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ACID-BASE PROPERTIES OF URBAN SOILS IN CHERKASSY

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Abstract. The characteristics of the soil cover of the city Cherkassy and the sources of anthropogenic changes of its acid-base properties are presented. The results of the research of soils from different functional zones of the city Cherkassy showed that its reaction is mainly alkaline. The cartographic model of experimental data was made with the program SURFER showing acid-base regime characteristics of soils in different functional zones of the city. This mapping allowed to identify the following soils: fertile (pH = 6.5–7.0) and potentially fertile (pH = 7.0–7.5), hardly suitable (pH = 7.5–8.0), moderately (pH = 8.0–8.5) and highly (pH = 8.0–8.5) toxic. It is concluded that only 60% of urban soils can be identified as fertile or potentially fertile in terms of characteristics of acid-base regime. The results of the evaluation of acid-base regime of urban soilsare correlated with the results of the previous studies of pollution of snow cover in the areas of permanent e-missions and the anionic composition of soils. The analysis of the cause-effect relationships in the impact of adverse environmental factors on urban landscapes showed that the formation of acid-base regime of soils is influenced both by the natural landscape, i.e. geochemical, and anthropogenic factors.

Keywords: urban soils, acid-base properties of soils, soil toxicity, cartographic modeling.

Introduction

The soil is an important component of geosystems forming in urban conditions as soils ensure their productivity and biodiversity. Urban soils are the basis for the existence of green areas. They are apowerful kind of filter that together with the plants absorbs and partially neutralizes toxic emissions. Soil microorganisms react quickly tothe change in the ecological functions and condition of soils, which is reflected in their biochemical activity (Svirskene 2003; Anan'eva 2003; Růžek *et al.* 2006; Garcıa-Gil *et al.* 2000). The sterilizing effect of different pollutants leads to loss of sensitive species of microorganisms, microbial decay cenosis, loss of biochemical activity of the soil, and the destruction of microorganisms leads to the degradation of ecosystems (Wilson 2008; Papa *et al.* 2010).

Soil acidity is of great importance for plants. For most species of deciduous trees slightly acidic or neutral environment is more favorable (Pн = 5.5–7.0).

As acidic soil reaction increases, the absorption of anions by plants also increases, but the absorption of cations becomes more difficult. As a result, mineral nutrition, ingress of calcium and magnesium into plants are disrupted, the synthesis of proteins and sugars slows down.

Alkaline reaction of soil enhances the cationic supply and impedes the anionic supply and starting from Ph = 8–9 makes the soil unsuitable for growth of most plants. In alkaline soil the availability of P decreases, many tree species suffer from micronutrient deficiencies (B, Cu, Fe, Mn, Zn) because these nutrients exist in insoluble forms that are unavailable for the plants (Mengel, Kirkby 2001). Fe or Mn deficiency impairs the ability of photosynthesis (Abadía *et al.* 1999; Dirr 1998), which can reduce tree growth and resistance to stress. In addition, in an alkaline reaction environment and wash regime the mobility of organic material increases dramatically, which leads to depletion of soil humus.

Elevated pH may also alter the composition and abundance of endomycorrhizal fungi that inhabit soil (Porter *et al.* 1987), which could influence root system colonization and therefore nutrient uptake capacity.

On the other hand, the solubility of certain elements, such as Al and Pb, which are toxic to the tree roots, decreases in alkaline soils.

In urban areas the soils are usually alkalized (Susan *et al.* 2010; Lutsyshyn *et al.* 2011), though there are also soils with low pH values (Pouyat *et al.* 1995; Graul 1999; Alamgir *et al.* 2015).

Most researchers link high alkalinity of urban soils to the transferof mainly calcium and sodium chloride as well as other salts, which are sprinkled on sidewalks and roads in winter, through run-off and drainage water. Calcium leaching also occurs under the influence of deposits from building rubble, cement, bricks, etc. which are of alkaline character (Wong *et al.* 2006). Industrial calcinated dust shifts the pH of the soil solutions from the range of values 4.0–4.5 to 6.0–6.5 and above; this pH shift has a long-term nature (Bockheim 1974; Craul 1999).

In conditions of the crisis levels of technogenic pollution in the soil-plant system and the catastrophic functional state of the street plantings it becomes important to study the ecological state of the soils in the zone of the root system of plants.

The territory of Cherkassy is polluted by the complex of different sources that are both immobile (industry) and mobile (transport). Anthropogenic soil disturbance and technogenic pollution of soil have led to the formation of specifically transformed natural and man-made system. Physicochemical properties and chemical composition of the soil are modified, and soil, being one of the most important biogeochemical barriers to migration of phytotoxiccompounds, deteriorates and partially loses its basic functions.

Most of the green areas of the city, especially the southern and north-eastern parts, are in poor condition. Typical lesions of plants are: ulcer (all tree species), tumor (*Populusbalsamifera, Aésculushippocástanum, Tiliacordata*), wet bacteriosis (*Fráxinusexcélsior, Aésculushippocástanum*), scaly peeling of bark (*Aésculushippocástanum*). On the leaves of 60% of the trees edge andpoint necrosis was identified. The thinning of the crown of *Populusdeltoides* ranges from 40 to 90%, the trunks of 80% of the trees have ulcers. In the south-eastern part of the city *Aésculushippocástanum* and *Robíniapseudoacácia*are in poor condition. Up to 50% of the surfaceof the leaves is damaged by necrosis. Thinning of the crown is observed in 40% of the trees. Theleaves are damaged by brown spots (up to 20%). An increase of the number of dry branches of 1-3d order is observed in 30% of plantings. The plants are under stress as a result of the toxic effect of emissions of enterprises and motor vehicles (Kornelyuk *et al.* 2007; Chemerys *et al.* 2013).

From the point of view of ecology, urban soil is a deposit environment that accumulatestechnogenic pollutionfora long-term period. The degree of contamination of urban soils depends on the rate of emissions from the industrial facilities and transport, on the time of exposure to emissions, and on the sustainability of soil affected bycontamination.

The lithogenicbase of Cherkassy landscapes consists of loess and loess-like loams, sandy loams of various origins. The soil cover of the city is characterized by high heterogeneity, light texture (with predominance of large and medium sand), a high degree of base saturation (86–99%). Among the most common types of soil in urban areas typical low-humus and meadow black soils on the loess rocks can be distinguished. Humus content ranges from 1.7 to 4.3%, with an average value of 2.9%. The values of this indicator are less in the residential areas on the alluvial sands, in the central part of the city, particularly areas of high-rise buildings, and in the industrial zone, which were for a long time under the influence of urbanogenic factors.

The formation of different genetic groups of soils can be explained by complex mutual influence of the forest and steppe vegetation, moisture regime, the introduction of contaminants and other types of human impact. The soil cover has been transformed due to urban development, the creation of the Kremenchug reservoir, the subsequent developments of the coastal zone, cultivation in gardens, orchards, parks. In the new areas of high-rise buildings a significant part of urban soils have no signs of zonal soils, their profiles are formed by bulk soils of different particle size distribution, carbonate rubble, etc.

Aerotechnogenic pollution has a significant influence on the formation of the quality of soils. The analysis of the meteorological conditions (Kornelyuk *et al.* 2007) shows that the processes of accumulation of contaminants dominate in the region rather than their dispersion. Frequent calms, light winds, fog, low precipitation (amount of annual precipitation is 450–480 mm, the minimum figures – 255–390 mm) contribute to the stagnation of polluted air masses and determine the significant increase of the concentration of impurities in certain periods due to extremely adverse conditions for their dispersion. Under adverse weather conditions the high level of pollution is observed in the southern and south-eastern regions. The residential area of the central part of the city is characterized by an increased level of contamination (Fig. 1). The map was prepared by the Regional Committee for Nature Protection on the basis of calculations of air pollution in the city of Cherkassy under the program “Ether-6.03”. Data from all immobile sources and background values of mobile sources were incorporated into the program (Rodzha 1994).

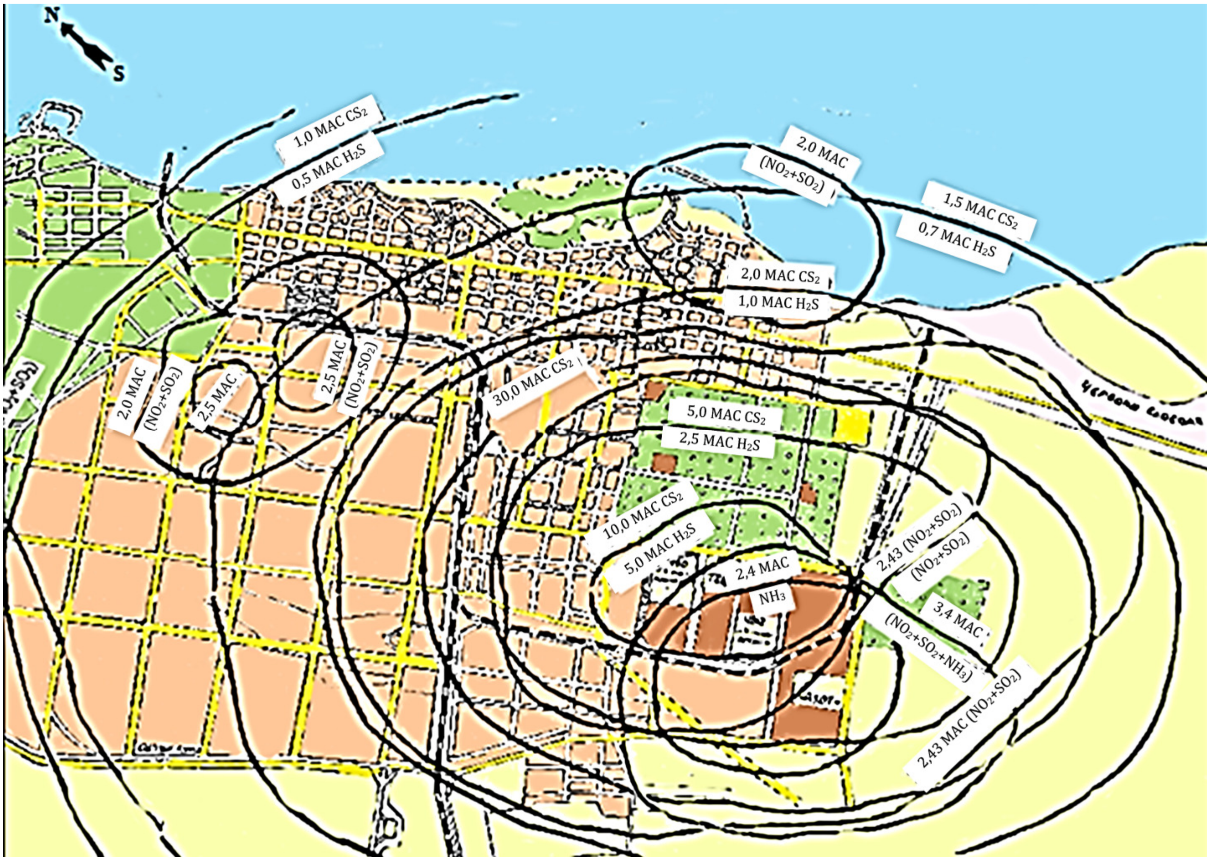

Fig. 1. Map of the most probableone-off surface concentrations of harmful substances in the air of the city of Cherkassy under the most adverse weather conditions

In Cherkassy there are about 200 immobile sources of aerotechnogenic contamination of urban landscapes.

More than 150 dangerous substancesthat are subject to registration are emitted into the atmosphere.

The main contribution to the total air pollution belongs to the enterprises which are located in two industrial zones – southern and eastern industrial agglomerations. During the year 2014,50.7 thousand tons of pollutants from immobile and mobile sources of pollution got in the air basin of the city. The main environmental pollutants are Cherkassy Chemical Company (plant "Azot") and power (CHP Cherkassy) industry that are located in the southern industrial and road transport zone (Table 1).

The emissions of these enterprises contain substances which are potentially capable of acidification (NO_2, SO_2) and alkalization (NH_3, alkali and heavy metals contained in the discharged ash) of soils. Under the transition of Cherkassy CHP from natural gas to coal (with high ash and high sulfur content) the aerotechnogenic load on urban landscapes has increased. Over the past 10 years, SO_2 emissions increased 2.2 times, NOx – 6.8 times, Hg – 2.75 times, Pb – 13.3 times, Cr – 17.8 times, Zn – 16.7 times.

In the south-eastern industrial agglomeration and transport zone air dust is 2–14 times greater than the background, and this leads to an increase of the role of suspended particles as carriers of chemical elements.

Table 1. The main pollutants emitted into the atmosphere of the city of Cherkassy, tons/year

Pollutant	Impurity	Environmentalemission
Cherkassy CHP	SO_2	18899.141
	NO_2	6329.544
	Substance in the form of suspended solids	3897.461
Plant "Azot"	Substance in the form of suspended solids	1924.380
	NO_2	1142.254
	NH_3	951.833
	CO	911.301
Motor transport	NO_2	1579.7
	SO_2	162.5
	CO	11869.2
	Carbon soot	201.6

All this presents a danger of increasing technologic loads, including the acidifying agents, to critical values and as a consequence, transformation of urban soils which may be accompanied by increased soil acidity, change of their physicochemical properties and functions.

The typical signs of anthropogenic transformation of soils in the city of Cherkassy today area heavy increase of the degree of spatial heterogeneity of the anionic composition of soil compared to natural zonal soils, technogenic salinization, changes in the acid-base balance under the influence of a complex combination of natural processes of self-organization and varying urbanogenic actions.

The aim of this work is 1) to study the acid-base properties of soils in the city of Cherkassy and the peculiarities of their changes in different functional areas of the city, 2) to identify the cause-and-effect relationship in the impact of adverse environmental factors on urban landscapes and 3) to map the research results.

This work is relevant due to the intensive technogenic impact on urban landscapes of Cherkassy that leads to chemical degradation of soils and malfunction of geobiocoenosis.

This work novelty is in using a software package SURFER that helped to create a map of soil acidity of Cherkassy and to zone the city according to the impact of pollution factors and changes of the urban ecosystem quality.

Materials and methods

The object of the study is the soils, selected from 65 trial grounds in different functional areas of the city of Cherkassy (marked with triangles on the map). The geographic location of sampling points was carried out by GPS-receivers. The sampling depth was 0–20 cm. An average sample for analysis was prepared by quartering. Soil acidity was measured using the potentiometric method, sulfates were measured using the gravimetrical method, nitrates were measured by the potentiometric method using an ion-selective electrode, bicarbonates andchlorides were measured by thetitration method.

The choice of test sites was based on the results of the previous research of pollution of urban landscapes in the areas of permanent emissions (Myslyuk *et al.* 2010, 2011) and calculation of the total environmental load index (Tarasova *et al.* 2004).

In order to identify spatial patterns of formation of zones of acidification (alkalizing) the software package SURFER was used. On the basis of the raster map of the city of Cherkassy through digitizing its electronic form was created and the grid was built on an irregular array of 65 data points. The construction of grid functions was done according to the Kriging method that is effective enough and gives a good representation of the data, regardless of the size of the original set of experimental points, and allows to build a map that would be the best way to display the data of field research.

When characterizing the acid-alkaline regime of soils, the following gradationswere specified: suitable and fertile (pH = 6.5–7.0); potentially fertile (pH = 7.0–7.5); unsuitable, slightly toxic (pH = 7.5–8.0); intermediately suitable, intermediately toxic (pH = 8.0–8.5); unsuitable, highly toxic (pH>8.5) (Metodicheskie…2003).

Results and discussion

Taking into account the fact that the soils of the city of Cherkassy in the areas of creating outdoor spaces are generally complex formations of natural and human origin, which are impacted by the action of toxic man-made factors, we investigated the changes in physical and chemical properties of technogenically modified soils in the zone of the root system of woody plants in different areas of the city.

One of the main indicators of change in the chemical composition of the soil under the conditions of technogenic pollution is the dynamics of changing of acidity of the soil solution. The pH-reaction of the soil solution is a general environmental factor that characterizes the nutrient regime of the soil, affects the growth and development of woody plants. The proper initial assessment of soil conditions in urban areas will optimize their settings and ensure good survival of planted plants.

The investigation of acid-base properties of the soil showed that under the active aciditythe urban soilsare characterized by neutral, slightly alkaline and alkaline reaction of the environment.

The pH value is in the range of 6.0–9.2. In spring the pH offset is observed as upward alkalinity in all areas, which is probably due to alkaline agents coming to the soil during snow melting and due to dissolving alkaline source rocks (reaction of the environment of loess rocks of pH changes within 6.7–8.9).

Mapping of the experimental data by the acid-base characteristics of soils using the software package SURFER (Fig. 2) allowed to specify 4 zones of toxicity (Fig. 3).

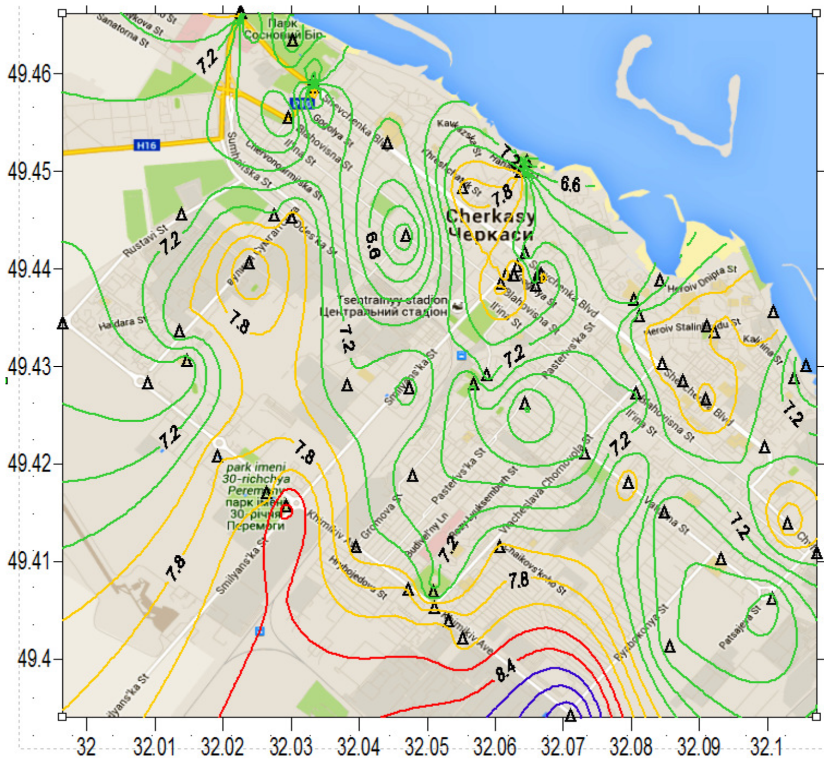

Fig. 2. Contour map of active acidity (pH) of soils

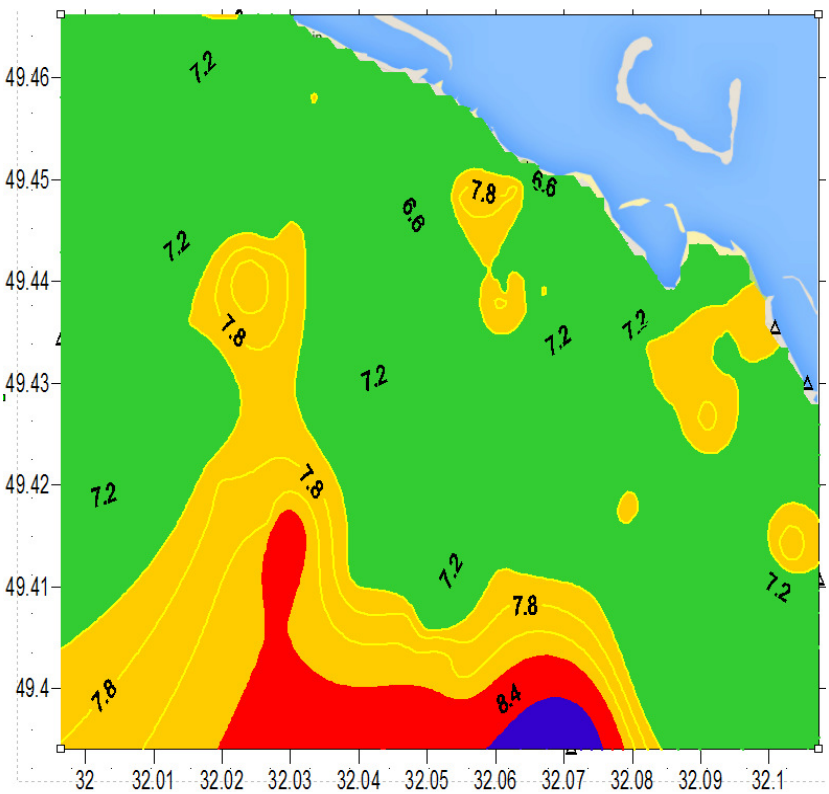

Fig. 3. Landzoningmapoftoxicity

The zones of strongly (pH>8.5) and moderately (pH = 8.0–8.5) toxic soils (marked accordingly blue and red on the maps) are confined to the southern industrial site, where the company for the production of mineral fertilizers plant "Azot" and Cherkassy CHP are situated. Increased alkalinity of the soils is probably due to the emissions of ammonia and its compounds from the plant "Azot".

Unsuitable (slightly toxic) soils (pH = 7.5–8.0, marked with yellow on the maps) are confined to residential areas of multi-storey buildings with a heavy traffic and pollution from enterprises of southern and eastern areas of industrial zones (factory for the manufacture of paints and varnishes "Aurora", machine building plant, plant "Khimreaktiv", woodworking plant, etc.). Alkalization of the soil occurs as a result of using the anti-icing salts. Water-soluble sodium chloride and exchangeable sodium are present in soils of roadsides.

Potentially fertile (pH = 7.0–7.5, marked with green on the maps) soils are typical for the areas of residential mixed zone with less intensive traffic, as well as for areas of low-rise buildings with the prevailing agro-urban soils of adjoining gardens (preservation of natural soil formation processes, as similar as possible to natural soils).

Along with urban soils with alkaline soil properties there are soils on the outskirts of the city, called park "Sosnovyjbor" (recreation area), with a level of acidity close to neutral (pH = 6.5–7.0). It is known (Vozbuckaya, 1968) that conifers contribute to increasing the acidity of soils due to the acidic properties of their organic remnants (pH = 3.6–4.0). Alkalinization of soils of this outskirt parkland, located at a distance of 14 km from the main sources of emissions of acid-base agents, proves a significant aerotechnogenic pollution of urban landscapes.

The analysis of acidity maps showed that only 60% of soils can be characterised as fertile and potentially fertile.

The reduction of soil acidity of the soil solution can be the reason for increasing the hydrolytic acidity. According to our data, hydrolytic acidity ranged from 2 to 69 mmol/kg of soil. The lowest values of this indicator are typical for the zones where there is a tendency to alkalization of soils.

The results of the evaluation of the acid-base regime of urban soilscorrelate (r = 0,63) with the results of the previous studies of pollution of snow cover in the areas of permanent emissions (Myslyuk *et al.* 2010) and the anionic composition of soils.

Studies of snow cover as an indicator of aerogenic landscape pollution (Ehkologicheskaya... 1996; Nazarov *et al.* 1978; Gorodskaya… 2013) allowed to simulate the spread of flue gases from the enterprises of southern industrial zone and to show that aerosols and products of gas transformation, settling on landscapes, form a significant area of pollution of the city and as a result covers the entire territory of the city. The chemical composition of the melt water indicates the higher level of technogenic pollution of snow cover. The map zoning of the territory of the city according to the indicator of total technogenic impact (the ions HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-) shows that 48% of the city can be estimatedas if it did not experience a significant aerotechnogenic load (N_{sum}<50 tons/km^2·year), 27% of the territory experienced moderate pollution (50 tons/km^2·year <N_{sum}<100 tons/km^2·year), 21% experienced severe pollution (100 tons/km^2·year <N_{sum}<200 tons/km^2·year), 4% of the territory experienced a very strong pollution exceeding the maximum permissible load (N_{sum}> 200 tons/km^2·year) (Myslyuk O. *et al.* 2010).

The exceedance of the background values was recorded for all ions in the selected snow samples. The highest values of the concentration ratio were observed at sulfate ions. Thus, in the north-west direction (2km from CHP) the level of sulfates was 872 mg/l, which is 79 times higher than the background concentration. In spring, after the melting of snow, in the same direction the sulfate concentration was 34 mg/kg of soil, which is 6.4 times higher than the background concentration. The contour of maximum sulphate content in the snow cover (Fig. 4) is elongated in the direction of the prevailing winds (in winter the winds with the eastern directions dominated), which indicates mainly aerogenic income of these aerosols to urban landscapes(Myslyuketal. 2010).

The comparison of the chemical composition of snow infiltrate and the water of the river Ros showed that the content of sulfate ions in the snow infiltrate is much more above the background levels in the surface waters. This confirms our assumption that the main flow of sulfate ions into the natural environment and, as a consequence, acidification of soils, is technogenic, which is associated with the use of coal with high sulfur content by Cherkassy CHP.

The features of changes in the chemical composition of snow in the area of CHP is the change of the ratio of natural anions in soils HCO_3^-> SO_4^{2-}> Cl^-> NO_3^- on technogenic SO_4^{2-} (24.7)> HCO_3^- (5.7)> NO_3^- (3.6)> Cl^- (1.7), and in the area of plant "Azot" –on technogenic HCO_3^- (11.3)> NO_3^- (7.2)> SO_4^{2-} (4.9)> Cl^- (1.9), that correlates with the composition of technogenic emissions into the atmosphere.

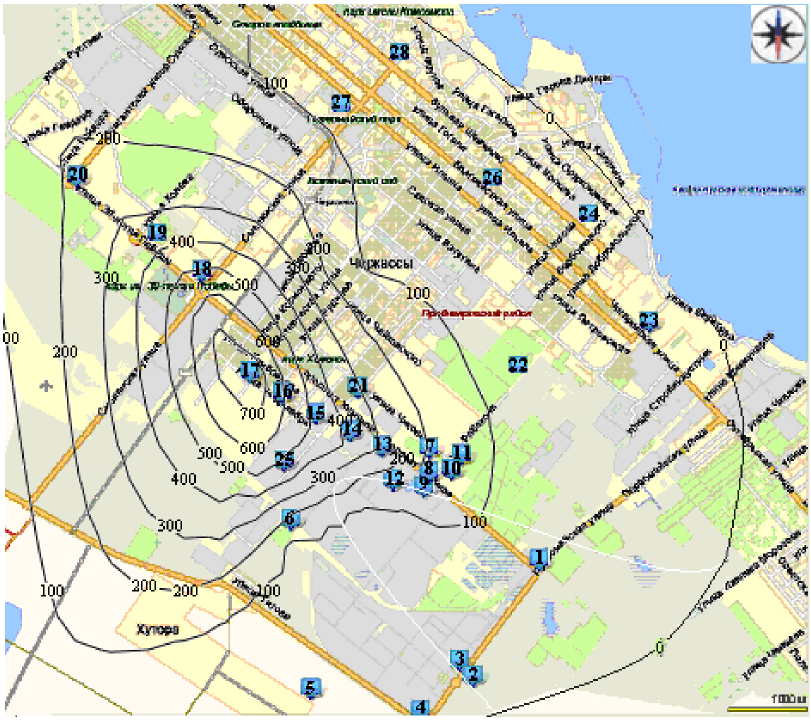

Fig. 4. The content of sulfate ions in the snowcover (mg/l of meltwater)

The connection of aerotechnogenic load with heavy traffic is also identified, especially on the roads of high technical category and with technological parameters of the roadway. The influence of motor transport can be classified as chronic. A significant number of cars, trucks and buses on the main transport thoroughfares of the city leads to pollution of urban landscapes. The conducted studies of soil samples by atomic absorption spectrometry showed that roadside zones of the areas with high traffic rate are under a heavy load of substances-toxicants, exceeding the maximum permissible level. The average concentration of mobile lead, which is an indicator of soil pollution with the emissions of motor transport, is 2.7 times higher than the background concentration in the soils of the city. Among pedogeochemical lead anomaliesthe soils of the central and western parts of the city (12.9 mg/kg, 6.4 MAC), that are maximally saturated by the traffic flow,stand out (Myslyuk *et al.* 2011).

The results of the research of the anionic composition of soils in autumn showed high content of ions of the main salt composition (Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-). The priority substances by the value of concentration ratio were chloride ions (3–13), nitrate ions (1.4–7.7), bicarbonate ions (2.5–5.4). This can be caused by both natural (salting with highly soluble saltsis typicalfor the loess soils) and technogenic factors. Studies have shown that the highest concentration ratios for nitrate ions in the soils are in the northern and south-western directions, which correlates with wind rose and pollution areas of CHP and the plant “Azot” located there. According to the salinity type the soils are slightly saline, chloride salinity prevails, especially in the east and west directions. Soil salinity with chlorides exceeds allowable values.

Natural leaching regime does not provide the necessary decrease of salinity. The change of the concentration of chlorides and nitrates from autumn to spring is not clear: in different sections both an increase and a decrease of the content of these ions were observed. This can be explained both by their higher solubility as compared with other ions and, as a result, migration into the lower layers of the soil with the melt water, and by filtration properties of soils and a different character of urbanogenic factors.

The response of the underlying surface on the atmospheric depositions of sulphate, nitrate and chloride delivery to de-icing agents may be acid leaching of soil-forming rocks.

Preliminary studies have found that urban soils of the city of Cherkassy are predominantly characterized by a very high, high and medium buffering to the acid load and a high and medium buffering to the alkaline load. The difference of stability of individual soil horizons to the acid-base impact is due to the peculiarities of their particle size distribution, the different degree of saturation by bases and humus content.

There is the neutralization of the acids coming in the aerotechnogenic way in calcareous saturated soils of the city of Cherkassy, so the reaction of their solution is neutral or even alkaline. The duration and regularity of pollution (emissions from enterprises, use of a large number of anti-icing agents in winter, contact of carbonate construction waste with soil, removal of topsoil) are responsible for the tendency of urban soils to alkalization.

With a further increase or even maintaining of the existing rate of energy sources (coal and natural gas) by the Cherkassy CHP, the estimation of soils in terms of acid-base buffering becomes important. This will allow to identify the vulnerable ecological and geochemical ecosystems and to develop effective environmental protection measures.

Conclusions

1. The results of the study of acid-base properties of soils from different functional areas of the city of Cherkassy showed that 40% of urban soils have an alkaline reaction, which is of little use for the growth and development of tree vegetation stands. They need correction of acid-base properties.

2. The analysis of the cause-effect relationship in the impact of adverse environmental factors on urban landscapes showed that the formation of acid-base regime of soils is influenced by both natural landscape-geochemical and anthropogenic factors.

3. Based on the theoretical, statistical and visual interpretation of cartographic material, zoning of the city into zones of influence of pollution factors and changes in the quality of the urban ecosystem was done.

4. The created map models will make it possible to analyze space-time changes of the urban landscapes and to identify locations of dangerous ecological processes.

5. The information obtained during the research is viewed as a preliminary guide for objective and scientifically based assessment of the ecological state of the urban landscapes of the city of Cherkassy, and for the development of environmental measures and selection of woody plants for landscaping.

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RŪGŠTINĖS ŠARMINĖS ČERKASŲ MIESTO ŽEMĖS SAVYBĖS

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Santrauka

Pateikta Čerkasų miesto dirvožemio dangos ir jos rūgštinių šarminių savybių antropogeninių pokyčių charakteristika. Dirvožemio iš skirtingų Čerkasų miesto funkcionalinių zonų tyrimų rezultatai parodė, jog jie turi išskirtinai šarminę reakciją. Panaudojus programinį SURFER paketą pagal dirvožemio rūgštinio šarminio režimo charakteristiką skirtingose funkcionaliose miesto zonose atlikta eksperimentalių duomenų kartografija, kuri suteikė galimybę išskirti: derlingas (pH = 6,5–7,0) ir potencialiai derlingas (pH = 7,0–7,5) žemes, mažai tinkamus (pH = 7,5–8,0), vidutiniškai (pH = 8,0–8,5) ir stipriai (pH = 8,0–8,5) toksiškus dirvožemius. Parodyta, kad pagal rūgštinio šarminio režimo charakteristiką tik 60 % miesto žemės galima išskirti kaip derlingas ir potencialiai derlingas žemes. Nepalankių ekologinių faktorių miesto landšaftui poveikio priežasties pasekmės ryšių analizė parodė, kad rūgštinio pagrindinio dirvožemio režimo formavimą veikia gamtiniai landšaftiniai– geocheminiai bei antropogeniniai faktoriai.

Reikšminiai žodžiai: miesto žemė, rūgštinės–šarminės dirvožemių savybės, dirvožemio toksiškumas, kartografinis modeliavimas.