ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal
www.orientjchem.org

Est. 1984

ISSN: 0970-020 X
CODEN: OJCHEG
2016, Vol. 32, No. (6):
Pg. 3015-3019

Biodiagnostics of the Azov Sea Solonchaks Condition at Chemical Contamination

SERGEY I. KOLESNIKOV, NATALYA A. VERNIGOROVA, KAMIL SH. KAZEEV, SVETLANA A. TISHCHENKO, EVGENIA V. DADENKO and YULIYA V. AKIMENKO

Southern Federal University, 194/1 Stachki, Rostov-on-Don 344090, Russia.

http://dx.doi.org/10.13005/ojc/320621

(Received: November 21, 2016; Accepted: December 12, 2016)

ABSTRACT

In studies on chemical contamination of soils, little attention is paid to disguised solonchaks. This is due to the low significance of disguised solonchaks for agriculture and the lack of significant pockets of chemical contamination in the areas of their extension. At the same time, these soils are widely extended in the coastal landscapes and perform important ecological functions. They are involved in the maintenance of biodiversity and the sustainable functioning of natural ecosystems. As shown by the current study, the contamination by Cr, Ni, Cu, Pb and oil leads to a deterioration of the biological properties of the hydromorphic estuary carbonate solonchak. This means decrease in the total number of bacteria, the activity of catalase and dehydrogenase, cellulolytic ability, abundance of the *Azotobacter* genus bacteria, as well as worsening indicators of radish seeds germination and initial growth. In terms of toxicity to the biological properties of the investigated marsh solonchak the studied elements form the following sequence: Cr>Cu>Ni>Pb. High toxicity of Cr compared to Pb, Ni and Cu in marsh solonchak is explained by weak alkaline reaction, in which CrO_3 is transformed into highly toxic chromate.

Keywords: Chrome, Copper, Nickel, Lead, Salt-marshes, Soil contamination, Biological condition, Taman.

INTRODUCTION

In studies on chemical contamination of soils, little attention is paid to disguised solonchaks. This is due to the low significance of disguised solonchaks for agriculture and the lack of significant pockets of chemical contamination in the areas of their extension. At the same time, these soils are widely extended in the coastal landscapes and perform important ecological functions. They are involved in the maintenance of biodiversity and the sustainable functioning of natural ecosystems[1, 2]. Furthermore, taking into account the significant increase of traffic flow to Crimea via Taman and the development of associated infrastructure, studying the effects of chemical contamination of littoral soils of the Azov Sea, largely consisting of disguised solonchaks, becomes quite relevant.

The aim of this work is to assess the condition of marsh solonchaks of the Azov Sea region under the conditions of contamination by oil and heavy metals (Pb, Cr, Ni, and Cu) based on biological parameters.

METHODS

Hydromorphic estuary carbonate solonchak from Taman Peninsula (Krasnodar Krai, Temryuk district, Sennoy settlement, 45°19.460' N 37°00.222' E) was selected as the study object. Soil for the study was sampled from the 0-10 cm layer, where the concentration of contaminating substances is the highest.

The investigated soil is characterized by psammitic granulometric composition, low humus content of 1%, a neutral medium, pH = 7.5, poor aggregation, though quite high biological activity: the total number of bacteria was 2.4 bln/g of soil, the activity of catalase - 8.6 ml O_2/g of soil for 1 min, the activity of dehydrogenase - 9.0 mg TPP/10 g of soil for 24 hours, and the abundance of the *Azotobacter* genus bacteria - 100% of lumps fouling.

Oil and heavy metals (in the form of oxides), namely PbO, CuO, CrO_3 and NiO were used as contaminants.

Among heavy metals, Cr, Cu, Ni and Pb were chosen because they are major contaminants of the soils of Azov Sea region[3]. In addition, they can be used to compare the degree of toxic effect, as their maximum permissible concentration (MPC) is 100 mg/kg of soil. We used MPC values developed in Germany[4]. First, because the values of maximum permissible concentration of total (gross) amount of copper and nickel in Russia are lacking. Second, the "Russian" MPC of lead often cannot be used in practice because its value is less than the actual content of this element in many types of soil.

In addition, the MPC of oil content in the soil has not been developed. Therefore, to express the oil concentration in the soil we used its percentage composition.

Heavy metals were introduced into the soil in quantities of 1, 10, and 100 MPC that corresponds to 100, 1000 and 10,000 mg/kg, the oil dosages were 1, 5 and 10% by weight of the soil.

The soil was incubated in vegetation vessels at room temperature (20-22°C) and optimum moisturization (60% of normal field capacity) in triplicates.

The soil condition was determined 30 days after contamination. This period proved to be the most informative in the study of the chemical contamination effects on biological properties of the soil.

Laboratory and analytical studies were performed using conventional ecological methods[5,6]. We have carried out biochemical, microbiological, and phytotoxic tests, analyzed the total bacterial abundance, the abundance of *Azotobacter* genus bacteria, assessed soil cellulolytic activity and determined phytotoxic properties of the soil as well as activity of catalase and dehydrogenase. The total number of bacteria in the soil was accounted by fluorescent microscopy according to Zvyagintsev and Kozhevin method, bacteria of the *Azotobacter* genus – by lumps fouling method using Ashby medium, cellulolytic ability – by decomposition ratio of cotton fabric, phytotoxicity – by change in the length of radish roots, catalase activity – by Galstyan technique, and dehydrogenase activity – by Galstyan technique in Khaziyev's modification.

Based on the above mentioned biological parameters we determined the integrated indicator of biological condition (IIBC) of soil[6]. To calculate the IIBC, the values of each of the above indicators in the control (uncontaminated soil) were taken as 100%, and the percentages of indicators in all other test options (in contaminated soil) were expressed with regard to reference values. Further, the average values of the five selected indicators for each test option were determined. The obtained value of IISC was expressed in percentage relative to control (100%).

This technique allows integrating the relative values of different indicators, whose absolute values cannot be integrated, as they have different units of measurement.

Table 1: The effect of chemical contamination on biological properties of hydromorphic estuary carbonate solonchak

Element (substance)	Contaminant dose Control	1 MPC	10 MPC	100 MPC	HCP05
The total number of bacteria, bln per 1 g of soil					
Cr	2.4	1.8	1.1	1.0	0.3
Cu	2.4	2.3	1.5	1.2	0.2
Ni	2.4	2.1	1.4	1.2	0.2
Pb	2.4	2.4	2.4	2.2	0.2
oil	2.4	1.3	0.9	0.8	0.3
HCP05		0.2	0.2	0.2	
The catalase activity, ml of O_2 per 1 gr of soil for 1 min					
Cr	8.6	8.4	8.1	4.2	1.4
Cu	8.6	8.4	7.5	4.7	0.7
Ni	8.6	8.1	8.2	6.6	0.7
Pb	8.6	8.5	8.2	7.1	0.7
oil	8.6	8.6	7.9	6.2	1.3
HCP05		0.7	0.9	0.8	
The dehydrogenase activity, mg of TPP per 10 g of soil for 24 hours					
Cr	9.0	4.1	3.5	2.9	1.1
Cu	9.0	5.6	3.9	4.4	0.8
Ni	9.0	9.3	6.8	3.5	0.7
Pb	9.0	9.0	8.3	3.0	1.0
oil	9.0	8.8	6.8	3.6	1.0
HCP05		1.0	1.0	0.6	
Soil cellulolytic activity, % of the control					
Cr	100	61	54	38	15
Cu	100	83	61	36	9
Ni	100	79	58	46	7
Pb	100	88	64	59	10
oil	100	91	77	68	11
HCP05		10	9	10	
The abundance of *Azotobacter* genus bacteria, % of the lumps fouling					
Cr	76	49	44	32	6
Cu	76	55	38	24	7
Ni	76	43	35	25	6
Pb	76	41	33	27	6
oil	76	35	29	23	5
HCP05		5	4	4	
The root length of radish (phytotoxicity), % of the control					
Cr	100	50	28	2	11
Cu	100	69	37	11	9
Ni	100	63	30	11	8
Pb	100	72	34	12	10
oil	100	26	18	0	9
HCP05		5	3	1	
The integrated indicator of soil condition (IISC), % of the control					
Cr	100	66	53	34	
Cu	100	80	57	39	
Ni	100	81	60	42	
Pb	100	85	72	52	
oil	100	69	56	41	

To check the received data for fidelity we have conducted variance analysis determining the least significant difference (LSD).

RESULTS

Based on the results of the study it was found that contamination of the hydromorphic estuary carbonate solonchak by Pb, Cr, Ni, Cu and oil leads to deterioration of its biological condition. In most cases there was a significant reduction in the studied biological parameters (Table 1): the total number of bacteria, the abundance of *Azotobacter* genus bacteria, cellulolytic activity, catalase and dehydrogenase activities, root length of radish, and the IISC.

A similar pattern was obtained in studies conducted earlier with other soils of the South of Russia: ordinary chernozem, southern chernozem, typical chernozem, leached chernozem, compact chernozem, brown and gray forest chernozems, sod carbonate chernozem, alpine humus chernozem, and chestnut chernozem[7-11].

The degree of reduction of biological parameters in most cases was in direct proportion to the concentration of soil contaminants.

Biological parameters, used in the present work (activity of catalase and dehydrogenase, cellulolytic ability, abundance of *Azotobacter* genus bacteria, and root length of radish), can be employed for monitoring, diagnostics and standardization of chemical contamination of disguised solonchaks by Pb, Cr, Cu, Ni and oil.

A range of toxicity of the investigated elements in terms of the degree of negative impact on the biological properties of the hydromorphic estuary carbonate solonchak is as follows: Cr (63) > Cu (69) > Ni (71) > Pb (79). However, such a sequence of toxic elements according to their ecological hazard for soils does not fully coincide with the results obtained in other studies[12-14]. The high toxicity of chromium is determined by the fact that we have used high chrome oxide (CrO_3), in which the chromium is in the oxidation degree equal to +6 and has a significant oxidative capacity. This kind of oxide was used in the experiment since it contaminates soil most commonly[4].

Besides, the toxicity of Cr was significantly higher in hydromorphic estuary carbonate solonchak comparing to the other three metals, namely Pb, Ni and Cu. This is due to the faintly alkaline reaction of the soil, in which CrO_3 is transformed into the highly-mobile and highly-toxic chromate[15]. Similar effects of Cr were observed in the other alkaline and neutral soils[8, 9].

CONCLUSION

Contamination by Cr, Ni, Cu, Pb and oil leads to a deterioration of the biological properties of the hydromorphic estuary carbonate solonchak. This means decrease in the total number of bacteria, the activity of catalase and dehydrogenase, cellulolytic ability, abundance of the *Azotobacter* genus bacteria, as well as worsening indicators of radish seeds germination and initial growth.

As a rule, the abatement of biological parameters is directly dependent on the concentration of soil contaminants.

In terms of toxicity with regard to the biological properties of the hydromorphic estuary carbonate solonchak, the investigated elements form the following sequence (the range is averaged according to the doses of contaminants): Cr (63) > Cu (69) > Ni (71) > Pb (77).

ACKNOWLEDGEMENTS

The research was supported by the Ministry of Education and Science of the Russian Federation (6.345.2014/K) and state support of leading scientific schools of the Russian Federation (NSH-9072.2016.11).

REFERENCES

1. Shishov L.L., Pankova E.I., **2006**, Zasolennye pochvy Rossii [Saline soils of Russia] [Text], Moscow, IKC "*Akademkniga*", **2011.,**854.
2. Kolesnikov, S.I., Spivakova, N.A., Vezdeneeva,

L.S., Kuznetsova, Yu.S., and Kazeev, K.Sh., , Modeling the effect of chemical pollution on biological properties of hydromorphic solonchaks in the dry steppe zone of Southern Russia. *Arid Ecosystems*, **2011.,** *1*(2),. 83-86.

3. Alekseenko, V.A. Suvorinov, A.V., and Vlasova, E.V., , Metally v okruzhayushchey srede. Pribrezhnye akvalnye landshafty Chernomorskogo poberezhya Rossii. [Metals in the environment. Coastal aquatic landscapes of the Black Sea coast of Russia] [Text]. *Moscow, FSBSI SRI PMT,* **2012**., 360.
4. Kabata-Pendias, A.,. Trace elements in soils and plants. *4th edt. Boca Raton, FL, Crc, Press*, **2010**.,548.
5. Zvyagintsev, D.G., , Metody pochvennoy mikrobiologii i biokhimii [Soil microbiology and biochemistry methods] [Text]. Moscow*, Moscow State University*, **1991.,**304.
6. Kazeev K., Kolesnikov, S., Biodiagnostika pochv: metodologiya i metody issledovaniya [Biodiagnostics of soil: methodology and research methods] [Text]. Rostov-on-Don, Southern Federal University, **2012.** ., 260.
7. Kolesnikov, S.I., Zharkova, M.G., Kazeev, K.Sh., Kutuzova I.V., Samokhvalova, L.S., Naleta, E.V., and Zubkov, D.A.,. Ecotoxicity assessment of heavy metals and crude oil based on biological characteristics of chernozem. *Russian Journal of Ecology*, **2014.,***45*(3),. 157-166.
8. Kolesnikov, S.I., Spivakova, N.A., and Kazeev, K.Sh.,. The effect of model soil contamination by Cr, Cu, Ni, and Pb on the biological properties of soils in the dry steppe and semidesert regions of Southern Russia. *Eurasian Soil Science,* 44(9), **2011.,**1001-1007.
9. Kolesnikov, S.I., Yaroslavtsev, M.V., Spivakova, N.A., and Kazeev, K.Sh.,. Comparative assessment of the biological tolerance of chernozems in the South of Russia towards contamination by Cr, Cu, Ni, and Pb in a model experiment. *Eurasian Soil Science,* **2013** 46(2),. 176-181.
10. Kolesnikov, S.I., Tatlok, R.K., Tlekhas, Z.R., Kazeev, K.Sh., Denisova, T.V., and Dadenko, E.V., , Biodiagnostics of the resistance of highland and mountain soils in the Western Caucasus to pollution with crude oil and oil products. *Russian Agricultural Sciences*, **2013.,** 39(2). 151-156.
11. Kolesnikov, S.I., Tlekhas, Z.R., Kazeev, K.Sh., and Val'kov, V.F., Chemical contamination of Adygea soils and changes in their biological properties. *Eurasian Soil Science,* **2009,** *42*(12), 1397-1403.
12. Crommentuijn, T., Polder, M.D., Van de Plassche, E.J., , Maximum permissible concentrations and negligible concentrations for metals, taking background concentrations into account. RIVM Report 601501001. Bilthoven, Netherlands, **1997.,** 260 .
13. Van de Plassche, E.J., De Bruijn, J.H.M., , Towards integrated environmental quality objectives for surface water, sediments and soil for nine metals. RIVM Report 679101005. Bilthoven, Netherlands, **1992.,**130.
14. Vodyanitsky, Y., , Standards for the contents of heavy metals and metalloids in soils. *Eurasian Soil Science*, **2012.,** 3. 321-328.
15. Zachara, J.M., Ainsworth, C.C., Cowan C.E., and Resch, C.T., Adsorbtion of chromate by subsurfase soil horizons. *Soil Sci. Soc. Am. J.*, **1989,** *53*.. 418-428.