20-osios Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis“ teminė konferencija
Proceedings of the 20th Conference for Junior Researchers “Science – Future of Lithuania”

APLINKOS APSAUGOS INŽINERIJA / ENVIRONMENTAL PROTECTION ENGINEERING

2017 m. kovo 20 d. Vilnius
20 March 2017, Vilnius, Lithuania

ISSN 2029-7157 / eISSN 2029-7149
ISBN 978-609-476-073-0 / eISBN 978-609-476-072-3
Article Number: *aplinka.011*

Aplinkos apsaugos inžinerija
Environmental protection engineering

https://doi.org/10.3846/aainz.2017.011

ASSESSMENT OF ACID-BASE BUFFERING PROPERTIES OF SOILS OF THE CITY OF CHERKASSY

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Abstract. The research carried out showed that the amount of the buffering capacity of soil in acid and alkaline ranges varied within 27–98% (from low to very high) and 31–81% (from medium to very high) respectively. The specific features of acid-base buffering capacity of soils are in asymmetry with buffering areas. For the first time the computer generated models were created using the software package SURFER that will allow to monitor the urban soils’ state in time and space, to estimate the degree of their degradation under the influence of growing technogenic load, to specify the peculiarities of the formation of ecogeochemical situation in the city. The city map was zoned by acid-base buffering properties of soils based on the theoretical, statistical and visual interpretation of cartographic data.

Keywords: urban soils, acid-base properties of soils, acid-base buffering, geoinformation technology, cartographic modeling.

Introduction

The study of the ecological state of an urban system of industrial centers is one of the priority areas of environmental monitoring. The topicality of such studies is due to the necessity to decrease dangerous environmental consequences of urbanization and the optimization of the ecological status of the city.

The optimal target for assessment of environmental pollution is a ground coating. The soil, which is a deposit environment, reflects the processes of breaking geochemical cycles, affects the structure of man-made geochemical anomalies in man-made landscapes and is an indicator of the territory geoecological status.

Anthropogenic disturbance and technogenic soil pollution lead to the formation of a specifically transformed natural-technological system. Properties and chemical composition of the soil are modified; the soil becomes degraded and partially loses its ecological and regulatory functions (Yang, Zhang 2015).

One of the specific directions of soil transformation is the acidity change, the most dynamic indicator of its physical and chemical properties. The acidity actively changes in space and time depending on changes in the basic soil processes and is influenced by anthropogenic evolution of soils. In turn, the process of soil acidity is altered, resulting in a change of its properties (the structural damage, change in the elemental composition and physico-chemical properties), violation of soil-geochemical processes, reduction of the ecosystem stability and vegetation deterioration.

Soil buffer properties play an important role in the formation of acid-base mode despite the fact that they are poorly studied, especially neutral-alkaline soils (Huang *et al.* 2009; Weaver *et al.* 2004; Bartminski *et al.* 2012; Luo *et al.* 2015).

Buffer properties are among the indicators which show the resistance of soil to degradation, including anthropogenic degradation (Bednarek *et al.* 2005; Rizea *et al.* 2009). Buffer properties are understood to denote the soil's ability to maintain a relatively stable pH value despite the action of acidifying or alkalinising agents. The soil’s ability to neutralise the compounds which modify its pH value results from the presence of certain specific buffering substances the action of which is similar in terms of results but it is associated with the processes which are different in terms of the pH values at which they can run, the buffering capacity understood as the amount of acid or base which can be neutralised by a specific volume (or mass) of the soil and primarily the course of the chemical reaction (Bloom *et al.* 2005).

Due to the buffer properties, within small changes of the medium reaction (pH), the soil does not experience negative consequences. When the soil reaction (both acescency and grassing down) and the process impact duration change, there occurs soil degradation and alterations in its properties.

The study of quantitative and qualitative parameters and regularities of formation of acid-base buffer properties of soil is both theoretically and practically important. Parameters of acid-base buffering, and in particular, the extent of the buffer capacity in the acid and alkaline ranges can be taken for standard of physical and chemical indicators of the soil for background monitoring (Nadtochiy, Myslyva 2014).

The aim of the current study was to determine the resistance of urban soils of Cherkassy to degradation associated with intensive anthropopressure. The topic is relevant to the city of Cherkassy, which undergoes a significant aero industry-related activity, especially during the transition of the Cherkassy CHP from natural gas to coal as the primary fuel, which is reflected in the state of urban landscapes (Myslyuk *et al.* 2010a; Myslyuk *et al.* 2010b; Myslyuk, O., Myslyuk, Ye. 2011), on the functioning of the biogenocenosis (Kornelyuk, Myslyuk 2007; Chemerys *et al.* 2013).

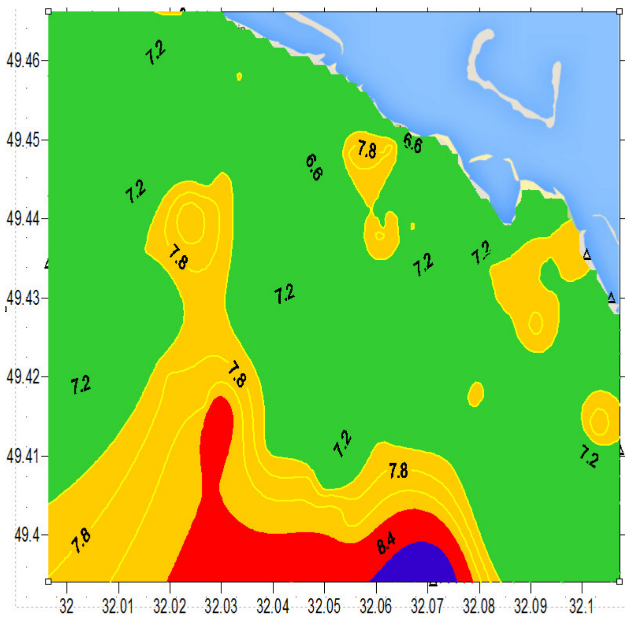

Fig. 1. Land zoning map for pH

The study of the acid-base properties of the soil in Cherkassy (Hovorun, Myslyuk 2016) showed that they are mostly weakly alkaline and alkaline (Fig. 1). 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. High sensitivity and vulnerability of a soil cover to the anthropogenic load may be caused by its limited buffering. The growth of the anthropogenic load on the urban ecosystems can lead to a drastic change of buffer properties of soils.

Materials and methods

Field and analytical studies were performed during 2013–2016 years. Buffer properties of the industrially modified soils in different functional areas of the city were examined. 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.* 2010a; Myslyuk *et al.* 2010b; Hovorun, Myslyuk 2016). 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. All studies were conducted in three replications. The results were obtained by means of variational methods of statistics at the level of significance $P \leq 5\%$ (Lakin 1990); mathematical-statistical analysis was conducted on the basis of the standard computer software Microsoft Office Excel 2010.

The soil buffer capacity was assessed according to the procedure (Nadtochiy, Myslyva 2014). It is based on the potenciometric determination of the soil suspension pH shift depending on changes in the acid (HCl) and alkaline (NaOH) concentration, on the standard ratio of water: soil = 2.5 recommended by the International Congress of soil analysts in Oxford. The land area of soil buffering of the conditioned completely buffering reference sample and soil buffering in the acid (alkaline) range was calculated on the Excel program on the basis of the obtained buffering curves (Fig. 2) by means of the numerical integration method according to Simpson's rule. The extent of the buffer capacity (in percentage) was calculated according to the ratio of soil buffering areas in the acid (alkaline) range and soil buffering in the conditioned completely buffering reference sample.

Ranking of soils by acid-base buffer capacity is given in Table 1 (Nadtochiy, Myslyva 2014).

In order to detect spatial regularities of geochemical zones formation for the acid-base buffer properties of soil SURFER software package 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 90 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.

Table 1. Assessment Scale of Natural Acid-Base Buffer Capacity of Soils (per cent)

Index assessment	Acid range	Base range
Very low	<15	<10
Low	16–40	11–30
Medium	41–60	31–50
High	61–80	51–70
Very high	>81	>71

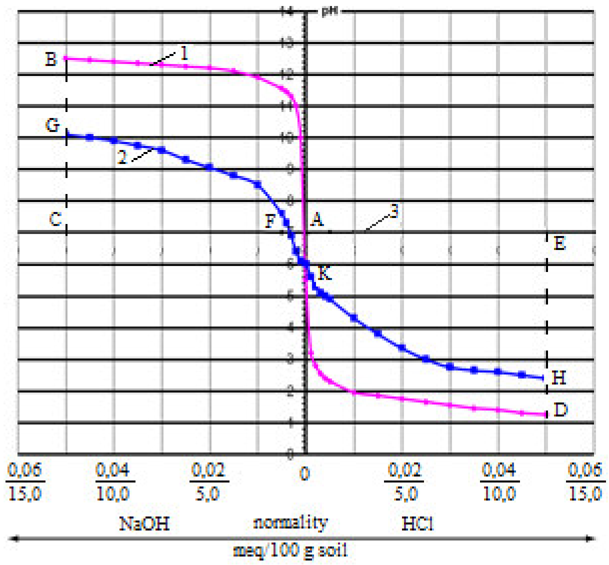

Fig. 2. Graphical models of the acid-base buffer soil: 1 – Curve of relationship between pH values of HCl and NaOH solutions and the changes in concentration; 2 – buffer curve of sample; 3 – line of soil buffering of the conditioned reference buffering sample; ABC and ADE are areas of the soil buffering of the conditioned reference buffering sample; FABG and DKH are areas of the soil buffering in the acid and alkaline ranges

Results and discussion

The alkaline soils in urban areas not only induce nutrient imbalance but also change the metal speciation and activities (Ge *et al.* 2000; Yang, Zhang 2015). The values of the soil pH in Cherkasy are in the range of 6.0–9.2 (Hovorun, Myslyuk 2016), alkaline soils dominate (Fig. 3).

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 environment and wash regime the mobility of organic material increases dramatically, which leads to depletion of soil humus.

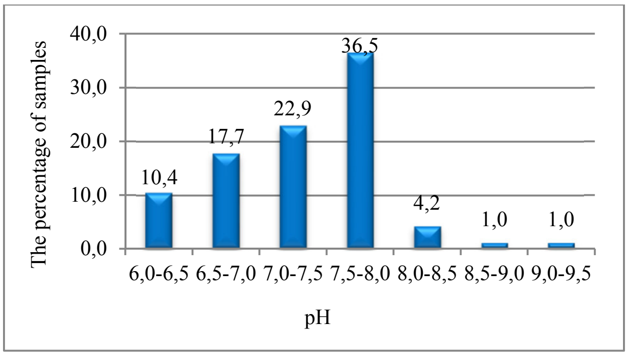

Fig. 3. Soil ranking according to pH

As it was noted above, buffer properties play an important role in the formation of acid-base ground mode. Soil buffering is determined by means of a quite intricate complex of physical, chemical and biological processes and depends, above all, on the reaction of the soil solution, carbonate content, and composition of organic matter, the capacity of cationic exchange, the degree of saturation of the soil absorption complex bases. Soil buffering capacity depends on the external influences: chemical composition of substances coming, intensity and duration of their receipt (Vinogradova 2013).

The studies of soils in Cherkassy showed that the extent of the buffer capacity in acid and alkaline ranges varied within 27–98% and 31–80% range respectively. In accordance with the scale of assessment of acid-base buffering (Table 1) the extent of the buffer capacity of the investigated soils ranged in the acid range from low to very high, in the alkaline range – from medium to high (see Fig. 4).

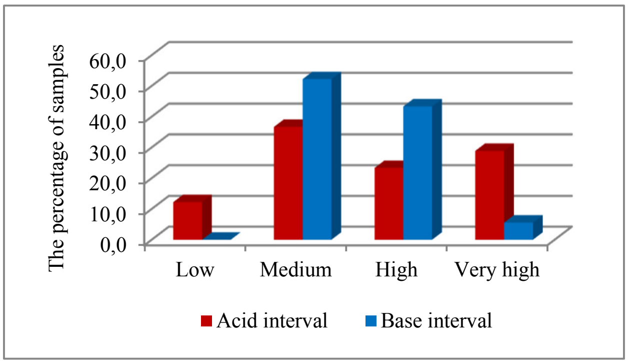

Fig. 4. Ranking of soils by acid-base buffer capacity

The soils with the average degree of the acid-base buffer capacity (36.7% of the samples) in the acid range and the medium (52.2% of the samples); high (43.3% of the samples) is in the alkaline range. 12.2% of soil sampling is in the acid range, the low degree of acid-base buffer capacity. A very high degree of acid-base buffer capacity of soils on the action of acidifying substances is inherent in the areas confined to the areas of influence of such powerful sources of pollution of landscapes of the city as a factory for the production of mineral fertilizers "Azot", the Cherkassy CHP and transport.

The particularities of manifestation of the soil acid-core buffer capacity are in the asymmetry of the buffer area. 58% of the samples had the best buffer properties in the acid range than in the alkaline one, 20% – in the alkaline range, 22% of the samples had the same buffer properties both with acids and alkali. The overwhelming asymmetry of buffer areas is caused by physical and chemical properties of the soil. As it is known, calcerous soils, due to their saturation with calcium and magnesium, have buffer mechanisms with the pronounced asymmetric function that is manifest in prevalence of the proton neutralization processes (H^+), that is these soils show a significant anti-acid capacity. Humic acids can actively neutralize both acidic and alkaline loads (Capko 2008; Nazyrova, Garipov 2011).

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 (Hovorun, Myslyuk 2016).

While analyzing the soil acid-base buffer properties, as well as any complex natural process, a systematic approach must be used, when it is quite natural to process large amounts of the specifically structured geographically distributed information, thus the traditional methods do not fully provide the desired results. In these cases it is necessary to use new tools and methods of the information analysis in the form of the computer-based GIS technologies.

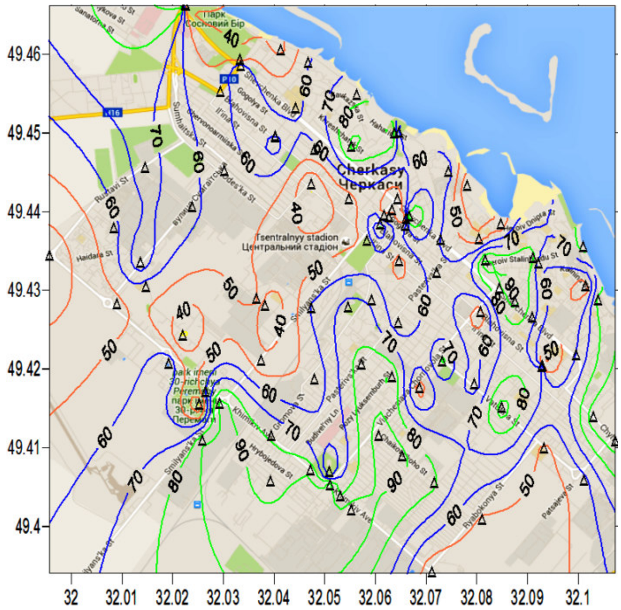

Fig. 5. Contour maps of soil buffering in the acid range

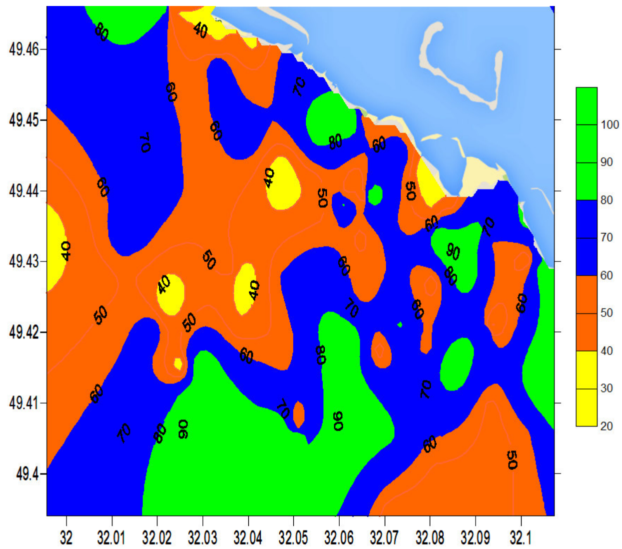

Fig. 6. City zoning by the buffering of grounds in acidic range

Mapping of experimental data using SURFER software package. (Fig. 5–8) and the comparative analysis of the buffer properties of soil in the acid and alkaline ranges allowed to reveal a significant diversity of the city territory according to the degree of the soil acid-base buffer capacity in the acid range (Fig. 6). The difference is the stability of individual soil horizons to acid-base effects due to the peculiarities of their grain composition, different degrees of saturation of bases, humus content and man-made factors.

Thus, it can be argued that today soils in Cherkassy have a relatively high buffer capacity to counter the influx of both acid and alkaline compounds. However, it is necessary to understand that the soil buffer mechanisms function steadily until their capacity is exhausted. When the soils, even with the high carbonate content, are constantly loaded with acid, there may come a threshold limit when the stocks of Ca^{+2} and Mg^{+2} run out or decrease, thus leading to the destruction of buffer mechanisms. The following algorithm of changes in the buffer properties is more appropriate for Cherkassy undergoing in recent years a significant anthropogenic acid load in connection with the transition of the Cherkassy CHP to coal as a primary fuel (Hovorun, Myslyuk 2016). The response of the underlying surface on the atmospheric depositions of sulphate, nitrate and chloride delivery to de-icing agents, acid leaching of soilforming rocks may be a change in the buffer properties of soils.

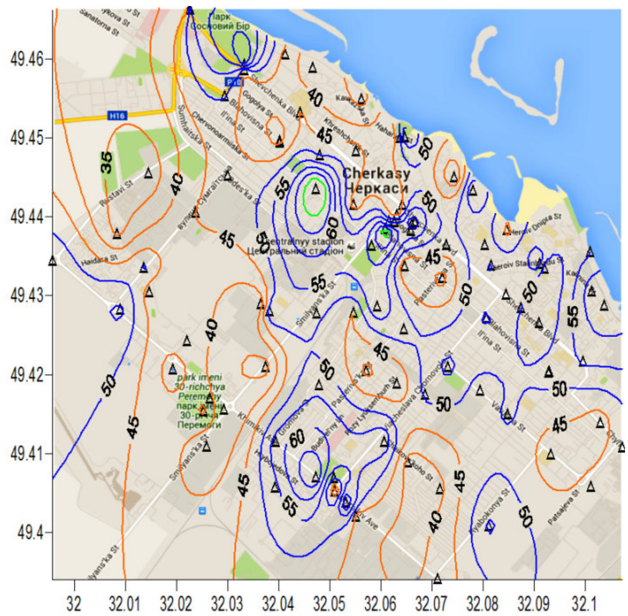

Fig. 7. Contour maps of soil buffering in the alkaline range

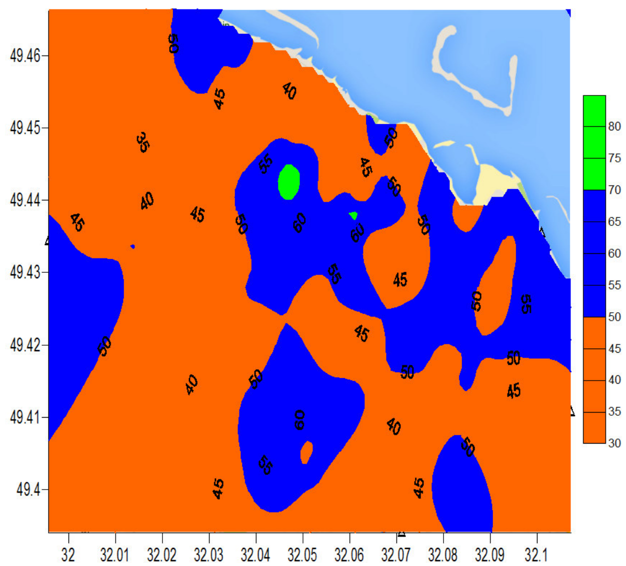

Fig. 8. City zoning by the buffering of grounds in alkaline range

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 study of soils in Cherkassy showed that they have a relatively high buffer capacity to counter the influx of both acid and alkaline compounds. The extent of the buffer capacity of soil in acid and alkaline ranges varied within 27–98% (from low to very high) and 31–81% (from medium to very high), respectively.
2. On the basis of the SURFER software package, soil buffer maps of Cherkassy were created.
3. Based on the theoretical, statistical and visual interpretation of the obtained cartographic material, the territory of the city was zoned according to the soil buffer properties.
4. The peculiarities of manifestation of the soil acid-base buffer capacity lie in the asymmetry of buffer areas and spatial diversity of the city according to the buffer capacity of the soil to resist the action of acidifying substances, and are likely determined by the anthropogenic decalcinacion.
5. The map models created will make it possible to analyze space-time changes of the urban landscapes and to identify locations of dangerous ecological processes.

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ČERKASŲ MIESTO DIRVOŽEMIŲ BUFERINIŲ RŪGŠTINIŲ–BAZINIŲ SAVYBIŲ ĮVERTINIMAS

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Santrauka

Tyrimai parodė, kad dirvožemio buferinė geba rūgštiniame ir šarminiame diapazone svyruoja 27–98 % intervalu (daugiausia nuo mažo iki labai aukšto) ir atitinkamai 31–81 % intervalu (nuo vidutinio iki labai aukšto). Specifinė dirvožemių rūgščių–šarmų buferinė geba asimetriškai koreliuoja su buferinėms sritims. Pirmą kartą kompiuteriniai modeliai buvo gauti naudojant programinės įrangos paketą SURFER, kuris leido stebėti miesto dirvožemių būklę laiko ir erdvės atžvilgiu, siekiant įvertinti dirvožemio degradacijos laipsnį atsižvelgiant į oro technogeninę apkrovą, įvertinant eko-geocheminės situacijos susidarymo mieste ypatumus. Miesto žemėlapis buvo suskirstytas pagal dirvožemio rūgštines–bazines buferines savybes, remiantis teoriniais, statistiniais ir vizualiniais kartografiniais duomenų interpretavimais.

Reikšminiai žodžiai: miesto žemė, rūgštinės–šarminės dirvožemių savybės, rūgščių ir šarmų buferinė, geoinformacinių technologijų, kartografinis modeliavimas.