Assessment of the current state of agricultural land pollution with heavy metals

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Abstract. In the modern period the quality of the land, especially for agricultural production is an especially important aspect. For evaluation of agricultural lands pollution, a on land pollution by heavy metals, related to 1 and 2 hazard class study was conducted. The study of these metals was carried out in one of the industrial districts of the Irkutsk region – Usol’sky. The study of soils on the content of heavy metals Hg, Cu, Cd, Pb, Zn, Ni, Cr, As was carried out on different agricultural lands for different landscape structures. Grounds for selection of soil samples laid with uniform soil, vegetation conditions and uniform mechanical composition of the soil. The grounds were laid out in distant from the industrial sources, the land located under the ”torch” Heating Electrical Station (HES) and the land along Federal highway and the land adjacent to industrial sites. The content of mobile forms of heavy metals are given in tabular material. Analysis of soil samples was carried out for humus horizon (0-10 cm), where the accumulation of heavy metals occurs. From the above factual (tabular) material it follows that the current state of agricultural lands of the Usol’sky district is satisfactory, with the exception of lands located along the Federal highway and land adjacent to the industrial site of OJSC (OAO) ”Usol’e - Khimprom”. As studies have shown the anomalous accumulation of heavy metals in the soils of this area doesn’t occur, which can be explained by the conditions of leaching regime, the mobility of metals, light and middle loam and sandy loam mechanical composition of the soil.

Pollution of agricultural land by technogenic pollutants affects the quality of food grown on such soils, leads to a change in the function of soils, to their qualitative deterioration and degradation, which ultimately affects the normal functioning of the ecosystem as a whole. Land degradation poses a growing threat to global food security [1,2]. The priority and most common pollutants are heavy metals - Hg, Cu, Cd, Pb, Zn, Ni, Cr, As, which enter the soil from various technogenic sources and are highly technophilic [3]. Also, these heavy metals tend to accumulate in soils and plants that a person consumes as food and belong to the 1st and 2nd hazard classes.

Therefore, the aim of our research was to assess the pollution of agricultural land in one industrial and at the same time agricultural region – Usol’sky in the Irkutsk region. Agricultural lands occupy 12% of all lands of the Usol’sky district and are located in the northern lowland part of the Angara river valley, where they are a zone of almost continuous agricultural use [4], and are represented by gray forest soils of light and medium loamy and sandy loam texture.

The material used for the study was soil samples taken on various agricultural lands. Sites for the selection of soil samples were laid on lands with a uniform soil and vegetation cover; on arable land
samples with the same mechanical composition were taken. The selection of soil samples was carried out according to GOST 17.4.3.01-83 [5], the number of samples studied was 56.

The analysis of soil samples was carried out by the atomic absorption method [6] using the Shimadzu AA-7000 atomic absorption spectrophotometer.

The main source of heavy metals entering the soils of the Usol’sky district are dust emissions from coal burning from heating electrical stations, small boiler houses, and home furnaces; ash and slag storage sites, gas and dust emissions of enterprises, vehicles [7].

The accumulation of heavy metals in soils occurs in the upper (humus) horizons of soils, and directly depends on the thickness of the humus horizon and the content of organic matter, and their further migration depends on the mechanical composition of soils. Since the task of assessing the pollution of agricultural lands was faced, the excess of pollution was estimated by the maximum permissible concentrations (MAC) and background values of the content of heavy metals in soils.

The content of heavy metals in the arable layer, represented by loamy mechanical composition, is below the MAC (table 1).

| Item to be defined | Unit of measurement | MAC value | Background values | Actual concentration | Accuracy indicator,± Δ |
|--------------------|---------------------|-----------|-------------------|---------------------|------------------------|
| Lead (Pb)          | mg / kg             | 6.0       | 1.08              | 4.1                 | ±1.5                   |
| Zink (Zn)          | mg / kg             | 23.0      | 3.19              | 10.5                | ±4.6                   |
| Nickel (Ni)        | mg / kg             | 4.0       | 0.74              | <2.0                | -                      |
| Cadmium (Cd)       | mg / kg             | 1.0       | 0.13              | <0.5                | -                      |
| Copper (Cu)        | mg / kg             | 3.0       | 0.28              | 2.2                 | ±0.9                   |
| Chromium (Cr)      | mg / kg             | 6.0       | -                 | <2.0                | -                      |
| * Arsenious (As)   | mg / kg             | 2.0       | -                 | 0.17                | ±0.09                  |
| * Mercury (Hg)     | mg / kg             | 2.1       | -                 | 0.015               | ±0.007                 |

* in all tables, mercury and arsenious are gross forms; A dash indicates that the item is not detected.

Table 2 presents the results of the content of heavy metals in the humus horizon (0-10 cm) of gray forest soils on a natural meadow field used for grazing, where their content is also lower than the MAC.

| Item to be defined | Unit of measurement | MAC value | Background values | Actual concentration | Accuracy indicator,± Δ |
|--------------------|---------------------|-----------|-------------------|---------------------|------------------------|
| Lead (Pb)          | mg / kg             | 6.0       | 1.08              | 3.6                 | ±1.3                   |
| Zink (Zn)          | mg / kg             | 23.0      | 3.19              | 9.2                 | ±4.0                   |
| Nickel (Ni)        | mg / kg             | 4.0       | 0.74              | 2.8                 | ±1.2                   |
| Cadmium (Cd)       | mg / kg             | 1.0       | 0.13              | <0.5                | -                      |
| Copper (Cu)        | mg / kg             | 3.0       | 0.28              | 1.8                 | ±0.7                   |
| Chromium (Cr)      | mg / kg             | 6.0       | -                 | 2.5                 | ±1.4                   |
| * Arsenious (As)   | mg / kg             | 2.0       | -                 | 0.2                 | ±0.01                  |
| * Mercury (Hg)     | mg / kg             | 2.1       | -                 | 0.015               | ±0.007                 |

The content of heavy metals was also determined in the humus horizon on a meadow field used for perennial grasses for haymaking, where their content is lower than the MAC (table 3).
As the above results show, the determined heavy metals are below the MAC on the studied agricultural lands. However, in addition to MAC, the state of soils is estimated by background values, including in relation to heavy metals. Naturally, the background values of the elements will vary even within the same region and depend on the underlying rocks and the introduced diffuse industrial emissions. So, for the soils of the Usol’sky district, according to the data of the Federal State Institution Agrochemical Service Center (ASC) “Irkutsky”, the background values of heavy metals are lower than the MAC. Therefore, the actual concentrations of Pb, Zn, Ni, Cu were 2-3 times higher than the background.

Some agricultural land is located directly under the "torches" of industrial enterprises, heating electrical stations. Industrial emissions of these enterprises directly affect agricultural land [8]. So, soil samples taken in the zone of influence of heating electrical stations show an increased content of Pb, Ni, and Cu, but not exceeding the MAC, but above background values (tables 4,5).

**Table 3.** The content of mobile forms of heavy metals in the humus horizon on a meadow field under perennial grasses (hayfields).

| Item to be defined | Unit of measurement | MAC value | Background values | Actual concentration | Accuracy indicator, ± Δ |
|--------------------|---------------------|-----------|-------------------|----------------------|-------------------------|
| Lead (Pb)          | mg / kg             | 6.0       | 1.08              | 4.2                  | ±1.5                    |
| Zink (Zn)          | mg / kg             | 23.0      | 3.19              | 8.8                  | ±3.9                    |
| Nickel (Ni)        | mg / kg             | 4.0       | 0.74              | 2.1                  | ±0.9                    |
| Cadmium (Cd)       | mg / kg             | 1.0       | 0.13              | <0.5                 | -                       |
| Copper (Cu)        | mg / kg             | 3.0       | 0.28              | 1.6                  | ±0.6                    |
| Chromium (Cr)      | mg / kg             | 6.0       | -                 | 2.9                  | ±1.7                    |
| * Arsenious (As)   | mg / kg             | 2.0       | -                 | 0.2                  | ±0.01                   |
| * Mercury (Hg)     | mg / kg             | 2.1       | -                 | 0.015                | ±0.007                  |

**Table 4.** The content of mobile forms of heavy metals in the humus horizon on the meadow field in the heating electrical stations zone of influence.

| Item to be defined | Unit of measurement | MAC value | Background values | Actual concentration | Accuracy indicator,± Δ |
|--------------------|---------------------|-----------|-------------------|----------------------|-------------------------|
| Lead (Pb)          | mg / kg             | 6.0       | 1.08              | 5.7                  | ±2.1                    |
| Zink (Zn)          | mg / kg             | 23.0      | 3.19              | 14.2                 | ±6.2                    |
| Nickel (Ni)        | mg / kg             | 4.0       | 0.74              | 3.9                  | ±1.6                    |
| Cadmium (Cd)       | mg / kg             | 1.0       | 0.13              | <0.5                 | -                       |
| Copper (Cu)        | mg / kg             | 3.0       | 0.28              | 2.8                  | ±1.1                    |
| Chromium (Cr)      | mg / kg             | 6.0       | -                 | 3.6                  | ±2.1                    |
| * Arsenious (As)   | mg / kg             | 2.0       | -                 | 1.3                  | ±0.7                    |
| * Mercury (Hg)     | mg / kg             | 2.1       | -                 | 0.026                | ±0.012                  |

**Table 5.** The content of mobile forms of heavy metals in the humus horizon on a meadow field under perennial grasses in the heating electrical stations zone of influence.

| Item to be defined | Unit of measurement | MAC value | Background values | Actual concentration | Accuracy indicator,± Δ |
|--------------------|---------------------|-----------|-------------------|----------------------|-------------------------|
| Lead (Pb)          | mg / kg             | 6.0       | 1.08              | 5.9                  | ±2.1                    |
| Zink (Zn)          | mg / kg             | 23.0      | 3.19              | 14.4                 | ±6.3                    |
| Nickel (Ni)        | mg / kg             | 4.0       | 0.74              | 3.7                  | ±1.6                    |
| Cadmium (Cd)       | mg / kg             | 1.0       | 0.13              | <0.5                 | -                       |
| Copper (Cu)        | mg / kg             | 3.0       | 0.28              | 2.9                  | ±1.2                    |
| Chromium (Cr)      | mg / kg             | 6.0       | -                 | 4.1                  | ±2.4                    |
| * Arsenious (As)   | mg / kg             | 2.0       | -                 | 1.3                  | ±0.7                    |
| * Mercury (Hg)     | mg / kg             | 2.1       | -                 | 0.027                | ±0.012                  |
Soil samples studied on agricultural land through which the federal highway runs in the Usol’sky district were taken on abandoned self-growing lands and a natural meadow with gray forest soils.

The heavy metal content in the surface horizon of self-growing soils is almost 2 times higher than the MAC for Pb, 1.4 times for Ni, 3.4 times for Cu, 1.5 times for Cr, and almost like MAC for Hg (table 6).

Table 6. The content of mobile forms of heavy metals in the surface horizon in self-growing lands.

| Item to be defined | Unit of measurement | MAC value | Background values | Actual concentration | Accuracy indicator, ± Δ |
|-------------------|---------------------|-----------|-------------------|----------------------|-------------------------|
| Lead (Pb)        | mg / kg             | 6.0       | 1.08              | 11.8                 | ±4.2                    |
| Zink (Zn)        | mg / kg             | 23.0      | 3.19              | 15.9                 | ±7.0                    |
| Nickel (Ni)      | mg / kg             | 4.0       | 0.74              | 5.5                  | ±2.3                    |
| Cadmium (Cd)     | mg / kg             | 1.0       | 0.13              | 0.55                 | ±0.3                    |
| Copper (Cu)      | mg / kg             | 3.0       | 0.28              | 10.2                 | ±4.1                    |
| Chromium (Cr)    | mg / kg             | 6.0       | -                 | 9.1                  | ±5.3                    |
| * Arsenious (As) | mg / kg             | 2.0       | -                 | 1.2                  | ±0.6                    |
| * Mercury (Hg)   | mg / kg             | 2.1       | -                 | 1.91                 | ±0.86                   |

The heavy metal content in the humus horizon in a natural meadow 500 m from the passing federal highway showed an abnormally high content of Pb - excess of MAC by 4.4 times, As by 3.5 times, Cu by 2.4 times, Ni by 1.5 times, and Cr by 1.2 times (table 7). High concentrations may also occur due to proximity to the industrial enterprise of Usol’ye Khimprom (sampling was carried out 1.5 km from the reduction area).

Table 7. The content of mobile forms of heavy metals in the humus horizon in a natural meadow.

| Item to be defined | Unit of measurement | MAC value | Background values | Actual concentration | Accuracy indicator, ± Δ |
|-------------------|---------------------|-----------|-------------------|----------------------|-------------------------|
| Lead (Pb)        | mg / kg             | 6.0       | 1.08              | 26.4                 | ±9.5                    |
| Zink (Zn)        | mg / kg             | 23.0      | 3.19              | 18.9                 | ±8.3                    |
| Nickel (Ni)      | mg / kg             | 4.0       | 0.74              | 6.1                  | ±2.6                    |
| Cadmium (Cd)     | mg / kg             | 1.0       | 0.13              | 0.9                  | ±0.4                    |
| Copper (Cu)      | mg / kg             | 3.0       | 0.28              | 7.1                  | ±2.8                    |
| Chromium (Cr)    | mg / kg             | 6.0       | -                 | 7.4                  | ±4.3                    |
| * Arsenious (As) | mg / kg             | 2.0       | -                 | 6.9                  | ±3.5                    |
| * Mercury (Hg)   | mg / kg             | 2.1       | -                 | 1.64                 | ±0.74                   |

The studied soil samples from various agricultural lands corresponding to different landscape structures and located at different distances from pollution sources showed different degrees of pollution with heavy metals. And the farther from the source of pollution the agricultural land is located, the lower is the content of heavy metals in the soil.

It should be noted that the soils of the Usol’sky district are in satisfactory condition in terms of heavy metal content, i.e. their content in soils does not exceed MAC.

The most contaminated soils with heavy metals are confined directly to the sources of pollution, the main of which is the federal highway and existing industrial facilities.

Anomalous accumulation of heavy metals in soils does not occur, despite the long industrial development of the area, which can be explained by the conditions of the leaching regime, high mobility of metals, light and medium loamy and loamy soil texture.

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