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# Heavy Metal Migration in Soil-Plant System in Conditions of Urban Environmental Pollution

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**ABSTRACT:** This study is devoted to heavy metal soil migration to coltsfoot in urban pollution of Tyumen city. Soil and plant samples were collected in the summer of 2017 to 2020 at the control site, highway, engine-building, oil refinery, battery manufacturing, and metallurgical plants. Heavy metals (Cu, Zn, Fe, Mn, Pb, Cd, Ni, Co, and Cr) mobile and acid-soluble forms in soils, and metals concentration in plants were analyzed by atomic absorption and atomic emission spectroscopy. Metals concentration in soils of urban area exceeded the control by 1.1 to 20 times. Relative accumulation of metals decreased in the order: Pb > Cu > Zn > Ni > Cr > Fe > Co > Mn > Cd. Heavy metals mobility in soils decreased in the order: Cd > Mn > Pb > Zn > Ni = Cu > Co > Cr > Fe. Coltsfoot metal accumulation changed in the order: Fe > Zn = Mn > Pb > Cu > Cr > Co > Ni > Cd. The highest contamination for most of the metals was at the metallurgical plant, while Ni and Co concentrations were maximum at the oil refinery. Content of Cu, Zn, Fe, Cd, Ni, and Co in coltsfoot correlated with a concentration in soils. Bioconcentration factor showed the following metal bioavailability: Cu > Zn > Cd > Pb > Ni > Mn > Cr > Co > Fe. Heavy metal accumulation in coltsfoot should be taken into account during sanitary control of herb drugs based on this plant.

**KEYWORDS:** Heavy metals, soils, plants, accumulation, bioconcentration factor

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## Introduction

Heavy metals (HM) are one of the most abundant environmental pollutants. Metals sources may be natural (wildfires, rock erosion, and volcano eruptions), but anthropogenic pollution (metallurgy, agriculture, transport) exacerbates the metals contamination issue (P. K. Rai et al., 2019; Uchimya et al., 2020). The atmospheric HM pollution is related to power plants (27%), ferrous metallurgy (24.3%), oil extraction and refinery (15.5%), transport (13.1%), and non-ferrous metallurgy (10.5%; Zwolak et al., 2019).

After precipitation on the soil surface, HM accumulate in soil, especially in humus rich layers (Q. Li et al., 2022). The main risk of HM pollution is the long half-life and ability to migrate by trophic chains (Nagajyoti et al., 2010; Zwolak et al., 2019). Metals half-life may take 70 to 510 years for Zn, 13 to 110 years for Cd, 310 to 1,500 years for Cu, and 770 to 5,900 years for Pb (Kabata-Pendias & Pendias, 2011). Metals mobility in soil is stipulated by many factors: organic substance, clay minerals, oxides, and anions (carbonates, phosphates, silicates, and sulfides). All of these components determine soil ability to bind HM and prevent their further migration (Q. Li et al., 2022). Besides, soil pH, redox potential, and humidity are of high importance for metal mobility (R. Kim et al., 2015).

Bioavailable of mobile HM form in soil include water-soluble compounds, free metal ions, and soluble metal complexes with organic and inorganic ligands (R. Kim et al., 2015; Q. Li et al., 2022). Besides, HM exchangeable forms, adsorbed on clay minerals by electrostatic forces, are also considered mobile. Various reagents and mixtures are used for the extraction of metal mobile forms in soil, such as acetate ammonium buffer

(pH = 4.8), 1 M  $\text{NH}_4\text{NO}_3$ , 0.02 M  $\text{CaCl}_2$  + 1 M  $\text{CH}_3\text{COONH}_4$ , 0.005 M DTPA (diethylenetriamine pentaacetate) + 0.01 M  $\text{CaCl}_2$  + 0.1 M triethanolamine. Hydrochloric acid (1 M solution) is often used for the extraction of mobile forms, however, in this case not only bioavailable form is extracted, but also less plant available metal reserve in soil (R. Kim et al., 2015; Q. Li et al., 2022).

HM transport in plants can be passive (without energy consumption), and active (metabolic) with energy consumption to transport ions in opposition to electrochemical potential gradient. Passive transport is implemented via cation non-selective channel, while for active transports selective protein transporters are used. For instance, there are proteins, selectively transporting  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  (Nagajyoti et al., 2010). Metals ions are transported to stem and leaves via xylem, after which can enter phloem and redistribute in plant organs (DalCorso et al., 2013).

The rate of metal accumulation in plants is species-specific. According to Baker's (1981) classification there are accumulators, indicators, and excluders plant species. Accumulators absorb high metal concentration in the overground part, despite low metal content in soil. Indicators accumulate metals in such way, that content in plant change proportionally to that in soil. Excluders slightly accumulate metals in overground part, but after metal concentration in soil reach certain critical point, plant start to accumulate HM in an uncontrolled way.

Many HM (Cu, Zn, Fe, Mn, Mo, Ni, and Co) are essential for normal plant growth and development (Ghori et al., 2019). All plants need to absorb these elements from soil in certain amount. These metals implement various physiological functions:



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participate in redox enzymes, photosynthesis, respiration, protein biosynthesis (Andresen et al., 2018). However, excessive HM concentration leads to toxic effect (Edelstein & Ben-Hur, 2018; Riyazuddin et al., 2022).

Metals can have various negative impacts on plants vital functions. HM can oppress plant growth by lowering cell division intensity, and violate cell elongation, binding to -SH groups of cell wall proteins (Bharti & Sharma, 2022; Kupper & Andresen, 2016). Metal accumulation leads to oppression of plants development, delay in phenological phases, and disturb mineral nutrition (Rhiyazuddin et al., 2022). Photosynthesis is very sensitive to HM accumulation, photosynthetic enzymes, chloroplasts membranes, and photosystem in whole can be targets for HM (R. Rai et al., 2016). Besides, HM decrease activity of respiration enzymes and electron transport in respiration chain (Bharti & Sharma, 2022). Finally, HM disturb water balance in plants, by decreasing water volume in cells, osmotic potential, and transpiration rate (Kabata-Pendias & Pendias, 2011; P. K. Rai et al., 2019).

There have been numerous studies on heavy metal concentration in soils and plants in various countries (Baltas et al., 2020; Demkova et al., 2017; Dong et al., 2018; Galal & Shehata, 2015; Gupta et al., 2021; H. S. Kim et al., 2016; Kumar et al., 2020; Noli & Tsamos, 2016; Rutigliano et al., 2019; Shaheen et al., 2016; Sulaiman & Hamzah, 2018; Swiercz & Zajecka, 2018; Varol et al., 2021; Wang & Zhang, 2018; Wu et al., 2018). However, there are few studies associated with HM translocation in Russia (Chaplygin et al., 2018; Minkina et al., 2017; Popova, 2019). Tyumen is a fast-developing industrial city with oil and gas, engine-building, and metallurgical enterprises, as well as a high number of vehicles per capita. This creates the risk of HM contamination. Earlier in some studies, HM content in soils was (Konstantinova et al., 2019; Seleznev & Rudakov, 2019; Shigabaeva, 2015), however, the issue of metal translocation to plants remains poorly investigated. This study attempts to fill the research gap of heavy metals translocation to plants of urban area, and metals bioavailability in disturbed urban soils in a case study of Tyumen.

Coltsfoot is a plant with widely recognized medicinal properties (Shikov et al., 2014). However, our previous research showed that it has a high capability of metal accumulation, compared to other herbs in the studied area (Petukhov et al., 2020). The purpose of this study was to investigate heavy metals soil migration to coltsfoot in Tyumen during 4 year period (2017–2020). Assumed metal accumulation in coltsfoot will limit its use in medicinal purpose. The data on HM concentration in soils and herbs of Tyumen can be recommended to apply in the development of environmentally justified norms of human activity on wildlife. The investigation of quantitative relation of metal concentration in soils and plants can predict the possibility of phytoextraction, and limit herbal materials from polluted areas.

## Materials and Methods

### Study area

Soil and plants samples were collected at the end of July 2017 to 2020 in Tyumen at the control site (30 km from the city, and 5 km from anthropogenic sources), highway (30 km from the city), and 200 m distance at plants in the city: engine-building, oil refinery, battery manufacturing, and metallurgical plant (UMMC). Tyumen (57°09'N, 65°32'E) is situated in Western Siberia and is the capital of the Tyumen Oblast in the Russian Federation.

### Sample collection and analysis

Soil samples were collected at 0 to 10 cm depth. Air-dried soils were averaged by quartering, ground, and sifted through a 1 mm sieve. Heavy metal mobile form in soil was extracted using acetate-ammonium buffer (pH=4.8; PND F 16.1:2:2.2:2.3.78-2013), acid-soluble fraction was extracted by 5 M HNO<sub>3</sub> (RD 51.18.191-2018).

Coltsfoot (*Tussilago farfara* L., 1753) overground part (leaves and stems) was collected at five spots at each site. Plants were washed and air-dried, and then ashed at 500°C for 3 hours. Then metals in plant ash were extracted by 5 M HNO<sub>3</sub> (Ministry of Agriculture of the Russian Federation, Central Institute of Agrochemical Treatment of Agriculture, 1992). Metal content analysis (Cu, Zn, Fe, Mn, Pb, Cd, Ni, Co, and Cr) in soils and plants was conducted by atomic absorption spectrophotometer “ContrAA 700” (Analytic Jena, Germany) and atomic emission spectrophotometer with inductively coupled plasma Plasma Quant PQ9000 (Analytic Jena, Germany). Analysis was conducted at the Center for Collective Usage “Rational nature management and physicochemical research.”

The plants ability to accumulate HM was estimated by Bioconcentration factor (BCF), which was calculated as the ratio of the metal content in the plant to that acid-soluble fraction in soil:

$$BCF = \frac{C_{plant}}{C_{soil}}$$

### Quality control and assurance

Sample using a known amount of metal standard was examined for verification of the accuracy of the analytical procedure. Recoveries of the heavy metals ranged between 85% and 110%. All reagents used were analytical reagent grade. A pre-cleaning regime, that is, acid washed was applied for each glassware apparatus prior to use. Double-distilled water was used throughout this study for laboratory applications including reagents, blanks, and standard preparation. Soil and plants sample preparation was conducted twice, while measurements were conducted in three parallel.

### Statistical analysis

Statistical analysis was conducted by calculating the mean value and mean deviation. Normal distribution was confirmed by Kolmogorov–Smirnov test. Mean values comparison was done by Student's *t* coefficient, confidence interval was calculated for  $p \leq .05$ . Bivariate correlations were analyzed at  $p \leq .05$ .

### Results and Discussion

The content of Cu mobile form in soil ranged from 0.07 to 0.94 mg kg<sup>-1</sup> (Table 1). In 2017, 2018, and 2020 Cu concentration in urban soils was higher than in control by 1.6 to 4 times. The maximum permitted concentration of Cu mobile form in soil (3 mg kg<sup>-1</sup>) was not reached. Acid-soluble Cu fraction in soils of Tyumen ranged from 1.2 to 24 mg kg<sup>-1</sup> (Table 1) and exceeded concentration at the control site in urban area in 2017 to 2020. Mobility of Cu in soil (ratio of mobile form to acid-soluble) ranged from 0.2% to 37%, mostly from 1% to 18% (Figure 1).

Elevated Cu content in urban soils may be stipulated by a high amount of vehicles, fossil fuel burning, and likely the historic application of pesticides and fertilizers at the city outskirts. In previous research Cu content in soils of Tyumen ranged from 11 to 28 mg kg<sup>-1</sup> (Shigabaeva, 2015), while in another study the mean Cu content was estimated at 30 mg kg<sup>-1</sup> (Konstantinova et al., 2019). Cu content in soils was close to its content in another city of Russia, Yoshkar-Ola (Voskresenskaya et al., 2013), soils of Slovakia (Demkova et al., 2017), and Northern India (Gupta et al., 2021). The comparison of results in this research with other studies is presented in Table 2.

The Cu concentration in coltsfoot ranged from 6 to 24 mg kg<sup>-1</sup> (Table 3). The plant accumulation was not observed in 2017, while in 2018 to 2020 Cu concentration in coltsfoot from highway, oil refinery, engine-building, and metallurgical plants exceeded the control by 20% to 140%. The highest concentration was at highway and metallurgical plant. Cu content in plants correlated with Cu mobile form in soils during 2017 to 2020 ( $R = .43$ ). The Cu content in coltsfoot turned out to be close its concentration in vegetables, grown in HM polluted soil in Bangladesh (Shaheen et al., 2016) and India (Gupta et al., 2021).

The content of Zn mobile form in soils ranged from 0.7 to 13 mg kg<sup>-1</sup> (Table 1). The maximum permitted concentration of Zn in soils is 23 mg kg<sup>-1</sup>, there was no exceeding of this value (Chief State Sanitary Doctor of the Russian Federation, 2021). In most cases, Zn mobile form in urban area was higher than that of control at least by 1.5 times, the highest concentration was at oil refinery and metallurgical plant.

The concentration of Zn acid-soluble fraction in soils of Tyumen ranged from 7 to 67 mg kg<sup>-1</sup>. Zn content in soils from industrial plants was higher than control at least by 15%, with maximum at metallurgical and battery-manufacturing plants, exceeding control by four times. The increase in Zn content at metallurgical plant may be connected to application of

zinc-coated scrap in steel production. Zn mobility in soils ranged from 5% to 20% (in average 5%–10%; Figure 1). Zn concentration in our study was close to another research in Tyumen (Boev et al., 2019; Shigabaeva, 2015), as well as study from Middle Urals copper smelter (Trubina & Vorobeichik, 2013). The content of Zn in Tyumen soils was similar to other countries: Poland (Swiercz & Zajecka, 2018), Italy (Rutigliano et al., 2019), and India (Gupta et al., 2021).

The content of Zn in coltsfoot ranged from 17 to 160 mg kg<sup>-1</sup> (Table 3). The relative Zn accumulation of at least by 15% to 100% was at all sites, except for battery-manufacturing plant. The maximum Zn accumulation was at metallurgical plant, exceeding control by 2.5 to 4 times. Zn concentration in plants correlated with its mobile form in soil ( $R = .40$ ). Coltsfoot at highway, engine-building, oil refinery, and metallurgical plant accumulated Zn higher than its maximum permitted concentration in plants (50 mg kg<sup>-1</sup>; Governmental Agricultural Committee of USSR, 1987). Zn concentration in coltsfoot was close to that of plants from Novocherkassk (Chaplygin et al., 2018) and Yoshkar-Ola cities (Voskresenskaya et al., 2013), vegetables in Greece (Noli & Tsamos, 2016), and lettuce in Italy (Rutigliano et al., 2019).

The concentration of Fe mobile form in soils ranged from 16 to 207 mg kg<sup>-1</sup> (Table 1). Fe content at highway and metallurgical plant in 2018 and 2020 was elevated, compared to control. Fe acid-soluble fraction in soils ranged from 15,000 to 95,000 mg kg<sup>-1</sup> (Table 1). Fe content exceeded the control at all sites, except highway. The maximum Fe concentration was at battery manufacturing and metallurgical plants, where it exceeded control at least by two times. Similar Fe concentration in soil was reported in Turkey (Baltas et al., 2020), and Mn mining area from southern China (M. S. Li et al., 2007). Environmental pollution by Fe is likely to appear from chimneys of steel production and iron-nickel battery manufacturing wastewaters. Fe mobility in soils was extremely low (0.03%–0.57%; Figure 1). This is probably due to iron presence in poorly soluble oxides and hydroxides (Colombo et al., 2013; Kabata-Pendias & Pendias, 2011).

The concentration of Fe in coltsfoot ranged from 95 to 8,500 mg kg<sup>-1</sup>. Coltsfoot accumulated Fe at all sites compared to control (Table 3). The greatest Fe accumulation was at metallurgical plant (up to 17 times) and highway in 2019. This may be due to steel production waste and application of Fe-based octane rating booster. In 2017 to 2020 Fe concentration in coltsfoot correlated with its mobile form in soils ( $r = .44$ ). Fe concentration in plants is similar to that of plants from Malaysia (Sulaiman & Hamzah, 2018) and Egypt (Galal & Shehata, 2015).

The concentration of Mn mobile form ranged from 25 to 110 mg kg<sup>-1</sup> (Table 1). Maximum permitted concentration of Mn mobile form in soil is 100 mg kg<sup>-1</sup> (Chief State Sanitary Doctor of the Russian Federation, 2021). Mn content in soil at engine-building and metallurgical plant in 2019 exceeded

**Table 1.** Heavy Metal Content (mean  $\pm$  SD, mg kg<sup>-1</sup>) in Soils of Tyumen.

1	CU	ZN	FE	MIN	PB	CD	NI	CO	CR
2	3	4	5	6	7	8	9	10	
Control 2017	0.38 $\pm$ 0.06	1.64 $\pm$ 0.02	123 $\pm$ 6	57.5 $\pm$ 5.6	16.1 $\pm$ 4.8	0.31 $\pm$ 0.18	—	—	—
	3.77 $\pm$ 0.07	9.60 $\pm$ 3.33	32,600 $\pm$ 1,080	163 $\pm$ 8	13.3 $\pm$ 5.1	0.56 $\pm$ 0.07	—	—	—
Highway 2017	0.44 $\pm$ 0.07	1.45 $\pm$ 0.03	88.4 $\pm$ 11.1	62.1 $\pm$ 7.7	6.12 $\pm$ 1.87	0.40 $\pm$ 0.08	—	—	—
	1.19 $\pm$ 0.20	6.78 $\pm$ 0.11	15,600 $\pm$ 1,370	184 $\pm$ 12	10.3 $\pm$ 3.6	0.43 $\pm$ 0.08	—	—	—
Engine-building plant 2017	0.94 $\pm$ 0.15	3.45 $\pm$ 0.08	34.5 $\pm$ 3.2	56.1 $\pm$ 7.7	12.8 $\pm$ 6.8	0.17 $\pm$ 0.10	—	—	—
	5.93 $\pm$ 0.53	29.1 $\pm$ 6.8	40,000 $\pm$ 1,200	247 $\pm$ 27	10.5 $\pm$ 2.5	0.13 $\pm$ 0.09	—	—	—
Oil refinery 2017	0.77 $\pm$ 0.12	1.73 $\pm$ 0.12	39.5 $\pm$ 8.5	52.5 $\pm$ 5.1	9.44 $\pm$ 4.04	0.77 $\pm$ 0.14	—	—	—
	4.24 $\pm$ 0.22	17.4 $\pm$ 1.7	32,000 $\pm$ 3,690	272 $\pm$ 9	10.4 $\pm$ 3.9	0.63 $\pm$ 0.14	—	—	—
Battery manufacturing plant 2017	0.86 $\pm$ 0.14	2.46 $\pm$ 0.03	46.9 $\pm$ 2.6	86.6 $\pm$ 5.6	29.0 $\pm$ 2.2	0.26 $\pm$ 0.17	—	—	—
	13.6 $\pm$ 1.89	48.7 $\pm$ 7.5	79,800 $\pm$ 4,250	462 $\pm$ 18	91.1 $\pm$ 5.4	0.29 $\pm$ 0.04	—	—	—
Metallurgical plant 2017	0.84 $\pm$ 0.14	1.38 $\pm$ 0.01	38.2 $\pm$ 6.2	56.0 $\pm$ 2.3	13.6 $\pm$ 5.2	0.27 $\pm$ 0.13	—	—	—
	9.58 $\pm$ 0.35	29.1 $\pm$ 4.5	77,000 $\pm$ 6,280	372 $\pm$ 16	10.6 $\pm$ 2.6	0.24 $\pm$ 0.15	—	—	—
Control 2018	0.07 $\pm$ 0.01	2.30 $\pm$ 0.06	47.7 $\pm$ 2.6	37.8 $\pm$ 6.0	16.5 $\pm$ 3.2	0.53 $\pm$ 0.16	—	—	—
	1.78 $\pm$ 0.27	12.8 $\pm$ 5.0	24,500 $\pm$ 138	176 $\pm$ 24	10.4 $\pm$ 5.2	0.44 $\pm$ 0.10	—	—	—
Highway 2018	0.44 $\pm$ 0.07	0.94 $\pm$ 0.01	58.7 $\pm$ 7.1	60.1 $\pm$ 2.5	14.1 $\pm$ 3.5	0.48 $\pm$ 0.21	—	—	—
	3.66 $\pm$ 0.42	12.0 $\pm$ 1.5	22,000 $\pm$ 1,960	318 $\pm$ 19	10.5 $\pm$ 5.2	0.35 $\pm$ 0.10	—	—	—
Engine-building plant 2018	0.44 $\pm$ 0.07	2.89 $\pm$ 0.13	32.8 $\pm$ 0.7	94.0 $\pm$ 9.1	19.0 $\pm$ 5.2	0.48 $\pm$ 0.20	—	—	—
	9.67 $\pm$ 0.60	23.3 $\pm$ 3.4	41,600 $\pm$ 4,750	461 $\pm$ 13	18.3 $\pm$ 2.3	0.53 $\pm$ 0.10	—	—	—
Oil refinery 2018	0.32 $\pm$ 0.05	0.73 $\pm$ 0.05	25.0 $\pm$ 13.7	25.2 $\pm$ 1.0	27.2 $\pm$ 1.4	0.54 $\pm$ 0.20	—	—	—
	7.05 $\pm$ 0.32	14.2 $\pm$ 0.3	44,400 $\pm$ 5,770	265 $\pm$ 29	28.5 $\pm$ 3.3	0.46 $\pm$ 0.10	—	—	—

(Continued)

Table 1. (Continued)

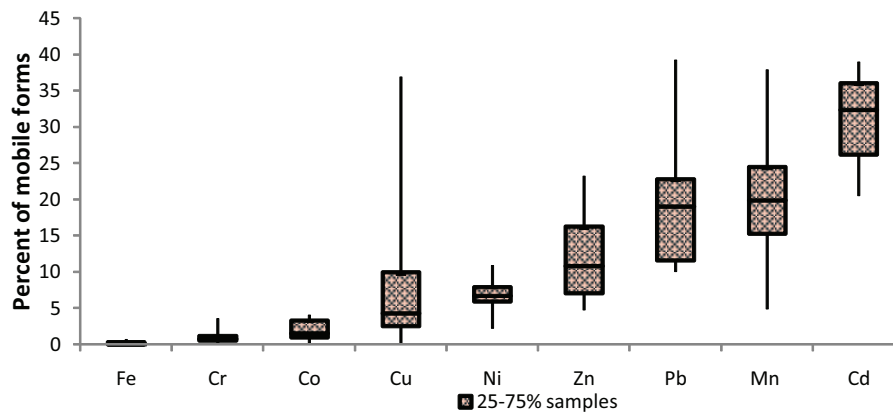
1	2	3	4	5	6	7	8	9	10
	CU	ZN	FE	MN	PB	CD	NI	CO	CR
Battery manufacturing plant 2018	0.45 ± 0.07	2.85 ± 0.01	22.7 ± 7.9	58.0 ± 5.4	49.0 ± 3.9	0.62 ± 0.12	—	—	—
	15.8 ± 1.00	55.5 ± 2.6	87,900 ± 2,200	488 ± 35	172 ± 6	0.52 ± 0.13	—	—	—
Metallurgical plant 2018	0.07 ± 0.01	2.55 ± 0.08	16.3 ± 2.2	69.5 ± 4.5	17.3 ± 0.8	0.46 ± 0.18	—	—	—
	8.49 ± 0.75	28.3 ± 3.9	58,500 ± 6,480	453 ± 88	17.9 ± 2.3	0.33 ± 0.10	—	—	—
Control 2019	0.58 ± 0.15	1.16 ± 0.05	207 ± 10	59.7 ± 6.0	4.30 ± 2.19	0.08 ± 0.03	—	—	—
	5.93 ± 0.29	16.5 ± 0.2	28,555 ± 833	171 ± 2	7.34 ± 3.57	0.33 ± 0.17	—	—	—
Highway 2019	0.55 ± 0.20	3.62 ± 0.10	172 ± 14	71.0 ± 0.9	4.35 ± 1.83	0.13 ± 0.04	—	—	—
	3.69 ± 0.95	15.6 ± 0.5	25,731 ± 1,126	390 ± 8	7.23 ± 3.73	0.33 ± 0.16	—	—	—
Engine-building plant 2019	0.50 ± 0.14	4.48 ± 0.16	67.8 ± 5.6	105 ± 2	5.19 ± 1.76	0.16 ± 0.08	—	—	—
	9.77 ± 0.46	28.0 ± 0.5	44,040 ± 1,008	276 ± 7	8.14 ± 3.63	0.34 ± 0.17	—	—	—
Oil refinery 2019	0.72 ± 0.20	2.44 ± 0.16	102 ± 7	68.4 ± 0.9	1.51 ± 0.87	0.13 ± 0.03	—	—	—
	6.67 ± 0.33	19.2 ± 0.6	43,714 ± 1,311	282 ± 10	7.29 ± 3.60	0.33 ± 0.17	—	—	—
Battery manufacturing plant 2019	0.49 ± 0.09	3.20 ± 0.08	49.3 ± 7.4	96.5 ± 0.5	34.9 ± 3.2	0.13 ± 0.06	—	—	—
	16.6 ± 0.9	45.5 ± 1.3	94,992 ± 2,265	448 ± 12	54.6 ± 3.7	0.34 ± 0.17	—	—	—
Metallurgical plant 2019	0.61 ± 0.20	7.28 ± 0.06	180 ± 5	110 ± 1	4.89 ± 3.37	0.14 ± 0.02	—	—	—
	10.8 ± 0.46	36.7 ± 2.2	53,544 ± 1,179	435 ± 11	7.61 ± 3.73	0.33 ± 0.17	—	—	—
Control 2020	0.27 ± 0.05	4.76 ± 0.62	17.0 ± 0.3	49.0 ± 3.0	0.67 ± 0.08	0.03 ± 0.01	1.2 ± 0.2	0.14 ± 0.02	0.07 ± 0.01
	7.0 ± 0.9	26.0 ± 3.2	37,650 ± 1,490	463 ± 83	6.70 ± 0.80	0.09 ± 0.01	14.0 ± 2.6	7.1 ± 1.3	11 ± 1.4
Highway 2020	0.31 ± 0.03	2.34 ± 0.13	12.0 ± 0.7	83.0 ± 5.2	1.20 ± 0.10	0.03 ± 0.01	2.4 ± 0.3	0.27 ± 0.02	0.15 ± 0.02
	9.0 ± 1.1	22.0 ± 1.4	43,210 ± 3,200	322 ± 20	7.9 ± 0.5	0.11 ± 0.02	22.0 ± 2.7	7.2 ± 0.4	17.0 ± 2.0

(Continued)

Table 1. (Continued)

1	2	3	4	5	6	7	8	9	10
	CU	ZN	FE	MN	PB	CD	NI	CO	CR
Engine-building plant 2020	0.44 ± 0.08	4.82 ± 0.31	9.0 ± 1.5	85.0 ± 5.2	4.70 ± 0.30	0.05 ± 0.01	2.5 ± 0.5	0.11 ± 0.02	0.13 ± 0.01
	18.0 ± 3.4	49.0 ± 9.0	75,170 ± 2,050	547 ± 34	21.0 ± 1.3	0.16 ± 0.03	38.0 ± 7.1	13.0 ± 2.4	28.0 ± 5.3
Oil refinery 2020	0.48 ± 0.03	13.0 ± 0.8	8.3 ± 0.9	97.0 ± 6.0	4.40 ± 0.30	0.06 ± 0.01	3.6 ± 0.2	0.36 ± 0.02	1.31 ± 0.24
	18.0 ± 1.3	62.0 ± 3.8	48,630 ± 2,410	410 ± 25	19.3 ± 1.2	0.15 ± 0.03	54.0 ± 3.4	9.0 ± 0.6	37.0 ± 2.3
Battery manufacturing plant 2020	0.18 ± 0.03	4.45 ± 0.32	6.3 ± 0.1	66.0 ± 4.0	55.0 ± 10.0	0.07 ± 0.01	0.8 ± 0.1	0.02 ± 0.01	0.01 ± 0.01
	24.0 ± 3.0	67.0 ± 12.0	95,240 ± 3,070	689 ± 43	141 ± 17	0.31 ± 0.04	37.0 ± 4.5	15.0 ± 1.0	30.0 ± 5.6
Metallurgical plant 2020	0.45 ± 0.08	7.00 ± 0.40	24.0 ± 1.8	77.0 ± 4.8	1.20 ± 0.10	0.05 ± 0.01	1.6 ± 0.2	0.13 ± 0.02	0.32 ± 0.02
	18.0 ± 2.2	58.0 ± 7.2	77,050 ± 4,970	606 ± 38	12.0 ± 0.8	0.25 ± 0.05	29.0 ± 3.6	11.5 ± 1.4	27.0 ± 5.0

Note. Above the line—mobile form, under the line—acid-soluble fraction.



**Figure 1.** Percentage of heavy metals mobile forms in soil of Tyumen in 2017 to 2020. Vertical lines indicate first and fourth quartile, and horizontal line inside the box is median.

maximum permitted concentration. Mn mobile form in soil from urban area exceeded the control by 1.1 to 2 times during 2017 to 2020 period.

The concentration of acid-soluble Mn fraction in soil ranged from 160 to 690 mg kg<sup>-1</sup> (Table 1). Mn content in urban area exceeded the control by 1.3 to 2.8 times, with highest concentration at metallurgical and battery-manufacturing plants. This is likely stipulated by Mn application in steel ligation. In previous studied Mn content in soils of Tyumen was estimated by 400 to 930 mg kg<sup>-1</sup> (Shigabaeva, 2015), while 170 to 770 mg kg<sup>-1</sup> in puddle sediments (Seleznev & Rudakov, 2019). The concentration of Mn in soil was similar to that in Hangzhou, China (Wang & Zhang, 2018). Mn mobility in soil ranged from 5% to 35% (mostly 10%–25%; Figure 1), which is explained by high solubility of Mn compounds and stability of its aqua complexes.

Mn concentration in coltsfoot ranged from 15 to 318 mg kg<sup>-1</sup> (Table 3). Mn accumulation compared to control was at highway, oil refinery, and metallurgical plant by 1.5 to 13 times, as well as engine-building plant in 2020. Elevated Mn content in coltsfoot at highway may. The usage of Mn in steel production leads to its accumulation by coltsfoot at metallurgical plant. Mn content in plants turned out to be similar to that in Egypt (Galal & Shehata, 2015), Novochoerkassk (Chaplygin et al., 2018), and vegetables in northern India (Gupta et al., 2021).

The concentration of Pb mobile form in soils ranged from 0.7 to 55 mg kg<sup>-1</sup> (Table 1). In most cases Pb concentration was at control level and in the range of 1 to 20 mg kg<sup>-1</sup> in 2017 to 2019. Pb content at oil refinery exceeded the control by 60% in 2018. In 2020 Pb mobile form concentration was higher than control at all sites, at least by 1.8 times. Besides, Pb mobile form at battery manufacturing plant greatly exceeded the control during all studied period. This is likely due to lead-acid batteries production.

The concentration of Pb acid-soluble fraction in 2017 to 2019 was roughly the same as mobile form. The exception was battery manufacturing plant, where 54 to 172 mg kg<sup>-1</sup> of Pb was registered (Table 1). In 2020 Pb acid-soluble fraction was,

at least two times higher in urban area than at control and highway. Pb content at battery manufacturing plant was 140 mg kg<sup>-1</sup>, which exceeded the control by 20 times. In previous study (Shigabaeva, 2015), Pb content in soil was 158 mg kg<sup>-1</sup>, which is similar to the results of this study. Pb mobility in soils was 10% to 64%, which creates the risks of Pb accumulation by plants. High Pb mobility in urban soils was previously registered in Samara (Morozova & Prokhorova, 2007). The Pb content in soil was similar to its level in urban soils of Slovakia (Demkova et al., 2017), and agricultural soils in Turkey (Baltas et al., 2020).

The concentration of Pb in coltsfoot from urban area in 2017 to 2019 was at the detection limit or similar to control (Table 3). In 2018 Pb concentration in plants from battery manufacturing plant exceeded control, which is due to lead-acid battery production. In 2020 Pb content in coltsfoot ranged from 0.7 to 11.5 mg kg<sup>-1</sup> (Table 3), with exceeding the control at all sites, at least by 1.6 times. The maximum Pb accumulation was at metallurgical and battery manufacturing plants, where, according to the Pharmacopeia of Russian Federation, maximum permitted concentration of Pb was exceeded (Ministry of Health of Russian Federation, 2015).

Cd mobile form concentration in soils of Tyumen ranged from 0.03 to 0.84 mg kg<sup>-1</sup> (Table 1). In 2017 to 2019 there were no statistically significant differences among studied sites. In 2020 Cd mobile form in soils of urban area exceeded the control by 60% to 130% (Table), but still remained low (0.03–0.07 mg kg<sup>-1</sup>). Cd acid-soluble fraction in soil ranged from 0.08 to 0.56 mg kg<sup>-1</sup> (Table 1). This is similar to Cd content in soil from Novochoerkassk power station (Chaplygin et al., 2018). In 2020 Cd content in urban soils was higher than control by 1.6 to 3.4 times (Table 1). Elevated Cd concentration may be due to accumulation and burn of municipal waste, and industrial and municipal wastewaters. According to the results of 2020, Cd mobility in soils was high (21%–39%).

The concentration of Cd in most plant samples in 2017 to 2019 was at the detection limit (0.02 mg kg<sup>-1</sup>) or at control level (Table 3). Low Cd content was previously observed in



Table 2. Heavy Metals Content in Soils and Plants in Various Studies.

LOCATION	CU	ZN	FE	MN	PB	CD	NI	CO	CR	REFERENCES
1	2	3	4	5	6	7	8	9	10	11
Soils										
Tyumen, Russia	1–24	6–67	15,600–95,240	163–689	10–172	0.13–0.63	14–54	7–15	11–37	In this study (acid-soluble fraction)
Tyumen, Russia	11–28	39–120		403–931	4–158		43–119	49–62	26–87	Shigabaeva (2015)
Novocherkassk, Russia	38–72	82–141		615–944	21–67	0.2–1.4	45–66		84–138	Chaplygin et al. (2018)
Hangzhou, China	2–198	43–885		92–770	2.13–346	0.03–2.41	6–75	1–16	20–255	Wang and Zhang (2018)
Skarzynsko-Kamienna, Poland	2–261	35–64			2–1,600	0.1–1.3	2–22		2–42	Swiercz and Zajecka (2018)
Yoshkar-Ola, Russia	20–45	5–174			18–146	0–1.63				Vokresenskaya et al. (2013)
Zagazig-Banaha highway, Egypt	23–77	49–372	8,600–47,955	408–1,246	10–30	<0.2	11–53	5–35	20–120	Galal and Shehata (2015)
North-East part of Slovakia	1.29–9.54	57–952	7,450–36,512	180–5,284	19–172	1.29–9.54	13–81	3–31	10–72	Demkova et al. (2017)
North-West part of Greece		10–506	20,000–38,000			0.5–4.1		12–20	156–9,983	Noli and Tsamos (2016)
Southern Italy	35–140	10–100			4–22	0.2–0.5	4–15	5–9	20–200	Rutigiano et al. (2019)
Northern India	5–34	25–63		2–68	4–22	0.4–24	5–49	3–14		Gupta et al. (2021)
Sinop province, Turkey	12–119	16–150	16,870–94,465		7–55		11–706		24–761	Baltas et al. (2020)
South-West part of China	7–83	36–226			18–46	0.1–0.7	12–78		40–115	Dong et al. (2018)
Northeastern Qinghai-Tibet Plateau	17–253	70–1,002			8–2,077	0.1–15	14–1,015	5–56	42–913	Wu et al. (2018)
WSA	38.9	70		488	27	0.41	29	11.3	59.5	Kabata-Pendias and Pendias (2011)
ESA	17.3	68.1		524	32	0.28	37	10.4	94.8	Kabata-Pendias and Pendias (2011)
UCC	28	67	39,200	774	17	0.09	47	17.3	92	Rudnick and Gao (2003)

(Continued)

Table 2. (Continued)

LOCATION	CU	ZN	FE	MN	PB	CD	NI	CO	CR	REFERENCES
1	2	3	4	5	6	7	8	9	10	11
Plants										
Tyumen, Russia	6–24	17–160	95–8,489	15–318	8–18	0.02–0.37	4–25	0.1–1.4	1–16	In this study
Novocherkassk, Russia Asteraceae and Poaceae families	1–21	2–86		2–119	1–34	0.07–1.20	1–17		9–24	Chaplygin et al. (2018)
Yoshkar-Ola, Russia <i>Plantago major</i> L., <i>Polygonum aviculare</i> L., <i>Matricaria suaveolens</i> L.	1.95–9.80	1.26–37.04			0.02–4.88	0.19–0.72				Voskresenskaya et al. (2013)
Namyangju city, Korea Chinese cabbage	23–40	22–110			0.24–1.47	0.22–0.52	5–40		20–70	H. S. Kim et al. (2016)
Zagazig-Banha highway, Egypt <i>Plantago Major</i>	17–75	25–68	108–24,215	73–98	1.8–5.6	0.5–4.2	2–9	1–6	7–74	Galal and Shehata (2015)
Jengka, Malaysia <i>Athyrium esculentum</i> , <i>Chromolaena odorata</i> , and <i>Lantana camara</i>	5–27		155–842		0.26–2.86	0.01–0.09				Sulaiman and Hamzah (2018)
North-West part of Greece vegetables		10–61	22–261					0.03–0.18	0.4–0.6	Noli and Tsamos (2016)
Bangladesh vegetables	2.2–9.7	0.07–3.5		7–28	0.01–0.06	0.01–0.06	0.6–2.3		0.5–1.1	Shaheen et al. (2016)
Southern Italy L. <i>sativa</i> , <i>C. pepo</i>	5–40	10–30				0.1–0.2	1–4		0.2–0.8	Rutigliano et al. (2019)
Northern India Vegetables	3–15	10–57		3–59	0.5–8.0	0.03–2.17	0.06–4.0	0.1–1.6		Gupta et al. (2021)

Table 3. Heavy Metal Content (Mean  $\pm$  SD, mg kg<sup>-1</sup>) in Coltsfoot From Studied Area in Tyumen in 2017 to 2020.

1	2	3	4	5	6	7	8	9	10
	CU	ZN	FE	MN	PB	CD	NI	CO	CR
Control 2017	21.1 $\pm$ 0.1	26.2 $\pm$ 1.5	94.6 $\pm$ 2.6	26.6 $\pm$ 3.6	9.0 $\pm$ 4.5	0.23 $\pm$ 0.11	—	—	—
Highway 2017	20.5 $\pm$ 0.1	23.9 $\pm$ 8.5	145 $\pm$ 9	33.2 $\pm$ 2.0	8.7 $\pm$ 4.3	0.24 $\pm$ 0.14	—	—	—
Engine-building plant 2017	20.0 $\pm$ 0.1	40.5 $\pm$ 0.4	123 $\pm$ 1	23.3 $\pm$ 0.2	9.2 $\pm$ 5.3	0.02 $\pm$ 0.10	—	—	—
Oil refinery 2017	18.0 $\pm$ 0.1	17.4 $\pm$ 0.3	192 $\pm$ 4	56.3 $\pm$ 3.4	9.0 $\pm$ 1.6	0.02 $\pm$ 0.10	—	—	—
Battery manufacturing plant 2017	15.0 $\pm$ 0.2	22.8 $\pm$ 0.8	127 $\pm$ 9	14.9 $\pm$ 0.6	9.1 $\pm$ 1.1	0.02 $\pm$ 0.10	—	—	—
Metallurgical plant 2017	19.0 $\pm$ 0.6	32.5 $\pm$ 0.4	992 $\pm$ 22	157 $\pm$ 5	9.0 $\pm$ 4.8	0.16 $\pm$ 0.12	—	—	—
Control 2018	7.8 $\pm$ 0.4	20.9 $\pm$ 0.3	359 $\pm$ 5	36.8 $\pm$ 0.5	8.4 $\pm$ 4.2	0.35 $\pm$ 0.14	—	—	—
Highway 2018	12.8 $\pm$ 0.2	41.0 $\pm$ 0.1	768 $\pm$ 4	62.0 $\pm$ 0.9	8.2 $\pm$ 4.1	0.48 $\pm$ 0.20	—	—	—
Engine-building plant 2018	5.9 $\pm$ 1.2	24.2 $\pm$ 1.1	482 $\pm$ 29	17.3 $\pm$ 0.1	8.2 $\pm$ 4.1	0.43 $\pm$ 0.17	—	—	—
Oil refinery 2018	10.0 $\pm$ 0.2	39.0 $\pm$ 4.6	733 $\pm$ 64	20.1 $\pm$ 0.3	17.8 $\pm$ 8.9	0.27 $\pm$ 0.11	—	—	—
Battery manufacturing plant 2018	5.9 $\pm$ 0.2	20.5 $\pm$ 0.4	874 $\pm$ 42	22.0 $\pm$ 0.7	18.2 $\pm$ 0.6	0.51 $\pm$ 0.28	—	—	—
Metallurgical plant 2018	9.5 $\pm$ 0.3	60.8 $\pm$ 7.5	6,143 $\pm$ 442	75.2 $\pm$ 3.2	11.9 $\pm$ 1.8	0.23 $\pm$ 0.10	—	—	—
Control 2019	8.5 $\pm$ 0.2	30.0 $\pm$ 0.6	1,013 $\pm$ 50	24.2 $\pm$ 1.0	$\leq$ 5.7	$\leq$ 0.14	—	—	—
Highway 2019	9.6 $\pm$ 0.2	37.7 $\pm$ 3.3	7,789 $\pm$ 78	53.1 $\pm$ 1.8	$\leq$ 5.7	$\leq$ 0.14	—	—	—
Engine-building plant 2019	8.9 $\pm$ 0.5	40.7 $\pm$ 1.1	1,473 $\pm$ 101	21.2 $\pm$ 1.8	$\leq$ 5.7	$\leq$ 0.14	—	—	—
Oil refinery 2019	8.6 $\pm$ 0.2	23.6 $\pm$ 0.6	1,391 $\pm$ 144	53.6 $\pm$ 3.5	$\leq$ 5.7	$\leq$ 0.14	—	—	—
Battery manufacturing plant 2019	9.8 $\pm$ 0.2	20.2 $\pm$ 0.5	2,026 $\pm$ 130	30.0 $\pm$ 2.5	$\leq$ 5.7	$\leq$ 0.14	—	—	—
Metallurgical plant 2019	13.5 $\pm$ 0.3	74.3 $\pm$ 1.8	8,489 $\pm$ 112	117 $\pm$ 3	$\leq$ 5.7	$\leq$ 0.14	—	—	—
Control 2020	9.9 $\pm$ 0.6	37.5 $\pm$ 2.3	154 $\pm$ 13	63.1 $\pm$ 3.9	0.69 $\pm$ 0.04	0.27 $\pm$ 0.05	4.2 $\pm$ 0.8	0.15 $\pm$ 0.02	1.0 $\pm$ 0.1
Highway 2020	11.8 $\pm$ 0.7	68.5 $\pm$ 8.5	257 $\pm$ 5	86.2 $\pm$ 5.3	1.14 $\pm$ 0.07	0.17 $\pm$ 0.03	3.8 $\pm$ 0.2	0.47 $\pm$ 0.09	2.0 $\pm$ 0.4
Engine-building plant 2020	20.4 $\pm$ 3.8	70.3 $\pm$ 8.7	331 $\pm$ 11	89.0 $\pm$ 16.0	2.1 $\pm$ 0.1	0.19 $\pm$ 0.02	4.9 $\pm$ 0.3	0.26 $\pm$ 0.05	3.6 $\pm$ 0.7
Oil refinery 2020	18.6 $\pm$ 1.2	59.4 $\pm$ 7.4	559 $\pm$ 18	64.0 $\pm$ 12.0	2.7 $\pm$ 0.5	0.28 $\pm$ 0.03	24.9 $\pm$ 4.6	1.35 $\pm$ 0.25	11.3 $\pm$ 2.1
Battery manufacturing plant 2020	13.5 $\pm$ 1.7	22.0 $\pm$ 2.7	173 $\pm$ 2	69.5 $\pm$ 4.3	7.4 $\pm$ 0.5	0.37 $\pm$ 0.02	4.6 $\pm$ 0.3	0.44 $\pm$ 0.03	1.5 $\pm$ 0.1
Metallurgical plant 2020	23.9 $\pm$ 1.5	160 $\pm$ 10	1,440 $\pm$ 64	318 $\pm$ 40	11.5 $\pm$ 0.7	0.29 $\pm$ 0.05	6.0 $\pm$ 0.4	0.48 $\pm$ 0.03	16.5 $\pm$ 2.0

floodplain plants in Tyumen (Motorin & Bukin, 2014). In 2020 Cd concentration in coltsfoot ranged from 0.09 to 0.37 mg kg<sup>-1</sup> (Table 3), only exceeding the control at battery manufacturing plant. In 2020 positive correlations between Cd content in plants and Cd mobile form in soils, as well as its acid-soluble fraction were established ( $R = .68$  and  $.72$  respectively).

In 2020 the concentration of Ni mobile form in soils ranged from 0.8 to 3.6 mg kg<sup>-1</sup> (Table 1). Ni content at all sites, except for battery manufacturing plant, exceeded the control at least by 1.3 times. The acid-soluble fraction of Ni in soil ranged from 14 to 54 mg kg<sup>-1</sup> and exceeded the control at all sites by 1.5 to 3.8 times (Table 1). The maximum Ni concentration was at oil refinery, which is likely due to application of Ni as catalyst in such petrochemical processes as hydrogenation and hydrotreating. Previous studies registered average of 46 mg kg<sup>-1</sup> (Konstantinova et al., 2019) and 75 mg kg<sup>-1</sup> Ni in soils of Tyumen (Shigabaeva, 2015). The mobility of Ni in soil was relatively low and ranged from 2% to 11%. Ni is known to have high affinity to clay minerals, and Fe, Mn hydroxides, which can explain its low mobility in soil (Kabata-Pendias & Pendias, 2011). Ni content in soil was similar to its concentration in many countries: roadside soils in China (Wang and Zhang, 2018), urban soils in Poland and Slovakia (Demkova et al., 2017; Swiercz & Zajecka, 2018), agricultural soils in India (Gupta et al., 2021).

The concentration of Ni in coltsfoot ranged from 2 to 25 mg kg<sup>-1</sup> (Table 3). Relative accumulation of Ni compared to control was only at oil refinery, which correlates with elevated Ni content in soil. Ni content in plants correlated with its concentration in soil ( $R = .79$ ). Ni content in plants is estimated to range from 0.1 to 2.7 mg kg<sup>-1</sup> (Kabata-Pendias & Pendias, 2011). The maximum permitted concentration of Ni in livestock plants is 1 to 3 mg kg<sup>-1</sup> (Governmental Agricultural Committee of USSR, 1987). Similar to this study Ni concentration in plants was at charcoal mine in China (Zhang et al., 2016), power plant in Novochoerkassk (Chaplygin et al., 2018), highways in Korea (H. S. Kim et al., 2016). All of this indicates Ni anthropogenic pollution in studied area.

The content of Co mobile form in soil ranged from 0.02 to 0.36 mg kg<sup>-1</sup> (Table 1). The concentration of Co at highway and oil refinery exceeded the control by 2 and 2.6 times respectively. Acid-soluble fraction of Co in soil was 7 to 15 mg kg<sup>-1</sup>, Co content at engine-building, battery manufacturing, and metallurgical plants exceeded the control by 1.6 to 2.1 times (Table 1). Co is used as additive to steel, which can explain its elevated content in soil. In previous study Co content in soil at oil refinery was 7 mg kg<sup>-1</sup> (Boev et al., 2019). Co mobility in soil was low and ranged from 0.1% to 4%. Low migration of soluble Co forms in soil is observed due to its sorption at Fe oxides and clay minerals (Kabata-Pendias & Pendias, 2011). Co concentration in soil of Tyumen was similar to the Co content in roadside soils in China (Wang & Zhang, 2018) and agricultural soils in Italy (Rutigliano et al., 2019).

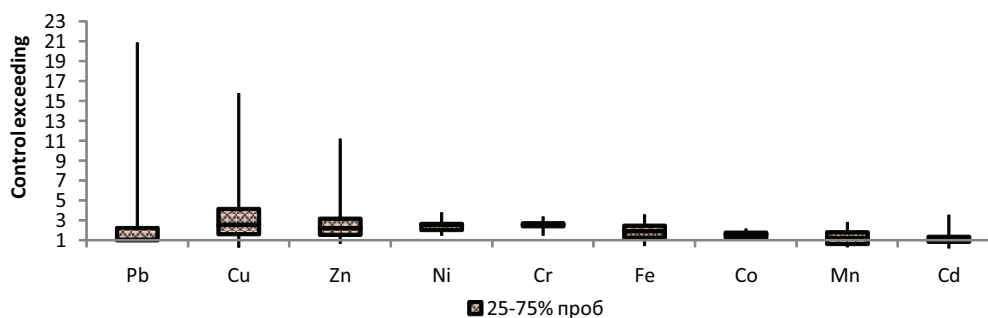
The concentration of Co in coltsfoot ranged from 0.16 to 1.35 mg kg<sup>-1</sup> in 2020 (Table 3). Co content at all studied sites exceeded the control at least by 70%. Co content in coltsfoot correlated with its mobile form in soil ( $R = .75$ ). As in the case of Ni, the highest accumulation of Co was at oil refinery. This is probably connected to application of cobalt-molybdenum-alumina catalysts in petrochemical processes. In previous study Co content in plantain in vehicles pollution conditions was 0.6 to 5.6 mg kg<sup>-1</sup> (Galal & Shehata, 2015). Co content in coltsfoot was close to its level in vegetables from India (Gupta et al., 2021).

The concentration of Cr mobile form in soils of Tyumen ranged from 0.01 to 1.31 mg kg<sup>-1</sup> (Table 1). Cr content in soils exceeded the control almost at all studied sites. The maximum Cr concentration was at oil refinery. Similar results were obtained for acid-soluble Cr fraction in soils (Table 1). Chromium (III) oxide is used as catalysts in petrochemical processes, which can explain elevated Cr content at oil refinery. Cr mobility in soils was low and ranged from 0.03% to 3.6%. Chromium compounds in soils are known to be stable and inert (Kabata-Pendias & Pendias, 2011). Cr content in soils of Tyumen was similar to Cr concentration in cities of Poland and Slovakia (Demkova et al., 2017; Swiercz and Zajecka, 2018).

The analysis of Cr content in coltsfoot registered from 0.4 to 16.5 mg kg<sup>-1</sup> (Table 3). The content of Cr in plants from urban area exceeded the control. Steel chromating and application of Cr in petrochemical catalytic processes led to maximum Cr accumulation at metallurgical plant and oil refinery. The maximum permitted concentration of Cr in herbs is 0.5 to 1.0 mg kg<sup>-1</sup> (Governmental Agricultural Committee of USSR, 1987), which was exceeded almost at all sites. Similar Cr content was previously registered in plants from Novochoerkassk power station (Minkina et al., 2017) and plantain at highway in Egypt (Galal & Shehata, 2015).

Thus, heavy metals mobility in soils of Tyumen can be decreased in the following order: Cd > Mn > Pb > Zn > Ni = Cu > Co > Cr > Fe (Figure 1). Metal accumulation in soils of Tyumen compared to control decreased in the order: Pb > Cu > Zn > Ni > Cr > Fe > Co > Mn > Cd (Figure 2). High Cd and Mn mobility in soils is likely due to its weak complexing ability, and stability of water-soluble compounds. This correlates with their low accumulation in soils. Fe mobility in soils is limited to low solubility of oxides and hydroxides. During 2017 to 2020 studied period Tyumen urban environmental contamination was stable, with such sources as vehicles (Fe and Mn), steel production (Fe, Mn, Cr, and Zn), iron-nickel and lead-acid batteries production (Fe and Pb), and petrochemical processes (Ni, Co, and Cr).

Heavy metal accumulation in coltsfoot decreased in the order: Fe > Zn = Mn > Pb > Cu > Cr > Co > Ni > Cd. There were seemingly opposite results of metal mobility in soil and accumulation in plants. For example, Fe has low mobility in soils, but actively accumulated by coltsfoot, when compared to control. However, high Cd mobility in soil does not provide its



**Figure 2.** Heavy metals in soils of Tyumen exceeding the control in 2017 to 2020. Vertical lines indicate first and fourth quartile, and horizontal line inside the box is median.

**Table 4.** The Results of Linear Regression Analysis ( $n=24$ ).

№	PARAMETERS (X-Y)	LINEAR REGRESSION EQUATION	CORRELATION COEFFICIENT R	P-VALUE
1	Pb mobile–Pb plant	$Y=0.177X + 5.53$	.564	.02
2	Fe mobile–Fe plant	$Y=19.8X + 685$	.441	.02
3	Cu mobile–Cu plant	$Y=9.69X + 8.42$	.430	.02
4	Zn mobile–Zn plant	$Y=0.0414X + 2.16$	.405	.03

**Table 5.** Bioconcentration Factor of Cu, Zn, Fe, Mn, Pb, and Cd for Coltsfoot.

	2017	2018	2019	2020
Cu	<b>4.95</b>	<b>1.43</b>	<b>1.34</b>	<b>1.12</b>
Zn	<b>1.53</b>	<b>1.52</b>	<b>1.57</b>	<b>1.68</b>
Fe	0.008	0.042	0.097	0.008
Mn	0.18	0.09	0.15	0.23
Pb	0.75	0.97	0.65	0.24
Cd	0.67	<b>2.38</b>	0.42	<b>1.69</b>
Ni	—	—	—	0.23
Co	—	—	—	0.06
Cr	—	—	—	0.22

Note. Mean value of studied sites during 2017 to 2020 period.  $BCF \geq 1$  is marked in bold.

accumulation by plants. This result can be explained by plants active participation on metal accumulation due to different biochemical functions of metals: absorption of essential Fe by specific proteins, and stopping Cd accumulation, which is toxic.

The HM concentration in soil positively correlated with its concentration in plants. Linear regression equations are presented in Table 4, which can forecast Pb, Fe, Cu, and Zn accumulation in coltsfoot by their mobile form content in soil.

The value of bioconcentration factor is presented in Table 5.  $BCF > 1$  indicates not only metal absorption, but plant accumulation as well.

Heavy metals bioavailability (according to the decrease in BCF value) changed in the order:  $Cu > Zn > Cd > Pb > Ni > Mn > Cr > Co > Fe$ . The order of metals bioavailability was closer to the order HM mobility in soil, compared to the order of metal accumulation in plants. Low Cr, Co, and Fe bioavailability correlates with their low mobility in soil. However, for other metals this correlation is not so straightforward. Probably, this is due to the important contribution of metabolic metal transport in plants via protein transporters. Earlier in other studies Cu (Sulaiman & Hamzah, 2018) and Zn (Popova, 2019) Bioconcentration factors were also high. The lowest bioconcentration factor of Fe was for herbs in Mn mining area (M. S. Li et al., 2007). Despite high Fe accumulation in coltsfoot, its translocation compared to soil is low, due to poor mobility in soil.

Coltsfoot can be attributed to heavy metals excluder species, despite metal accumulation in urban area compared to the control. In most cases, BCF in urban area was lower than control, despite elevated metal content in soils. Likely, plants in conditions of anthropogenic pollution develop heavy metals tolerance mechanisms and can emit metal chelators (citric acid, oxalic acid, and histidine) in rhizosphere to prevent its accumulation in plants (Thakur et al., 2016).

The investigation of metal translocation in soil-plant system depends on climate conditions, soil properties, and plant species. Therefore, the results of this study are recommended to apply in similar conditions of temperate climate, sod-podzolic soils, and related to coltsfoot plant species. For the demonstration of pollution source, samples in this study were collected close to industrial plants. However, in the future study more samples are needed to compose pollution map

and establish local background values. Besides, there is perspective in studying biochemical parameters and medicinal properties in plants under conditions of metal accumulation.

## Conclusions

Heavy metal content in soils of Tyumen exceeded the control by 1.1 to 2.0 times. Relative metal accumulation by soils decreased in the order:  $Pb > Cu > Zn > Ni > Cr > Fe > Co > Mn > Cd$ . The maximum Cu, Zn, and Pb content were at battery manufacturing plant, Ni, Cr—at oil refinery, while Fe, Mn—at metallurgical and battery manufacturing plants. Metal mobility in urban soils changed in the order:  $Cd > Mn > Pb > Zn > Ni = Cu > Co > Cr > Fe$ . Heavy metals accumulation in coltsfoot compared to the control decreased in the order:  $Fe > Zn = Mn > Pb > Cu > Cr > Co > Ni > Cd$ . The greatest metal accumulation of most metals was at metallurgical plant, while Ni and Co accumulated the most at oil refinery. Fe, Zn, Ni, and Cr content in coltsfoot exceeded the maximum permitted concentration for livestock plants. Cu, An, Fe, Cd, Ni, and Co content in coltsfoot correlated with their level in soil. Bioconcentration factor indicated the following metal bioavailability:  $Cu > Zn > Cd > Pb > Ni > Mn > Cr > Co > Fe$ . Heavy metal accumulation in coltsfoot should be taken into account during sanitary control of herb drugs based on this plant. The data on metal concentration in soils and plants of Tyumen can be applied in ecological monitoring of urban environment. Linear regression between metal concentration in soil and plant may forecast metal accumulation in plants. Heavy metal translocation in coltsfoot should be considered in sanitary control of medicine, containing coltsfoot leaves.

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