Problem of landflling environments pollution by heavy metals

V G Zilenina1,2, O V Ulanova1, L A Begunova1

1 Irkutsk National Science and Research Technical University, Lermontov St., 83, Irkutsk, Russia,
2 Technical University Dresden, Institute of Waste Management and Circular Economy, Pratzschwitzer St., 15, 01796 Pirna, Germany

E-mail: valeriia.zilenina@gmail.com

Abstract. The article discusses the problems of snow and soil pollution by heavy metals. The results of physical and chemical special features of the deposit environment are given. Also, the results of snow mantle research in Irkutsk are described. The problem of manganese degradation from electrochemical cells disposed in the SMW areas is being discussed.

1. Introduction

Geochemical transformation of nature affected by human activity is constantly increasing during the science and technical revolution. The changes led to the main problem of up-to-date ecological situation is the problem of environment pollution. The technogenic influence on a biosphere leads to the intensive pollution of soil, surface and ground waters, snow and atmosphere by the different chemical compounds such as heavy metals. The heavy metals (the density is more than 5.0) are such microelements which are important for the organism supplement (ferrum, manganese, zinc, copper, cobalt, molybdenum), elements with limited physiological functions (nickel, vanadium) or elements whose physiological functions are not studied completely (cadmium, arsenium, lead, chromium, mercury). According to the area pollution data, the most important elements of pollution are such deposit environments as soil and snow. [1]. Monitoring of soil composition changing allows to discuss soil as the most correct indicator of all environment. However, pollutants entering the soil as a rule occurs by means of temporary impacts. The processes of washing up by precipitations and falling air pollutants always have a great influence on the soil pollution. Snow has been studied for a long time to examine the process of falling air pollutants [2].

Snow obtains a high sorption capacities by absorbing gas and dust wastes from the atmosphere. This makes it to be a good pollution indicator not only for precipitations but also for the next water and soil pollution. It gives some information about the space distribution of chemical elements, the pollution sources of the intensity impact. The content of different heavy metals such as manganese, in the upper snow and ice layers exceeds their content in the lower layers. It can be explained by anthropogenic factor [3].

2. Materials and methods

In the areas exposed to the anthropological factor, there occur the pollutant detachment from the air. Thus, the concentration of chemical elements in snow is higher than in the air. Automobiles, railway, solid municipal wastes (SMW) storage release a high concentration of pollutants, which influence the
ecosystem negatively. Atmosphere (air environment), hydrosphere (water environment) and lithosphere (solid surface) are impacted by the pollutants as shown in Table 1.

### Table 1. Environment pollution

| Environment | Main sources of the pollution | Main pollutants |
|-------------|------------------------------|----------------|
| Atmosphere  | Industry, transport, heating stations | Carbon dioxide, sulfur oxide, nitrogen oxide, organic compounds, industrial dust |
| Hydrosphere | Waste waters, oil spills, automobiles | Heavy metals, oil, oil products |
| Lithosphere | Industrial and agricultural wastes the excessive use of fertilizers | Plastic, rubber, heavy metals |

The relationship between dry and wet precipitation depends on a lot of factors where the most important are: the length of a cold period, the intensity of snowfalls and physico-chemical properties of the pollutants, aerosol size.

The problem is actual because the municipal service doesn’t study the snow composition systematically as there is no areal monitoring subsystem as a part of a whole state of a monitoring system of the environment. Though the methods of the pollutants study could be rather simple and highly reliable.

According to the snow study in Irkutsk (Russia), the authors found a considerable snow pollution by manganese which is shown at the Table 2. Three areas were chosen for the studies aims are rail ways (RW), the park, the road (R) and the forest area (FA) out of the city. The given results vary from 0.05 to 0.97 mg/dm$^3$ that 20 times exceeds maximum permissible concentration in commercial fishing and drinking waters (for fishing water – 0.01, for drinking water – 0.05 mg/dm$^3$). Comparing with maximum permissible concentration in soils - their values are limited by the stated ones (MACs – 1500 mg/kg).

### Table 2. Mass manganese concentration in snow

|                       | RW- 0m | RW-2m | RW -4m | RW -6m | RW-8m | R-2m | R-4m | R-6m | City park 1 | City park 2 | FA |
|-----------------------|--------|-------|--------|--------|-------|------|------|------|------------|------------|----|
|                       | December | March | January | February | March | 2014 |  |  | 2015 | |  | |
| RW- 0m | 0.2514 | 0.8673 | 0.2514 | 0.83 | - | | | | | | | |
| RW-2m | 0.1130 | 0.5325 | 0.113 | 0.35 | 0.529 | | | | | | | |
| RW -4m | 0.1626 | 1.497 | 0.1626 | 0.25 | - | | | | | | | |
| RW -6m | 0.7493 | 0.865 | 0.7493 | 0.31 | 0.256 | | | | | | | |
| RW-8m | 0.1 | 2.595 | 0.1 | 0.32 | 0.785 | | | | | | | |
| R-2m | 0.2451 | 0.5845 | 0.2451 | 0.48 | 1.071 | | | | | | | |
| R-4m | 0.9348 | 1.817 | 0.9348 | 0.56 | 1.22 | | | | | | | |
| R-6m | 0.3409 | 1.930 | 0.3409 | 0.57 | 1.12 | | | | | | | |
| City park 1 | 0.8902 | 0.1475 | 0.1626 | 0.290 | 0.723 | | | | | | | |
| City park 2 | 0.2084 | 0.2445 | 0.8902 | 0.47 | 1.669 | | | | | | | |
| FA | 0.22 | 0.17 | 0.19 | 0.19 | - | | | | | | | |

### 3. Results and discussion

The results of chemical analyses of snow water introduced in the Table 3 prove that the data on the suspended matter possess the higher values than the values of maximum permissible concentration for surface waters. The suspended particles presence in snow could be explained by: 1) the use of sandy and chemically retarded acid as deicing matter where the base is sand; 2) by means of dust, ash, soot.
and smoke pollutants as the technological factors. In winter, the mass of buried fuel (coal) gets its maximum and suspended solids absorb by snow. Presence of the components snow and soil causes acidifying or alkalescency of media.

Table 3. Total suspended solids

| Total suspended solids in snow, mg/dm$^3$ | 2015 |
|----------------------------------------|------|
|                                        | February | March |
| RW-0m                                 | 2579.4 | 2510.5 |
| RW-2m                                 | 979.2  | 1701  |
| RW-4m                                 | 917.6  | 1535.7 |
| RW-6m                                 | 903.7  | 1434  |
| RW-8m                                 | 1151.4 | 1292.5 |
| R-2m                                  | 939.8  | 1750.5 |
| R-4m                                  | 2595.4 | 1328  |
| R-6m                                  | 938.8  | 1527.5 |
| City park 1                           | 879.9  | 978.2 |
| City park 2                           | 1049.58 | 946.6 |
| FA                                     | 648.5  | 756.9 |

In 2014-2015, the tests measuring data demonstrate a low ferrum concentration in snow which is varied from 0.001 to 0.9 mg/dm$^3$ (see Table 4) that does not exceed hygienic and epidemiological requirements [4].

Table 4. Mass ferrum concentration in snow

| Mass ferrum concentration in snow, mg/dm$^3.$ | 2014 | 2015 |
|---------------------------------------------|------|------|
|                                             | December | March | January | February | March |
| RW-0m                                       | 0.0359 | 0.022 | 0.0359  | 0.0178   | -     |
| RW-2m                                       | 0.0346 | 0.0245 | 0.0346  | 0.0031   | 0.012 |
| RW-4m                                       | 0.0293 | 0.0295 | 0.0293  | 0.0066   | -     |
| RW-6m                                       | 0.0241 | 0.0421 | 0.0241  | 0.0017   | 0.0030 |
| RW-8m                                       | 0.01096 | 0.01236 | 0.01096  | 0.0046   | 0.0054 |
| R-2m                                        | 0.0248 | 0.02869 | 0.0248  | 0.0175   | 0.0020 |
| R-4m                                        | 0.0315 | 0.091  | 0.0315  | 0.0144   | 0.0103 |
| R-6m                                        | 0.0032 | 0.0883 | 0.0032  | 0.0089   | 0.0086 |
| City park 1                                 | 0.0218 | 0.0136 | 0.0223  | 0.0080   | 0.0070 |
| City park 2                                 | 0.0223 | 0.0714 | 0.0218  | 0.0171   | 0.0073 |
| FA                                          | 0.0004 | 0.0025 | 0.0359  | 0.0012   | -     |

Manganese-zinc electrochemical cells, which are widely spread today, are also the source of manganese entering the soil. The length of the pollutant presence in the soils is much more than in the other parts of biosphere.

The ecological role of soil as a natural filter for the different technogenic pollutants among which the special part belongs to heavy metals (Tab.5). A part of some elements in common heavy metals concentration differs in soils enriched by them both naturally and anthropogenically. The toxic effect of heavy metals is determined not so by total content in the soil, as the concentration in an accessible
state for the organism. Such concentration nearby the natural deposits of heavy metals could be raised in 10-10000 times in comparison with ordinary concentration. It can reach such values in soils anthropologically enriched by heavy metals. The heavy metals concentration depends on lithological composition and acid and alkalized rock condition. In most cases the heavy metals concentration of clayed and loamy soils is higher than in sandy and sandy-loamy ones that is explained by a high sorption capacity of the previous ones. Besides manganese, they contain more than 30 chemical elements, twenty-two of them are metals in their elementary and ionic forms. The small electrochemical cells include in their composition: zinc, manganese, mercury, lead, nickel, cadmium, lithium, argentum, their oxides, organic matter paper, carton, starch, graphite). D.K. Agurakis and others studied the process of the heavy metals degradation from electrochemical cells while their burial proved that zinc and manganese concentrations in soil raised 70 and 11 times in comparison with initial concentration. Landfill soil possesses the ability to accumulate metals, and the level of pollution of landfill soil varies with depth and depends on the conditions of SNW storage.

The concentration of toxic, cancerogenic, hazardous and explosive substances in soil results from unseparated waste collection SMW landfill area with the other wastes. Also, it leads to the mentioned substances accumulation in food and water and afterwards to their concentration in the living organism. Cadmium, mercury, zinc and other metals accumulating in the living organism cause a serious impact for health. In human body, the excessive dose of manganese causes neurological diseases and vegetative-vascular dystonia. Also, it can influence cholesterol metabolism and atherosclerosis. When heavy metals get into the human body with food grown on the polluted soils, the first impacted system becomes a digestion one. If heavy metals get into the organism constantly, the biological magnification law starts working. It influences the other body systems: nervous, cardiovascular, excretory, reproductive. Subsequently, negative changes in the body occur at the cellular level.

If there are no electrochemical cells gathering and their following recycling in our country, they with other residual wastes are delivered to the landfill areas and damps and partly to the waste incineration plants. A number of experiments on the electrochemical cell degradation were carried out by S.M. Xara and others. Among all experiments there was a research carried out with a standard degradation procedure. (standard NEN 7343 “Leaching characteristics of solid earthy and stony buildings and waste materials”) [10] The study concluded the used electrochemical cells (using the existing waste division into: dangerous, non-dangerous, inert) belong to the hazardous group and they could not be incinerated with the residual wastes.

One of the important tasks when studying the landfill area influence on the environment components is to define chemical matter migration from the moment of getting into the landfill till the moment of its release into the environment during the whole period of landfill existence. During this period, there occurs the landfill gas formation. Precipitation seep through the landfill body and contact with SMW. As a result, there occur varied chemical and biological processes. Product of matter degradation obtained in the result of complex combinations of the mentioned processes then migrate with water and forming landfilling gas. By means of precipitation seeping through the landfill body and humidity coming out from the wastes in the landfill body, there forms the filtrate which is significantly polluted by different organic and non-organic matter. The landfill filtrate composition is identified by the types of wastes of the decaying organic matter and the landfill age. Besides organic matter, the filtrate contains: ferrum, mercury, lead and other heavy metals obtained from the waste electrical and electronical equipment such as electrochemical cells. Heavy metals migration in the environment is closely connected with the problem of their complexes formation with the organic matter of natural or technogenic origin. The filtrate forming inside the landfill body is saturated with organic matter which is delivered to the landfill area with the wastes of decay processes. In the process of organic matter metabolism there involved redox process where the oxidizing agent could be either oxygen (aerobic conditions) or transition elements Fe2+\Fe3+, Mn in different stages of oxidation, nitrogen oxides and others. Also, the oxidizer could be an organic matter (anaerobic conditions). While oxygen expending, anaerobic conditions start prevailing and such compounds as nitrates,
sulfates, ferrum oxides and manganese work as oxidizing agents. Anaerobic decay of organic matter of the SMW in the landfill has a lot of common with the fermentation of organic matter on other oxygen-free ecosystems.

The leading part in organic matter decay belongs to microbial processes. Anaerobic decay has two stages: acetogenic (acid) and methanogenic, which has also 2 stages: active and stable. The degradation processes in anaerobic conditions occur according to the similar processes in aerobic conditions. When strong oxidizers interreact with organic matter there can occur fully or partly completed oxidation of compounds. This environment creates the most comfortable conditions for complex compounds organization with metals existing in wastes, their possible transformation into solution forms and their migration with water to the environment. The common scheme of the flow of the filtrate is shown in Figure 1.

![Figure 1. The damp processes scheme.](image)

The most important physical and chemical processes in the landfill body are complex organization, sedimentation, dissolving, adsorption, ionic exchange, oxidation and deoxidization. According to the data it is stated that the period of the filtrate output (depending on the hydrogeological site structure) can vary from 1 (for sandy soils) to 25 (for clay soils) years after the waste burial in the landfill area. The zones of active water related to the upper part of the slit are highly affected be the filtrate pollution, especially ground waters. The filtrate enters the aquifer and the hazardous compounds could get into the drinking water.

Organic acid formation leads to the decreasing value of pH that can cause dissolving of a lot of metal compounds, the formation complex compounds with the dissolved organic substance and degradation are caused by forming and infiltrating waters. This phase could be possibly characterized by the maximum number of metals and filtrate, but the degradation rate at the early stages exponentially decreases till the methane starts its formation. Besides electrolyte (KOH), contained in the electrochemical cells, increases the soil pH. The pH increase could save metals in the soil upper layer, but it is not enough to stop metal migration. If the pH value is close to be about neutral, the chemical composition of a landfill does not change during a long period in the reductive environment. In such conditions, a lot of metals obtain a low solvability. Neutral reduction will prevail unless the buffer compounds appear. Oxidoreductive buffering capacity is mainly depends on be metals, pyrites, organic compounds. Buffering capacity of pH is produced owing to the presence of calcium oxide, hydroxides and carbon compounds and a piece of aluminosilicate compounds. In this case, acid rains
infiltration, oxygen diffusion and carbon dioxide accumulation will exhaust the buffer capacity and spoil acid-alkaline balance, reducing process. As a result, the metal activity will increase. Active ions of metals could be delivered to the lower part of damp, where pH value is still high and the reduction process is low. In this part of damp, metals could resettle. Thus, the reaction could spread inside the landfill deposit and later leave the damp [9].

Taking into account analyses of acid-alkaline balance of snow covering in Irkutsk (Russia), the value varies from 4 to 6, i.e. the range of neutral and partly acid values.

The pH landfill deposits study results give the values from 2.91 (acid media) to 10.54 (alkaline condition). The average value of pH at point is 9.8-10.1, that is in the limits of the values in the methanogenic phase [7].

Such characteristics of snow water as general rigidity is closely connected with the intensive pollution by the metal oxides and exhausted fumes. The maximum water rigidity is described in Table 5.

| Snow water rigidity, mg/l | pH of snow water.  |
|---------------------------|--------------------|
| 2015                      | Snow water rigidity, mg/l |
| February                  | February           |
| RW- 0m                    | 4.5                | 0.76 |
| RW-2m                     | 4.64               | -    |
| RW -4m                    | 4.68               | 0.3  |
| RW -6m                    | 4.67               | 0.23 |
| RW-8m                     | 6.2                | 0.35 |
| R-2m                      | 5.2                | 0.68 |
| R-4m                      | 5.63               | 0.85 |
| R-6m                      | 4.8                | 0.52 |
| City park 1               | 4.18               | 0.23 |
| City park 2               | 4.71               | 0.48 |
| FA                        | 4.78               | 2.25 |

4. Conclusion

On the territory of Irkutsk (Russia), the main factors influencing the trees growth and soil composition are the high level of technogenic air pollution and high recreation load. Among the technogenic pollutants of non-organic nature, the strongest influence on the trees and physic and chemical soil composition belongs to sulfur dioxide and heavy metals aerosols, especially lead.

In soils impacted by the silt, the landfill leachate contained such element as nickel, copper, barium, manganese, titanium, lead, zinc, cobalt, cadmium, mercury. The vegetation nearby the landfills area is polluted at the distance of 1.5 km. The heavy metal composition in the landfills deposit is 10 times more than permissible concentration in soil. It is noted that the soil is polluted by copper, zinc, cobalt. Though the soil pollution is revealed, it is more dangerous than air pollution as the generation or self-purification processes occur in soil more slowly than in the air and the toxic substances provides a slow chemical changing in soil.

The polluted soils negative effect on a human could be either direct (when soil dusting) or indirect (using food grown in the country or grown in the places of former unauthorized damp or using surface or ground waters as drinking one).

When designing the landfilling areas and waste storage, there exists a special damp bottom construction, which purpose is to protect from filtrate entering into the aquifer and into the ground waters. As a rule, there used clay soils for this purpose.

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