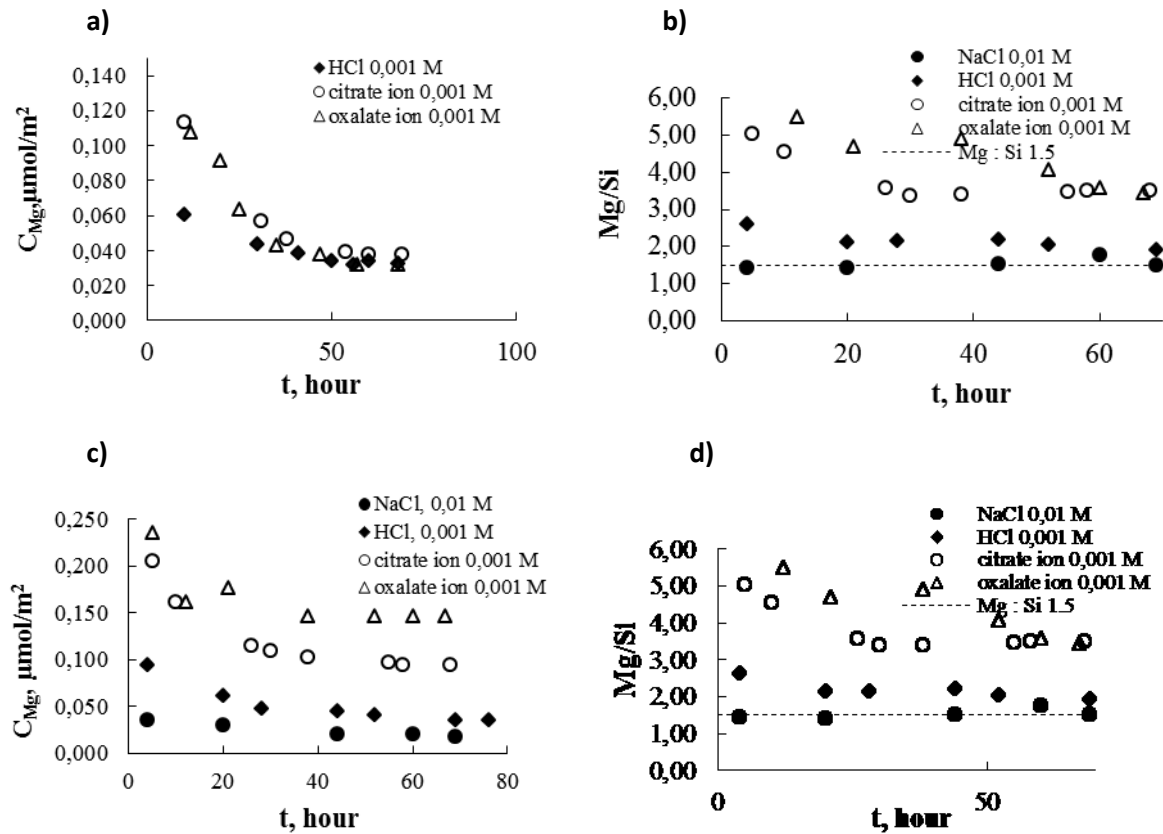


**Fig.1.** Installation scheme for conducting experiments on the minerals dissolution in a flow system.

**Results and discussion**

The change in the  $Mg^{2+}$  concentration during the experiment in a flow-through reactor indicates the rate of dissolution of talc and serpentine in solutions of various compositions (Fig. 2). The minimum dissolution rate of serpentine is observed in a neutral solutions (pH 6.5) and increases with a decrease in pH (Fig. 4). Since the specific surfaces of talc and serpentine differ by more than 10 times, the concentration of magnesium in the solution was reduced to the surface of the mineral. An active transfer of magnesium into solution the dissolution

of both talc and serpentine is observed during the first day of the experiment, after which it slows down significantly. After 40–45 hours the magnesium concentration practically does not change. The release of silica occurs to a much lesser extent, which is shown in Fig. 2, (b, d). The magnitude of the Mg/Si ratio can be used to conclude on the mechanism of mineral dissolution. In the case of talc, in the first hours of the experiment, the Mg/Si values in acid solutions significantly exceed Mg/Si in the solid phase (Fig. 2,b), which indicates incongruent dissolution.



**Fig.2.** Mg concentration changes in solution and the Mg/Si ratio over time during the dissolution of talc (a, b) and serpentine (c, d).

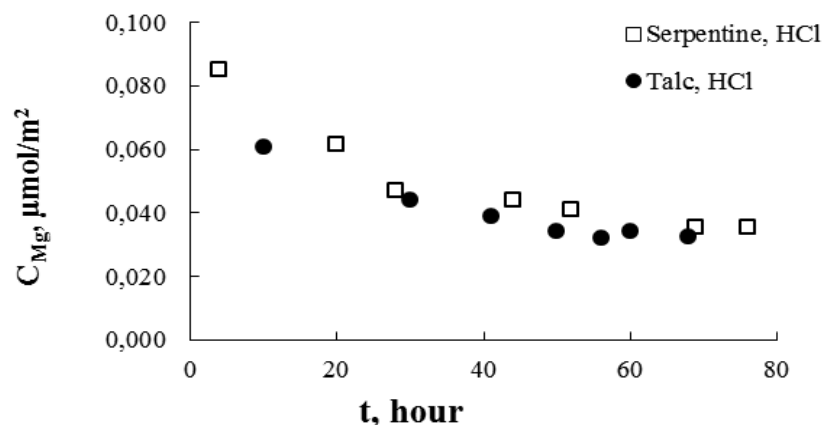
After two days the Mg/Si ratio approaches 0.75. It corresponds to the atomic ratio of magnesium and silica in the structure of the crystal lattice of talc and this value practically does not change with time. In the case of serpentine, when a steady state is established in NaCl and HCl solutions, a dissolution close to congruent is observed (Fig. 2, d). The Mg/Si value is practically constant and close to 1.5, that corresponds to the Mg/Si ratio in the crystal lattice of the mineral. The behavior of magnesium during the dissolution of serpentine and talc in a flow-through system without citrate and oxalate ions at the same acidity of the solution is identical (Fig. 3), as a result of which it can be concluded that the dissolution of minerals under these conditions is controlled by the

same processes.

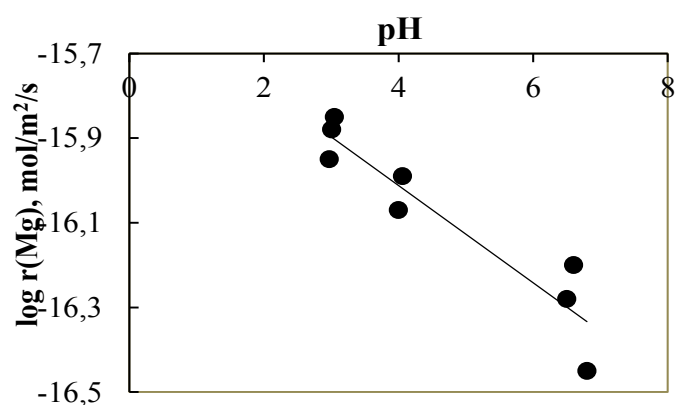
In natural magnesium silicates, the strongest covalent bond exists in tetrahedra between Si and O ions, and less strong ionic forces keep metal ions in the lattice (Lebedev, 1972). The initial stage of the dissolution mechanism consists in the formation of protonated (in an acidic solution) complexes on the surface of mineral particles (Stumm, 1992), which destabilize and polarize Mg-O bonds in the crystal lattice; therefore, the dissolution of minerals begins with a non-stoichiometric release of magnesium cations. As a result, a chemically altered leached layer is formed, through which ions must penetrate in order to continue dissolution (Newlands et al., 2017). The outer part of the leached layer can continuously

undergo repolymerization and reorganization of the silicate framework (Tsomaia et al., 2003). This leads to the formation of a dense layer of silica gel, which can passivate the dissolving surface and causes a

decrease in the dissolution rate (Gin et al., 2015; Wang et al., 2016).



**Fig.3.** Mg concentrations changes upon dissolution of talc and serpentine in 1 mM HCl



**Fig. 4.** Dependence of the dissolution rate of serpentine on pH.

The presence of organic ligands significantly increases the dissolution of silicates. For the case of serpentine, which has a large surface area this effect is most pronounced, and therefore the surface reactions are more intensive. Concentration of magnesium in the solution, both at the initial stage of the experiment and under steady-state conditions, is approximately 2-3 times higher compared to its concentration in experiments with talc (Fig. 2). The dissolution of talc in solutions of citric and oxalic acid is congruently at steady-state conditions. The authors (V. Prigiobbe, 2011, Grandstaff 1986, Wogelius and Walter 1991) also concluded that the dissolution of silicates is a completely stoichiometric process, i.e., the ratio Mg to Si in solution reflects the composition of the minerals. In our experiments on the serpentine dissolution in the presence of organic ligands, even when steady-state was established, the Mg/Si values significantly exceeded those in the solid phase. Probably, concentration of silica in the filtrate may be reduced due to the fact that part of the silica is deposited as a gel on the filter and thus a

smaller amount of dissolved silica enters the filtrate (Teir et al., 2007).

Knowledge of dissolution rates and understanding of the dissolution mechanisms of silicate minerals is essential for quantitative modeling and prediction of various CO<sub>2</sub> sequestration scenarios. The stationary rates of silicates dissolution in different solutions were calculated by the following equation:

$$r = (C_i * F) / (n * S * m), \quad (1)$$

where  $C_i$  is the molar concentrations of Mg or Si in the solution,  $F$  is the volumetric flow rate of the liquid, L/sec,  $n$  is the stoichiometric coefficient of Mg or Si in solid phase,  $S$  is the specific surface area of the mineral, cm<sup>2</sup>/g,  $m$  is the mass of the sample of the mineral, g.

Table 1 shows the stationary concentrations of magnesium and silica and the minerals dissolution rates calculated for (Mg and (Si). A clear linear dependence of the logarithm of dissolution rate on pH in an acidic environment was revealed (Fig. 4).

**Table 1.** Dissolution rates of talc and serpentine in acid solutions at 25<sup>o</sup> C. Volumetric flow rate 1.2\*10<sup>-5</sup> L/s.

Solutions	Minerals	C <sub>Mg</sub> , x 10 <sup>-5</sup> , mol/l	C <sub>Si</sub> , x 10 <sup>-5</sup> , mol/l	log r(Mg), mol/cm <sup>2</sup> sec	log r(Si), mol/cm <sup>2</sup> sec
0.01 M NaCl pH 6.5	serpentine	1.88	1.30	16.28	-16.25
0.001 M HCl pH 3	talc serpentine	0.43 5.0	0.6 2.69	-15.56 -15.85	-15.54 -15.94
0.0001 M HCl pH 4	serpentine	3.0	2.01	-16.00	-16.07
0.001 M C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> pH 3	talc serpentine	0.5 13.8	0.6 3.78	-15.50 -15.41	-15.54 -15.80
0.001 M C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> pH 3	talc serpentine	0.42 20.8	0.5 6.07	-15.58 -15.23	-15.62 -15.59

So, in the neutral solutions, the rate of silicate dissolution is minimal; it increases with a decrease in pH and in the presence of organic ligands: citrate and oxalate ions. The first stage of silicates dissolution proceeds incongruently with the predominant removal of magnesium cations into the solution. At the steady state (at minimal changes of pH, Si and Mg concentrations), the talc dissolution is close to stoichiometric. The lower Si concentration in the filtrates obtained in experiments with serpentine may be due to the formation of a silica gel layer on the filter. Obviously, the initial incongruent stage of dissolution may be the most promising in terms of the development of carbonation technologies, since the minimum removal of the network-forming elements Si and Al prevents the undesirable formation of secondary minerals (for example, clays), which excludes divalent cations from the carbonation process and greatly reduces the permeability of rocks.

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#### Rusakova M.-A., Drozdova O. Y., Lapitsky S.A. Forms of heavy metals in the river waters of the boreal zone during the summer low water

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**Abstract.** The study of the migration process of substances is one of the main tasks of geochemistry. The boreal regions play an important role in the transport of elements from the continents to the ocean at high latitudes. The work is devoted to the study of the forms of finding heavy metals in river waters. The objects of the study were the waters of five rivers located in different areas of the boreal zone.

Determination of metal forms was carried out using a combination of physical (filtration), chemical (ion-exchange chromatography) and calculation methods (Visual MINTEQ).



It was found that for all considered metals, the predominant form of occurrence is associated with organic matter. It was found that for all considered metals, the predominant form of occurrence is associated with organic matter. It was noted that for Fe and Cu, anionic complexes with organic ligands of the  $[MeL]^{n-}$  type predominate. The predominant form of occurrence of Pb and Cd is a neutral organic complex of the  $[MeL]^0$  type. Zn and Ni are characterized by both neutral and positively charged organic complexes of the form  $[MeL]^0$  and  $[MeL]^{n+}$ . Anionic complexes are presumably formed with high-molecular organic ligands, cationic and neutral, in turn, with low-molecular ones.

**Key words:** occurrence forms, heavy metals, complexes with organic ligands, boreal zone

Metals in natural waters exist in truly dissolved, suspended, or colloidal forms. Among metal complexes with organic substances, humic acids are particularly noteworthy as they have the highest ability to bind heavy metal ions (HM) into stable complexes with high stability constants. Among inorganic complexing agents with HM in river waters,  $OH^-$ ,  $HCO_3^-$ ,  $Cl^-$ ,  $F^-$ , and others are distinguished (Papina, 2001; Ilyina, 2011).

Metal compounds formed with different groups of organic substances also differ in properties, which affects the formation of migration flows

(Dobrovolsky, 2004).

In order to understand the role of organic colloids in river waters, it is important to first characterize their distribution and origin. Colloids enter surface waters from soils and can be organic, inorganic, or organomineral (Gustafsson, Gschwend, 1997; Gustafsson et al., 2000; Dahlgvist R. et al., 2004, 2007).

The forms of occurrence of HM in natural waters are of increasing interest and importance, as toxicity, bioavailability, and geochemical behavior strongly depend on the form of metal occurrence in river waters (Fytianos, 2001). Expanded knowledge about the forms in which trace elements are present in river waters is necessary to explain the different degrees of bioavailability and toxicity of various elements.

### Research objects and methods

The research objects were surface waters from five rivers in the boreal zone - Lundozhma (Vologda region), Koy (Vologda region), Kovzha (Vologda region), Mezha (Tver region), and Senga (Vladimir region). All of them are located in the European part of Russia. The physico-geographical characteristics of the research objects and the coordinates of the sampling points are presented in Table 1.

**Table 1.** Physico-geographical characteristics of research objects

River	Length, km	Drainage basin area, km <sup>2</sup>	Sampling coordinates	
			N	E
Senga	32	163	55°53.318'	39°31.23'
Mezha	168	2630	56°27.318'	32°57.794'
Lundozhma	18	72.8	62°32.324'	35°43.461'
Koy	14	2.1	59°47.974'	39°04.757'
Kovzha	108	1080	60°43.433'	37°10.010'

In situ measurements of conductivity (Hanna HI 9033 conductivity meter) and pH values (Hanna HI 9025 pH meter) were performed in natural waters. The content of bicarbonates was determined by titration method [GOST 31957-2012]. In laboratory conditions, the samples were analyzed for the content of inorganic anions using an ion chromatograph (Dionex ICS2000, Thermo) and dissolved organic carbon (DOC) using a LiquiTOC trace analyzer (Elementar).

The study focused on investigating the forms of HM in surface waters, as well as determining the proportion of colloidal and truly dissolved fractions. Separation of suspended forms from colloidal and truly dissolved forms was carried out by filtration through a membrane filter (Millipore) with a pore size of 0.22  $\mu m$ . Separation of colloidal forms and truly dissolved substances was carried out using ultrafiltration through a filter with pore size of 1 kDa. The determination of the content of anionic and

cationic compounds of heavy metals in the dissolved fraction was performed using ion exchange chromatography with the use of ion exchange resins - cationite (Dowex 50 WX 8, 200-400, Serva) and anionite (DEAE-cellulose, Sigma Aldrich). The amount of neutral complexes was calculated based on the difference between the initial concentration of the element and the sum of the cationic and anionic forms. The measurements of Fe, Ni, Cu, Zn, Cd and Pb content in the samples were carried out using inductively coupled plasma mass spectrometry (Elan 6100 DRC).

Taking into account all the obtained hydrochemical characteristics (pH, content of major cations and anions, and electrical conductivity) and the content of heavy metals, calculations of their forms in the studied water bodies were performed using the Visual MINTEQ ver. 3.1 program (Gustafsson, 2013) in combination with the SHM database and binding models of humic substances.

**Table 2.** Chemical characteristics of the studied objects (n.d. - not determined)

River	pH	$\alpha, \mu\text{s}$	DOC	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
							mg/l		
Senga	7.6	94	40	123	0.101	0.21	n.d.	n.d.	0.40
Mezha	7.6	36	19.4	35	0.060	1.18	0.119	1.15	0.62
Lundozhma	7.1	39	27	37	0.052	3.9	n.d.	0.28	0.68
Koy	7.8	214	20	176	0.021	0.62	n.d.	n.d.	1.53
Kovzha	7.9	26	13.4	0.40	0.14	2.3	n.d.	n.d.	18.1

### Results and Discussion

The main characteristics of the rivers are presented in Table 2. The laboratory analysis results did not reveal exceedances of MAC for iron, nickel, copper, zinc, cadmium, and lead.

Processing of the obtained data showed that for iron, the predominant form is colloidal (Table 3). Lead is also predominantly associated with colloids in most samples, except for the Senga River where it's truly dissolved form prevails. For nickel and cadmium, the predominant form in Senga and Lundozhma rivers is colloidal, while in Mezha, Koy, and Kovzha rivers it is truly dissolved. Copper is mainly in colloidal form in Mezha and Senga rivers, while in Lundozhma, Koy, and Kovzha rivers it is truly dissolved. Zinc, on the other hand, predominantly exists in truly dissolved form, except for the Koy river where it is mostly in colloidal form.

Calculations using the Visual MINTEQ program

showed (Fig. 1) that the predominant form of occurrence of Fe, Ni, Cu, Zn, Cd, and Pb in all studied objects and in any fraction (colloidal and truly dissolved) is associated with organic matter. Among the organic complexes of these heavy metals, negatively, positively, and neutrally charged groups can be distinguished (Fig. 2).

For iron and copper, anionic complexes with organic ligands of the type [MeL]<sup>n-</sup> predominate, presumably formed with humic substances or with two or more basic acids. The predominant form of occurrence of lead and cadmium is neutral organic complex of the type [MeL]<sup>0</sup>. Zinc and nickel are characterized by both neutral and positively charged organic complexes of the type [MeL]<sup>0</sup> and [MeL]<sup>n+</sup>, with positively charged and neutral complexes presumably formed with low molecular weight products of aquatic organism metabolism.

**Table 3.** Forms of metal occurrence (bold indicates the predominant form)

Metal	Form in solution (%)	Mezha	Senga	Lundozhma	Koy	Kovzha
Fe	colloidal	<b>97</b>	<b>94</b>	<b>99</b>	<b>81</b>	<b>94</b>
	dissolved	3	6	1	19	6
Ni	colloidal	10	<b>67</b>	<b>51</b>	23	39
	dissolved	<b>90</b>	33	49	<b>77</b>	<b>61</b>
Cu	colloidal	32	50	<b>56</b>	<b>82</b>	<b>60</b>
	dissolved	<b>68</b>	50	44	18	40
Zn	colloidal	31	3	8	<b>83</b>	31
	dissolved	<b>69</b>	<b>97</b>	<b>92</b>	17	<b>69</b>
Cd	colloidal	22	<b>67</b>	<b>58</b>	27	27
	dissolved	<b>78</b>	33	42	<b>73</b>	<b>73</b>
Pb	colloidal	<b>52</b>	25	<b>94</b>	<b>79</b>	<b>81</b>
	dissolved	48	<b>75</b>	6	21	19

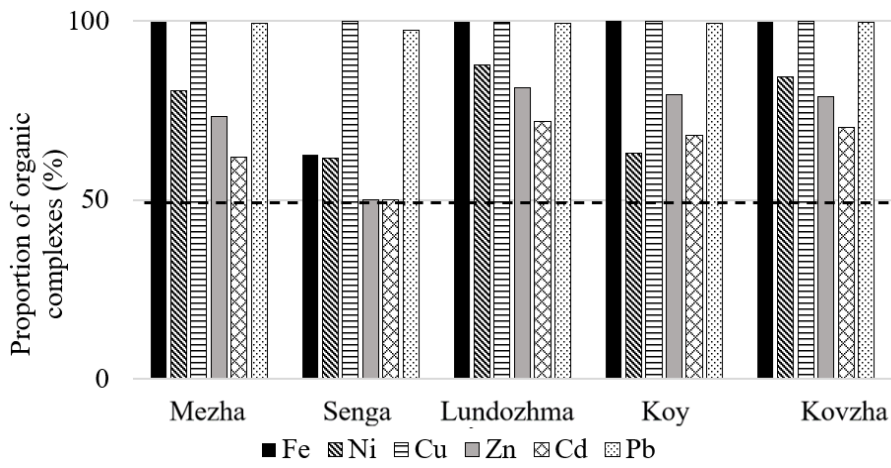


Fig. 1. Proportion of organic metal complexes in the studied waters

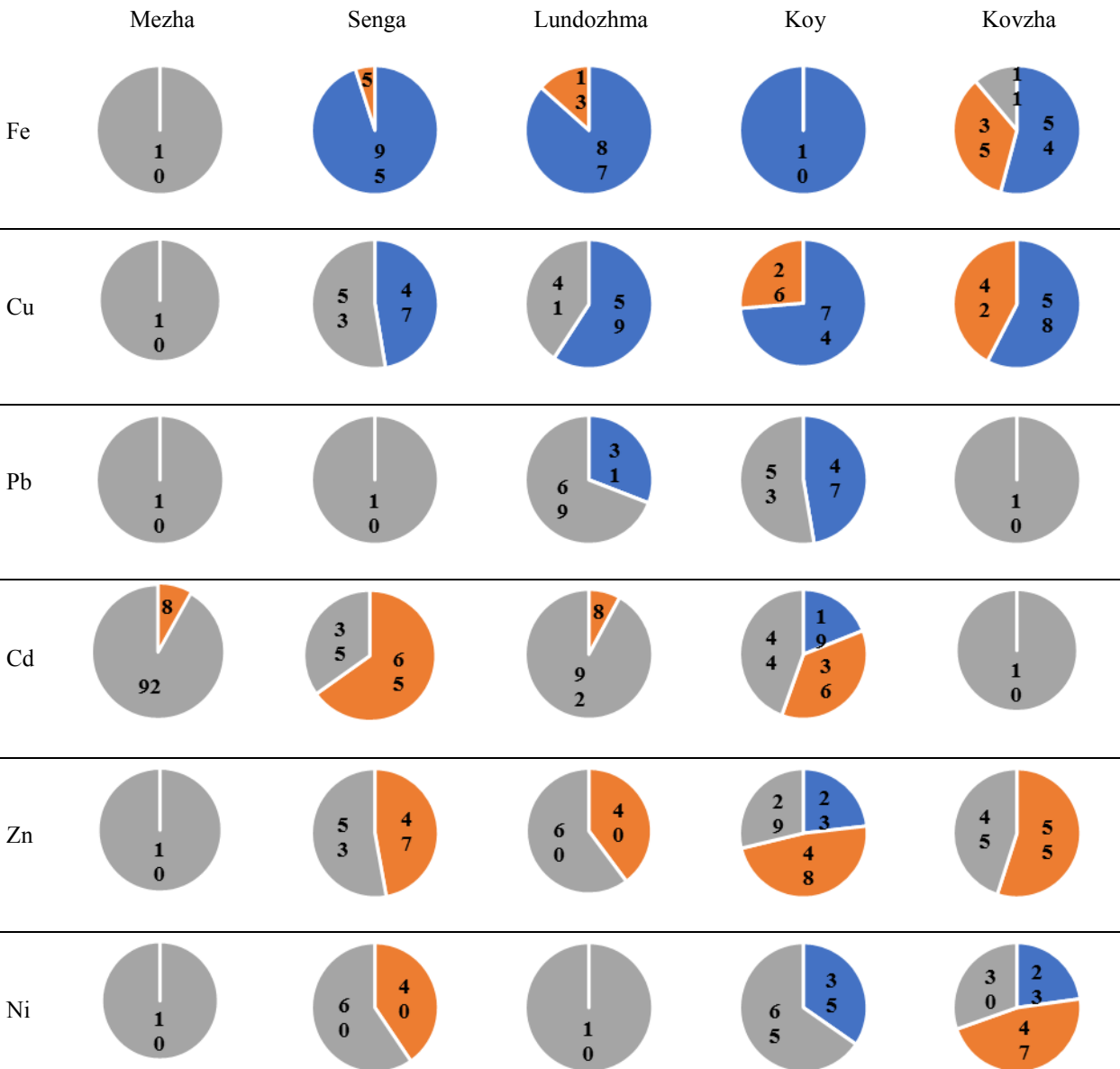


Fig. 2. Proportion of anionic, cationic, and neutral forms of heavy metals in the studied waters

**Conclusion.** In the rivers of the boreal zone, the predominant form of occurrence of Fe, Ni, Cu, Zn, Cd, and Pb is associated with organic matter. For Fe and Cu, anionic complexes with high molecular weight organic ligands of the type  $[\text{MeL}]^{n-}$  are characteristic. Pb and Cd are mainly found in neutral low molecular weight organic complexes of the type  $[\text{MeL}]^0$ . The main forms of occurrence of Zn and Ni are both neutral and positively charged low molecular weight organic complexes of the type  $[\text{MeL}]^0$  and  $[\text{MeL}]^{n+}$ .

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