Labile Components of the Amur River Flood Silts

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Abstract. The paper considers the possibility of inflow and accumulation of pollutants on the Amur River floodplain as a result of floods and deposition of the flood silts (FS). Labile components of FS – water-dispersible clays (WPC) – are a good indicator of transfer and removal of nutrients and contaminants. The study was focused on FS of the floodplain islands below the confluence of the Sungari River (near Khabarovsk, Far East, Russia). It is shown that, the content of major and trace elements in FS corresponds to the average values for sedimentary rocks independently of the flood power. However, after minor flood, there was a significant accumulation of calcium and phosphorus in WDC, which is accompanied by an abnormal accumulation of As up to 70 mg/kg. After the extreme flood, the As content in WDC fell by more than three times, which is associated with the duration of standing water in the floodplain. The latter causes the dissolution and leaching of apatite group phosphates and the arsenates contained in them as impurities. The process of As accumulation in WDC of the flood silts in low-water years (at minor floods) is not critical, but requires monitoring and further research.

1. Introduction
The formation of the river sediment composition is of interest both for solving fundamental problems of ecology, hydrology and geochemistry, and their individual issues. This is especially true for large transboundary rivers with frequent high to catastrophic floods, such as the Amur River. In floods, the bulk of river sediments is transferred. An important feature of the Amur River is their directional accumulation in the riverbed and floodplain [1]. The area of directional accumulation of the Amur River sediments covers the river valley from the confluence of the Sungari River to the mouth. The Sungari River is the largest tributary of the Amur River. In some years, its flow at the confluence exceeds the water flow of the Amur River. The amount of suspended sediments in the river during floods reaches 1500 mg/dm³ or more. The Sungari sub-basin is characterized by the highest anthropogenic load in the Amur basin (the influence of agriculture, industrial pollution, mining, hydropower dams) and the highest removal of suspended sediment. The extent of the involvement of the Sungari sub-basin lands in agricultural production is evidenced by the cartographic assessment of the spatial and temporal dynamics of the land used for arable land and rice fields [2, 3].

The aim of the work is to study the features and composition of the flood silts (FS) of the Amur River floodplain in the zone of influence of its main tributary, the Sungari River. The task of the work is to assess the possibility of inflow and accumulation of contaminants on the Amur floodplain as part...
of the FS. The study is a continuation of our research of the Amur River ecosystem. Earlier, for the area of modern directional sediment accumulation, we noted a significantly greater similarity of the water-dispersible clays (WDC) of the flood silts with suspended matter of the Sungari River than with the soils of the catchment area and suspended matter of the Amur River before the Sungari confluence [4, 5]. In this work, the main attention was paid to the analysis and detailing of the gross composition of the labile components of the flood silts – water-dispersible clays (WDC), good indicator of many processes involving water, and first of all soil water erosion, transfer and removal of nutrients and contaminants.

2. Objects and methods
The work was carried out in the basin of the middle Amur River. The climate of the territory is formed under the strong influence of oceanic factors. In the second half of summer–early autumn, tropical air masses penetrate deep enough into the continent. They cause intense precipitation, which is the reason for the formation of high (sometimes catastrophic) floods. The flood of 2013 was extraordinary: in the area of Khabarovsk, the maximum water level was 8.08 m (exceeding the level of the historical 1897 – 1.66 m). The duration of water standing on the floodplain was about three months, flooding depth exceeded 5.0 m.

Below the confluence of the Sungari River (within the Middle Amur Lowland), there are several floodplain extensions, where the rate of the flood wave decreases, contributing to the intensive sediment accumulation in the floodplain extension between the source of the Fuyuan Channel and the railway bridge near Khabarovsk. The Amur River in this area is characterized by a wide (about 20 km) floodplain, which has a much smaller width down- and upstream. It is the largest accumulation zone after the confluence of the Sungari [6].

The object of the study was the flood silts (FS) – silt-loamy sediment accumulated during the deposition of suspended matter from the water stream during a flood. Sampling was carried out during the summer and autumn periods of 2012–2014 on floodplain islands near Khabarovsk – the sources of the Beshenaya (site 713, 48°27.382′N 135°04.643′E) and Pemzenskaya Channels (site 714, 48°26.299′N 134°53.414′E). Samples of FS buried by the sand on the island levees (bars) were also collected (sites 711 11, 48°27.209′N 135°04.270′E 11, 48°27.196′N 134°57.757′E, respectively).

The study is based on gross analysis, which was supplemented by electron microscopic studies (SEM analysis). Gross composition (major and trace elements) of air-dry samples was determined by X-ray fluorescent analysis (RFA) on Pioneer S4 (Bruker AXS, Germany) and VRA-30 (Carl Zeiss, Germany). The reliability of the results was confirmed by the analysis of some samples by inductively coupled plasma-mass-spectrometry (ICP-MS Elan 9000, Canada). The SEM analysis was carried out on VEGA 3 LMH (TESCAN, Czech Republic). The INCA Energy 350 energy-dispersion spectrometer (Oxford Instrument, UK) was used to analyze the elemental composition of the most representative regions. Water-dispersible clay (WDC), aggregated clay (AC) fractions (particle size <2 μm) and residue from clay removal (RCR) fraction (particle size >2 μm) were identified with the method of fractional dispergeration of clay in water [7, 8]. The obtained suspensions of WDC, AC and RCR were dried in a water bath. The analyses were carried out in the analytical centers of Institute for Tectonics and Geophysics and Institute of Water and Ecological Problems, FEB RAS (Khabarovsk, Russia).

3. Results and Discussion
The composition and morphology of the individual fractions of FS presented in Table 1 and Figure 1. At different thicknesses (from 0.1 to 10 cm in the air-dry state) of the flood silts, the content of WDC, as well as AC, is close – about 2 and 9–10%, respectively. The WDC fraction content increases to 6–7% due to the AC fraction in the sand-buried flood silts. Since oxides/hydroxides Fe (III) are involved in the AC, its aggregation decreases under reducing conditions and part of fraction passes into the WDC. The increase of the AC content in the deeper layers of the buried FS may be associated with the
migration of clay during the fall of the Amur water level. Due to the additional differentiation in the profile, the spread of the AC content is from 2 to 13%.

### Table 1. Content of labile fractions in the flood silts.

| N | Site, depth (cm) | Year | Water level, cm | Particle size composition <2 µm, % |
|---|-----------------|------|-----------------|----------------------------------|
|   |                 |      |                 | Σ  | WDC  | AC   |
| 1 | 713 0–0.5(1.0)  | 2012 | 331             | 12.0 | 2.2  | 9.8  |
| 2 | 713 0–5(10)     | 2013 | 808             | 12.2 | 2.2  | 10.0 |
| 3 | 714 0–0.1(0.3)  | 2014 | 338             | 11.7 | 3.2  | 8.5  |
| 4 | 711 10–15       |      |                 | 8.7  | 6.6  | 2.1  |
| 5 | 712 5–19        |      |                 | 10.0 | 5.8  | 4.2  |
| 6 | 19–28           |      |                 | 14.7 | 1.6  | 13.1 |

In addition to the fractional composition (WDC, AC and RCR content), the sediments are characterized by a similar gross composition over different years (table 2). The latter is not obvious, but it is quite natural, since river suspensions are repeatedly redeposited in the process of transport, which leads to an averaging of the sediment composition. According to the RFA analysis, they are depleted of trace elements such as Cr, Cu, Ni, Sr, V and Rb. Some excess is observed only for Zr (250–310 mg/kg), which is typical for the Amur alluvium with an epidote-hornblende association of accessory minerals, including zircon. In general, the content of major and trace elements in the flood silts corresponds to the average values for sedimentary rocks (SR) [9].

However, a significant accumulation of calcium and phosphorus (in terms of oxides up to 7.0 and 0.5%, respectively) was observed for the WDC in low-water years. Their excess is more than 1.5 times in comparison with the flood silts, AC and RCR fractions. It is known that the gross concentrations of major and trace elements in the compared environments, which are 1.5 times more or less of typical content for the relatively homogeneous in landscape-geochemical relation natural site, can be attributed with a high degree of confidence to abnormal concentrations. The level of 1.5-fold variation in the concentrations of the detected elements smooths out the natural variation in the distribution of elements and possible errors in sampling and chemical-analytical studies [10, 11].

Usually, the accumulation of phosphorus in the edaphic components of ecosystems is associated with iron oxides/hydroxides due to the extremely low solubility of iron phosphates [12]. However, in our case, their distribution is antabile: the maximum content of phosphorus (phosphates) in WDC corresponds to the minimum content of Fe₂O₃. Calcium phosphates are also characterized by relatively low solubility. Indeed, changes in the calcium content are symbatic with that for phosphorus, which with a high degree of probability allows us to assert that "excess" phosphorus is associated with calcium. Accordingly, its transfer occurs in the composition of phosphates of the apatite group.

Apatite is one of the accessory minerals of granite-metamorphic rocks and their sedimentary derivatives of the Amur basin. It is diagnosed both in bottom sediments and the flood silts. But the almost three-fold excess of phosphorus in the composition of WDC in the low water level years allows us to assume its anthropogenic origin, namely as a result of its (apatite) use as fertilizers on farmland. Phosphorus content in the WDC decreases by 1.5–2 times after a extremely flood 2013, as a result of “forced washing”. Note that the content of phosphorus and calcium in AC and RCR varies within a 1.5-fold variation.

Phosphate minerals of apatite supergroup possess strong affinity for strontium and arsenic. As it was established in the laboratory, the substitution of calcium by strontium and phosphorus by arsenic leads to structural disorder of apatite resulting in a loss of crystallinity and formation of various defects including dislocations, stacking faults, grain boundaries and triple junctions whose type and density varies with dopant level. As a consequence, the apatite solubility is enhanced [13–16].
Figure 1. Micrographs of the river suspended matter (a, b) and fractions of the flood silts (c–f): a, b – typical microaggregates of river suspensions; c, d – WDC and AC respectively; e, f – partially dissolved and idiomorphic apatite microcrystals respectively (SEM, BSE – detector).

The analysis of the trace element composition of WDC confirmed the data obtained in laboratory conditions. The increase of phosphorus and calcium content in the WDC in the low-water years was accompanied by an abnormal accumulation of arsenic up to 70 mg/kg and an increase in the strontium content to average values in sedimentary rocks. After the flood 2013, the content of As fell by more than three times. It is important to note that fluctuations in the arsenic content occur symbatically not only with fluctuations in the Sr content, but also with calcium and phosphorus. The data of the SEM
analysis of RCR confirm the increased solubility of phosphates in the flood silts (figure 1e, f). Therefore, the accumulation of As in the WDC in low-water years can be associated with the use of phosphorus fertilizers on the catchment lands.

### Table 2. Gross composition of the flood silts and their fractions.

| Element, ppm/oxide, % | FS [9] | SR | WDC | AC | RCR |
|-----------------------|--------|----|-----|----|-----|
| As                    | –      | 6.6| 74  | 22 | 13  |
| Sr                    | 300    | 194| 135 | 153| 125 |
| Pb                    | 24     | 28 | 18  | 19 | 17  |
| Ni                    | 25     | 50 | 32  | 45 | 48  |
| Cu                    | 19     | 55 | 58  | 40 | 38  |
| Zn                    | 80     | 96 | 136 | 152| 132 |
| CaO                   | 1.62   | 2.46| 2.11| 1.48| 1.22|
| P2O5                  | 0.18   | 0.35| 0.29| 0.30| 0.29|
| Fe2O3                 | 4.80   | 9.43| 9.56| 9.81| 3.28|

*Flood silts 2012 (a), 2013 and 2014 (b), buried flood silts (c); dash – no data.*

The danger of arsenic accumulation in the edaphic components of ecosystems is due to the fact that all its compounds are toxic and carcinogenic, and inorganic arsenic compounds belong to the 1st category of carcinogens according to IARC (International Agency for Research on Cancer). The arsenic accumulation in the WDC of the flood silts in low-water years is not critical, since, taking into account the contribution of the WDC, the arsenic content in the flood silts does not exceed 5 mg/kg, with the average content of the latter in sedimentary rocks at 6.6 mg/kg. However, the observed accumulation of arsenic in the labile, the most chemically active fraction of the flood silts, requires further research and monitoring.

### 4. Conclusion

The composition of the Amur River flood silts deposited was studied in the most extensive zone of directional sediment accumulation (near Khabarovsk, Far East, Russia). The study of the flood silts by X-ray fluorescence analysis, scanning electron microscopy and energy dispersion analysis showed that they are characterized by a similar composition at minor and extreme floods. The content of the major and trace elements in them correspond to the average values for sedimentary rocks.

The detail of the composition of the flood silts fractions (water-dispersible clay WDC, aggregated clay AC and residue from clay removal RCR) showed that labile WDC fractions are a good indicator of transfer and removal of nutrients and contaminants by river sediments. The use of phosphorus fertilizers on the farmlands of the catchment leads to a significant accumulation of calcium and phosphorus in the WDC of the flood silts at low water level of the Amur River. It is accompanied by abnormal accumulation of As up to 70 mg/kg. At extreme flood and prolonged standing of water on the floodplain, phosphates of the apatite group and arsenates contained in them as impurities, dissolve and wash out from the labile fraction of the flood silts.

The arsenic accumulation in the WDC in low-water years is not critical, since the contribution of the WDC, the arsenic content in the flood silts does not exceed the average contents in sedimentary rocks. However, taking into account the trends in the targeted use of land in the Amur basin, the scale of land involvement in agricultural production in the Sungari sub-basin, the noted arsenic accumulation in the labile, the most chemically active fraction of the flood silts requires monitoring and further research.

### 5. References

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