City Soil Ranking According to the Level of Pollution: Approach Based on the Health Risk Assessment of the Child Population

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Abstract. Assessment of soil pollution with chemicals in certain districts (zones) of the city of Kazan was performed according to the data of the social-hygienic monitoring of the FBHI “Center of Hygiene and Epidemiology in Republics of Tatarstan” for the period of 2010 -2016. The indices of complex assessment of soil pollution with heavy metals (HM) and oil products in the zones under study did not exceed the established regulations. The results showed uneven distribution of pollutants on the territory of the city zones. The 3-rd zone (the Vakhitovsky district) is different, there the major contribution to the total risk level is made by lead (Pb) – 51.4%, cadmium (Cd) - 36.9%, mercury (Hg) – 3.53%, oil products, and copper (Cu) – 2.6%. The level of non-carcinogenic risk for the health of the child population aged 3-6 years old with application of regional exposure factors (THI 1.0 and less) corresponds to the target risk level. The maximum contribution to THI is caused by the dermal route of the oil products’ entry (from 94.0 to 98.9 %). Ranking of the city territory according to the total hazard quotient with the account of all routes of the chemicals’ entry identified two zones ranking first in the risk level: the 2-nd zone (the Sovetsky district) and the 3-rd zone (the Vakhitovsky district). The results indicate the necessity of revising the approaches to assessment of possible health risks associated with oil hydrocarbons on the basis of new scientific data.

1. Introduction

Compounds of heavy metals (HM) and oil products (OP) make up a considerable proportion of the environmental factors forming the population health risk in the industrially developed regions and cities of the country. Due to their high migration capability, tendency towards bioaccumulation and biomagnification, polytropic capacity metals are dangerous for human beings not only on direct effect on the human body, but through their impact on sanitary-hygienic indices of the environment as well [1, 2, 3]. Possible sources of the soil pollution with chemicals and HM include atmospheric deposition of dust and aerosols, vehicle emissions and various forms of industrial activities [8]. In recent years, the soils were assessed as a diagnostic tool for the environmental conditions having a significant impact on the human health. This problem is particularly topical for sensitive population groups (children aged 3-6 years old), the dose-effect and dose-response relationships in whom are responsible for their high vulnerability on exposure to chemicals [4, 5]. Taking into account the most significant routes and ways, which depend on the age and physiological peculiarities of children, is important as well.
The aim of the study is to carry out the ranking of urban territories according to the level of non-carcinogenic risk for the child population health based on dimensional analysis of distribution of chemicals in the soils in certain districts (zones).

2. Materials and methods

The content of chemical compounds and HM in the soil was assessed according to the data from the laboratory of the Testing Laboratory Center of FSFH “Center for Hygiene and Epidemiology in the Republic of Tatarstan (the years of 2010-2016). The research was performed with application of chromatographic (DDT- dichlorodiphenyltrichloroethane and its metabolites, HCCH - Hexachlorocyclohexane), stripping voltammetry (cadmium, lead, copper, zinc), potentiometric (nitrates), calculation (elemental sulphur) methods and IR-spectrometry (oil products). Assessment of non-carcinogenic risk was performed in keeping with Guidelines on the population health risk assessment (Guidelines P 2.1.10.1920-04) and the Environmental Protection Agency (US EPA) [6, 7, 8]. The assessment included inhalation, peroral and dermal routes of entry. The extrapolation of RfD values from peroral route of entry to conditions of dermal exposure was made according to formula 1:

\[ \text{RfDd} = \text{RfDo} \times \text{GIABS} \] (1)

- \( \text{RfDd} \) – an absorbed dose on dermal exposure, mg/ kg;
- \( \text{RfDo} \) – a reference dose on chronic peroral entry, mg/ kg;
- \( \text{GIABS} \) – the absorption ratio of gastro-intestinal tract.

Calculation of the body surface area of children aged 3-6 years old was made according to formula 2.

\[ \text{SA} = 0,007184 \times W^{0.425} \times H^{0.0725} \] (2)

- \( \text{SA} \) – the body surface area, m²; \( W \) – the body weight, kg; \( H \) – the body length (height), cm.

The surface area of certain body parts of children aged 3-6 years old was calculated in percentage of the total body surface area: the head – 8.0%, the arms (to the hands) – 41.2 %, the hands – 4.9%, the legs (to the feet) – 25.7%, the feet – 6.4% [8]. The regional exposure factors (REF) at the median level and the level of the 95-th percentile (95P) were determined based on the results of the questionnaire survey of parents, grandmothers and babysitters [12]. The assessment was performed in accordance with the risk level classification [9]. Zn, Pb, Cd, As, Cu, Ni, ammonia (in nitrogen), nitrates (in NO₃) and oil products as potential pollutants for the human health were included into the research.

3. Results and discussion

According to the State Standard (GN) 2.1.7.2511–09, the average annual concentrations of all substances under study at the median level and the level of the 95-th percentile in 5 zones of the city of Kazan did not exceed the values of MAC and TAC[10]. Hygienic normatives for MAC in the soils were developed for certain fractions of oil products: gasoline (MAC 0.1 mg/ kg), and benz(a)pyrene (MAC 0.02 mg/ kg), benzene, toluene, xylene (MAC 0.3 mg/ kg) [11, 12]. However MAC for the total oil content in the soil was not established. In the Republic of Tatarstan (RT), a hygienic normative for MAC of oil products in the soil – 1.5 g/kg was established by Decree of the Chief State Sanitary Physician “On implementation of MAC for oil products in the soils of the Republic of Tatarstan” No.18 of July 14, 1998 [13]. Comparison with the above mentioned standards revealed no exceedance of the oil products’ concentrations in the zones under study. According to the criteria of chemical pollution assessment, the soils of the city of Kazan fall under the category of “pure” – the content of chemicals in the soil does not exceed the background one, but it is not higher than MAC (TAC) as well. The results of the non-carcinogenic risk assessment in 5 zones of the city of Kazan (in accordance with monitoring points: the 1-st – Teplocontrol, the 2-nd – the Sovietsky district; the 3-rd – the Vakhitovsky district, the 4-th – Gorki and the 5-th – the Kirovsky district) on peroral entry showed that the level of total non-carcinogenic risk (HI) corresponded to a minimal level (1.0 and less). Hazard quotients (HQ) for certain substances did not exceed the minimal (target) level. Ranking of chemicals according to their contribution to the total risk level revealed a common pattern in four zones (apart from the 3-rd zone): the major contribution from 84.0% to 93.5% was determined by
proportion of oil products. The 3-rd zone (the Vakhitovsky district), where significant contribution to the total risk level was made by lead (Pb) – 51.4%, cadmium (Cd) - 36.9%, mercury (Hg) – 3.53%, oil products and copper (Cu) – 2.6%, distinguished itself particularly. The contribution ratio of the rest substances made not more than 1.2-2.1%. A certain variation, in contrast to other zones, was observed in the total form of mercury (Hg) in the 1-st zone, amounting up to 10.0% of contribution to the total hazard index (HI). Ranking of zones according to the total hazard index (HI) on peroral route of entry identified the following descending order of the zones: the Sovietsky and the Kirovsky districts, which were always characterized by a high level of the industry and production development, ranked first and second. The conditionally chosen zones of Gorki and Teplocontrol (HI 2.45E-05 – 2.62E-05) ranked third and fourth. And the Vakhitovsky district, which differed by specific character and proportion of HM (Pb, Cd, and Hg) and oil products’ contribution to the total risk level, ranked last. The fact that the central part of the city is characterized by the highest concentration of traffic and low traffic capacity of the old urban area can explain high concentrations of Pb in the soil, exceeding the levels in other zones by a factor of 2.0 – 2.5. The results indicate a minimal level of non-carcinogenic risk (HI 1.0 and less) for the health of the child population of the city on peroral route of the chemicals’ entry, irrespective of the zone of residence. (Table 1).

Table 1. Assessment of non-carcinogenic risk of the soil chemicals’ entry on peroral route.

| Substances       | The 1-st zone | The 2-nd zone | The 3-rd zone | The 4-th zone | The 5-th zone |
|------------------|---------------|---------------|---------------|---------------|---------------|
| Ammonia (in nitrogen) | 0             | 0             | 3.9E-07       | 0.15          | 2.8E-07       |
| Nitrates (in NO3) | 1.2E-07       | 6.8E-07       | 0.19          | 5.5E-07       | 2.1           |
| Elemental Sulphur | 0             | 0             | 4.1E-06       | 1.58          | 0             |
| Sulphates        | 0             | 0             | 9.7E-06       | 36.9          | 0             |
| Cadmium          | 4.9E-06       | 8.9E-06       | 2.50          | 1.3E-05       | 5.13          |
| Arsenic          | 0             | 0             | 7.6E-07       | 0.29          | 2.7E-06       |
| Mercury          | 2.8E-05       | 4.04E-07      | 0.11          | 9.2E-07       | 3.5           |
| Lead             | 7.4E-06       | 1.4E-05       | 3.97          | 1.3E-05       | 51.4          |
| Copper           | 1.9E-07       | 1.04E-06      | 0.29          | 6.9E-07       | 2.6           |
| Zinc             | 2.7E-07       | 5.4E-07       | 0.15          | 3.2E-07       | 1.2           |
| Oil products (total) | 0.00025     | 83.9          | 92.8          | 5.9E-07       | 2.3           |
| HI               | 0.00025       | 100           | 100.0         | 2.6E-05       | 100.0         |

The total risk on the dermal route of the soil chemicals’ entry was determined as the total impact on certain parts of the child body [7]. The exposure time at the level of the 95-th percentile made 100 days for the head, 130 days for the arms, 150 days for the hands and 80 days for the legs and feet. The value of total non-carcinogenic risk on the dermal exposure of the soil chemicals’ in all zones corresponded to minimal risk level (HI = 1.0 and less). The major entry from 30.0% to 43% fell on the arms and the legs, 13% - on the face and the head, taking into account the fact that the scenario included the summer period. The level of HI of the total risk in other zones varied from 0.365 in the 4-th zone up to maximum of 0.504 in the 2-nd zone.

Hazard quotients of certain substances did not exceed the minimal level, apart from oil products, HQ of which made 0.308 in the 1-st zone and the highest value of 0.49 was identified in the 2-nd zone, this fact corresponding to the allowable risk level. The major contribution to the total level of non-carcinogenic risk on the dermal route of chemicals’ entry in all zones was by 97.2 – 98.86% due to oil products. The results of the non-carcinogenic risk assessment on the inhalation route of the soil chemicals’ entry indicated a minimal risk level in all zones: the total hazard quotients were in the range from 1.52E-05 (the 1-st zone) to 5.5E-05 in the 2-nd zone (Table 2).
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Oil products (total)

Fluorine

Copper

Cadmium

Zinc

Mercury

Lead

The results showed that the examined elements of the soil in the zones of the city of Kazan differed

Figure 1. The carcinogenic risk (THI) assessment in various zones of the city of Kazan.

Table 2. Results of non-carcinogenic risk assessment on inhalation route of the soil chemicals’ entry in certain zones of the city of Kazan.

Table 3. Complex assessment of non-carcinogenic risk of the soil chemicals’ entry in certain zones of the city of Kazan.

The major differences between the zones were determined according to contribution of copper to HI:

the maximum values (76.3%, 72.6%, 70.6 %, and 69.5%) were identified in the 2-nd, the 3-rd, the 4-th and the 5-th zones, correspondingly. Certain peculiarities were revealed in the 1-st zone, where the percentage of copper made 49.9%, cadmium - 16.1% and zinc - 11.9%. The contribution of oil products to the total risk level ranged from 5.2% in the 2-nd zone, and up to 11.65% in the 1-st zone.

Ranking of zones according to the total risk level on the inhalation route of the chemicals’ entry with

soil identified in descending order: the Sovietsky and the Vakhitovsky districts, which were always characterized by a high level of the motor transportation loading under the conditions of old urban area, ranked first and second. The conditionally chosen zones of Gorki and the Kirovsky district (HI 2.38E-05 and 3.46E-05) ranked third and fourth. And an old industrial center of the city (Teplocontrol), which differs in the spectrum and the contribution ratio of Cd, Zn, Cu, Pb and Hg, ranked last. The complex assessment of non-carcinogenic risk with the account of all routes identified that the dermal route of the chemicals’ entry with soil was the major route (from 94.5 to 99.0%) for children in all city zones (Table 3).

Table 3. Complex assessment of non-carcinogenic risk of the soil chemicals’ entry in certain zones of the city of Kazan.

Assessment of the contribution ratio of certain zones in the city territory to the total risk value with the account of all routes of the chemicals’ entry identified two zones: the 2-nd zone (the Sovietsky district) and the 3-rd zone (the Vakhitovsky district) ranking first in the risk level. The obtained results indicate a minimal level of the total non-carcinogenic risk (THI 1.0 and less) for the health of the child population of the city on complex chemicals’ entry, irrespective of the zone of residence.

The results showed that the examined elements of the soil in the zones of the city of Kazan differed by various intensities of entry on the soil surface with technogenic and motor vehicle emissions. Asymmetric position of the central quartiles, shift of the median with respect to their center in certain zones proves that. It is most typical for Hg, Cd, Pb and oil products, and in a less degree – for Cu, Zn (in the 1-st and the 3-rd zones) and fluorine (in the 4-th zone). The soil pollution with chemicals under the conditions of old industrial region can be caused not only by atmospheric emissions of the enterprises working within the given city or close to it, but also by distant transfer of emissions and trace pollution from the enterprises, which were liquidated long ago, this fact being of key importance.
for the child population in the zone of Teplocontrol and the Kirovsky district. In spite of the fact that the total content of HM is one of the major indices applied on studying of the soil chemical pollution, many studies showed that the study of only this content in the soils was insufficient [14, 15]. Availability of various forms of the HM compounds, differing both in mobility and the mechanisms of fixation in the soil determines the extent of their ecological hazard and requires detailed study. Oil is a complex mixture of hydrocarbons with an admixture of various compounds, which can bioaccumulate (accumulate in the human body), have acute toxicity, mutagenic and carcinogenic activities [11]. The soils, into which 20-30 mln tons of hydrocarbons get annually for various reasons, and in addition to that 50-90 mln tons come from the atmosphere on combustion of oil products, are exposed to particularly intensive pollution with hydrocarbons [16]. The research shows the accumulation of lead and nickel in considerable concentrations in oil-polluted soils, and point out that new substances, which are foreign to natural ecosystems, the carcinogenic ones being among them, are included into biological cycle resulting from soil pollution [12]. This fact convincingly indicates the necessity of revising the approaches to assessment of possible health risks associated with oil hydrocarbons on the basis of new scientific data [20-23].

The major limitation of our research is caused by the absence of a possibility to identify the content of acid-soluble and mobile forms of HM, as well as the use of the results of subsequent fractionation of HM (which gets widespread use today), not allowing to correctly assess the ratio of technogenic contribution of the soil pollutants based on the results of probabilistic risk assessment.

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