The distribution and geochemistry of rare earth elements (REE) in anthropogenic, technogenic and natural surface waters of southern and eastern Primorye, Far East of Russia, are presented in this study. The obtained results indicated that most of REE (up to 70%) were transported as suspended matter, ratio between dissolved and suspended forms varying from the source to the mouth of rivers. It is shown that all REE (except Ce) in the source of the rivers are predominantly presented in dissolved form, however, the content of light and heavy REE is different. Short-term enrichment of light rare earth elements (LREE) caused by REE-rich runoff from waste dumps and mining is neutralized by the increase in river flow rate. Rivers in urban areas are characterized by high content of LREE in dissolved form and very low in suspended one.

1. Introduction
During the last decades, REE in various natural water sources have been the subject of intensive study. REE is often used as sensitive indicators of different water types and the degree of pollution by industrial, household, and agricultural wastewaters and nuclear power plant waste products. The insignificant differences in the chemical properties between the elements and their relative inertness provide grounds to assume that REE can be used as very sensitive indicators of geochemical processes that occur in water–rock–organic matter systems. The study of REE behavior in the natural water sources of the Russian Far East was initiated over 15 years ago [1-6]. First full data set on river waters of Primorye showed that obtained REE concentrations were at the detection limit of ICP-MS (Agilent 7500) for some rivers of Eastern and Southern Sikhote-Alin. A unique opportunity to measure REE concentrations in slightly mineralized waters in the rivers of eastern and southern Sikhote-Alin using the high resolution ICP-MS method appeared in 2014.

The purpose of this study is to measure the REE concentrations and the patterns of their fractionation in the rivers of eastern and southern Sikhote Alin, including relatively pure and polluted water streams crossing mining and urbanized areas.

Eleven rivers were sampled during 2014. On the north-east of Primorye, the Rudnaya River affected by mining has been investigated. From the north-east to the south-east of Primorye the following rivers with minimum anthropogenic impact have been tested: the Ayvakumovka, the Margaritovka, the Milogradovka, the Partizanskaya, the Sukhodol, the Petrovka, the Shkotovka, the Artemovka. The streams with anthropogenic impact are presented by the Vtoraya and the Pervaya
Rechka rivers within the territory of Vladivostok city, and a stream from purification plants of Dalnegorsk city. More details on sampling points can be found at https://www.google.com/maps/d/edit?mid=zw2CLGdOtNnE.k5G 87mVb IM&usp=sharing. Sampling methods, sample preparation and analytical peculiarities were discussed in [3].

2. Hydrochemical characteristics of rivers

In all the eastern and southern Sikhote-Alin rivers unaffected by anthropogenic impacts, mineralization is usually low (table), which reflects the wide distribution of crystalline rocks in the drainage areas and the low intensity of their chemical denudation. Increased mineralization is recorded within Vladivostok and in the Rudnaya River which is subjected to significant impacts of the mining industry (Table 1). The pH values typically varied from 6.0 to 7.0; in the Rudnaya River and Vladivostok water streams, they substantially exceeded 7.0. The content of dissolved oxygen in the unpolluted rivers was 9 mg/l. The turbidity of the water during the sampling period ranged from a few to tens of milligrams per liter. Cations in the %-equiv form are largely represented by Ca or Ca + Mg + Na mixture. The intensively polluted water streams frequently show a notable shift toward Na. Atmospheric precipitations are characterized by the mixed Ca–Na cation composition. Among the anions, the hydrocarbonate ion is dominant. A substantial shift toward the sulfate ion is observed in the mine waters and in a creek starting from the tailing storage. In the water streams of Vladivostok and its suburbs, the anion composition frequently exhibits a shift toward notable increase in Cl– and SO$_4^{2-}$.

Thus, the general hydrochemical parameters of the water in the studied rivers unaffected by anthropogenic impacts reflect insignificant erosion in the drainage areas composed mostly of acid and intermediate volcanic rocks.

3. Rare Earth Elements

Rare earth elements are transported by rivers both in solid (suspended particulate matter) and dissolved form. The content of REE transported in the form of suspended particulate matter by Primorye rivers may be as high as 70 % [6]. The proportions of REE transported in the solid and dissolved states are influenced by sorption/desorption processes and the pH of the medium [7]. Thus, to obtain a clear vision of REE fractionation, it is important to know REE concentrations in river water and suspended particulate matter.

The degree of fractionation depends on the physico-geographical conditions of the drainage area if the anthropogenic impact is negligible. The slight fractionation between light and heavy REE in the studied unpolluted rivers is explained by their hydrological features: steep profile; relatively small drainage area; low turbidity, total mineralization, and content of organic matter; and short interaction between water and suspended particulate matter. At the same time, in most large rivers with long interaction between suspended particulate matter and water, the water is enriched with heavy REE relative to LREE.

Very high concentrations of REE occur in mine water effluent and waste dumps of mining enterprises of the Rudnaya River basin. This is explained by lower pH values and higher TDS of water [6, 7]. While away from the pollution source (toward the mouth), the situation becomes similar to that in the unpolluted rivers of Sikhote Alin. Concentrations of LREE (La-Eu) in the rivers of Vladivostok city are tenfold lower. These concentrations are affected by of organic domestic wastes. LREE easily interact with organic matter and are removed from the solution. Figure 1 shows the results on total content of REEs (solid+dissolved), normalized to North-American shale composite (NASC). All lines were divided into three groups depending on presence/absence of anthropogenic or technogenic impact (A, B, C – see figure 1). The obtained data show that all lines demonstrate pronounced negative Ce-anomaly associated with the transition of Ce$^{3+}$ to Ce$^{4+}$ in oxygenated conditions (Eh$>0$), common for surface water streams. Four-valent cerium is inactive form and is derived from the solution [6, 8]. The actual fractionation between LREE and HREE doesn’t occur. We can clearly observe the separation of the REE concentration levels in the upper, middle reaches and mouth of the river.
Rudnaya River. Upper reaches are mostly affected by runoff from the tailings and mines which have high concentration of REEs (Table 1).

Towards mouth of the Rudnaya River, concentration of REE is reduced by dilution and sorption processes and falls dramatically in the mouth due to seawater influence [6]. Acidity growth results in a decreased REE concentration in water and increased fractionation to the suspended phase.

**Table.** Geochemical characteristic of watercourses of Southern and Eastern Primorye.

| Sampling point (ID number) | Chemical type of water | TDS, mg/l | pH | Eh, mV | LREE | HREE | $\Sigma_{REE}$, \( \mu g/l \) |
|---------------------------|------------------------|-----------|----|--------|------|------|-------------------|
| **Technogenous water streams** | | | | | | | |
| Streamhead of Krasnorechenskiy creek (1) | Mg–Ca-SO\(_4\) | 414 | 6.6 | 234.8 | 0.26 | 0.09 | 67.96 |
| Run off from the mine (2) | Na–Mg–Ca–SO\(_4\) | 1006 | 5.59 | 158 | 0.98 | 0.98 | 34.10 |
| **Rudnaya River** | | | | | | | |
| Streamhead | Na–Ca–HCO\(_3\) | 70 | 7.08 | 124 | 0.68 | 0.78 | 2.56 |
| After Krasnorechenskiy creek inflow | Ca–HCO\(_3\)–SO\(_4\) | 103 | 7.13 | 209 | 0.48 | 0.56 | 3.17 |
| After Taiga village waste water inflow | Na–Ca–SO\(_4\)–HCO\(_3\) | 92.1 | 7.28 | 286 | 0.36 | 0.44 | 3.66 |
| After Dalnegorsk city waste water inflow | Na–Ca–SO\(_4\)–HCO\(_3\) | 143 | 7.33 | 236 | 0.32 | 0.48 | 1.90 |
| Mouth | Ca–HCO\(_3\)–SO\(_4\) | 59.3 | 6.3 | 290 | 0.23 | 0.37 | 1.66 |
| **Natural water streams (rivers)** | | | | | | | |
| Avvakumovka (6) | Ca–Na–HCO\(_3\) | 70 | 5.91 | 254 | 0.19 | 0.22 | 11.20 |
| Margaritovka (7) | Na–Ca–HCO\(_3\) | 55 | 6.5 | 258 | 0.50 | 0.60 | 1.84 |
| Milogradovka (8) | Ca–Na–HCO\(_3\) | 51.4 | 6.17 | 296 | 0.45 | 0.48 | 3.51 |
| Partizanskaya (9) | Na–Ca–HCO\(_3\) | 76.2 | 6.88 | 246 | 0.38 | 0.47 | 0.32 |
| Sukhodol | Ca–Na–HCO\(_3\) | 44.6 | 6.38 | 277 | 0.30 | 0.35 | 0.77 |
| Petrovka (10) | Na–Ca–HCO\(_3\) | 57 | 6.92 | 263 | 0.39 | 0.40 | 0.80 |
| Shkotovka (11) | Na–Ca–HCO\(_3\) | 53 | 6.99 | 270 | 0.24 | 0.28 | 1.23 |
| Artemovka (12) | Na–Ca–HCO\(_3\) | 72.6 | 6.89 | 262 | 0.23 | 0.28 | 5.06 |
| **Anthropogenous water streams** | | | | | | | |
| Stream from purification plant of Dalnegorsk city (3) | NH\(_4\)–Na–Ca–Cl–SO\(_4\)–HCO\(_3\) | 300 | 6.96 | 40 | 0.82 | 0.94 | 0.20 |
| Vtoraya Rechka river (4) | Ca–Mg–Na–SO\(_4\)–HCO\(_3\)–Cl | 964 | 7.43 | 183 | 0.20 | 0.76 | 0.37 |
| Pervaya Rechka river (5) | Ca–Na–SO\(_4\)–HCO\(_3\)–Cl | 370 | 7.2 | 196.2 | 0.18 | 0.76 | 0.51 |

*Calculated the proportion of dissolved forms of REE on the sum of dissolved and suspended phase.

With increasing pH, the adsorption of lanthanides on suspended particles decreases from LREE to HREE [9]. The same patterns are observed for the proportion of the dissolved form, i.e. with a reduction of anthropogenic impact either the total REE content in water or the proportion of the dissolved forms of occurrence of REE decreases (Table).
Even more impressive difference between light and heavy REEs is observed in the streams of Vladivostok city (Figure 1C), as well as for purification plants of Dalnegorsk city. It reflects that this type of water is slightly alkaline (pH = 6.96–7.43) containing high concentrations of organic matter. REE Patterns for the Pervaya and the Vtoraya Rechka rivers demonstrate the same trend, but the last one has significant positive Gd anomaly, reflecting influence of health care facilities [10]. REE fractionation between dissolved and colloid forms is also different for various types of water streams. For example, almost 98% of REE present in the dissolved form in the runoff from the mine, showing the lack of organic contaminants and impurities capable of carrying REE adsorbed on colloidal particles. At the same time, the proportion of dissolved forms of REE in rivers was the least stable and varied from 0.19/0.22 for the Avvakumovka River to 0.5/0.6 for the Margaritovka River, reflecting the dependence of the total content of rare earth elements and the physic-chemical water parameters (pH, Eh), caused by a variety of flood characteristics.

Figure 1. Shale-normalized REE patterns in the watercourses: A – suffering technogenic impact; B – located in natural conditions; B – subject to anthropogenic pressure. Ordinate - normalized to NASC REE concentrations, the scale is logarithmic.

Previously, we calculated migration forms of some REE in sampled objects using the Selector software [3]. As a whole, it should be noted that most of them are mainly represented by the ion and carbonate forms, while their migration in water streams from tailing storages is largely provided by the sulfate form. For example, in the waters of the Avvakumovka and the Milogradovka rivers, La, Ce, and Nd migrate in the ion form, while the carbonate forms are subordinate. In the Avvakumovka River, this is also true for Eu, while in the Milogradovka River, the carbonate form slightly prevails over the ion one (51% vs. 43%). In the case of Yb, the ion and carbonate forms play approximately equal roles in its migration in the Avvakumovka River; in the Milogradovka River, migration of this element in the carbonate form sharply increases [3].

The proportions between the migration forms of Nd, Eu, and Yb in the Rudnaya River are slightly different. The migration of these elements is mostly provided by the carbonate form. Rather different proportions between migration forms are observed in the waters from the tailing storage, where La,
Nd, Eu, and Yb migrate mostly in the sulfate forms, while for Ce the ion form is the main one. Thus, these data demonstrate that the migration forms of some REE in the surface waters of three types with different REE concentrations (unpolluted water of the Avvakumovka and the Milogradovka rivers, the Rudnaya River waters subjected to the impact of the mining industry, and water from tailing storages) are different, as well.

4. Conclusion
Studies have established the following:
1. The content of REE and their fractionation in surface waters considerably varies depending on whether they are susceptible to the effects of mining enterprises or under impact of urbanized areas or located in natural conditions.
2. Host rocks, drained by rivers and, in urban areas, anthropogenic pressures have significant influence on the REE’s behavior and concentration.
3. REE fractionation between dissolved and suspended forms of transportation varies with distance from the upper reaches to the mouth. Most of the REE are transported in a suspended form (> 0.45) by the middle reaches of river, wherein the maximum concentrations are typical for light and medium REE, and the minimum – to heavy. In the upper reaches of the rivers all REE, with the exception of cerium, are predominantly in dissolved form. However, the division into groups (light+medium/heavy) is also common.
4. Effect of REE-rich runoff from waste dumps and processing enterprises drifts slightly against the general flow of the river. It is expressed in a short-term enrichment of LREE, but with the increase in the river flow, these anomalies are being leveled.
5. The rivers in urbanized areas are characterized by the most clearly expressed REE fractionation between suspended and dissolved forms. Effluents from purification plants and small rivers experiencing high human pressure are characterized by high content of LREE in dissolved form and very low concentrations of LREE in suspended one. This can be caused by high content of organic substances in wastewater and low concentrations of complex agents.

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