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Heavy metals pollution in children playgrounds -an environmental modelling and statistical analysis

Šapčanin A[1,2]*, Čakal M[2], Ramić E[1], Smajović A[1], Pehlić E[3]

[1]*Faculty of Pharmacy, University of Sarajevo, Zmaja od Bosne 8, 71 000 Sarajevo, Bosnia and Herzegovina*
[2]*Faculty of Mechanical Engineering, University of Sarajevo, Vilsonovo šetalište 8, 71 000 Sarajevo, B&H*
[3]*Faculty of Biotechnical Sciences, University of Bihac, Luke Marjanovića bb, 77 000 Bihac, Bosnia and Herzegovina*

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***Corresponding author:**
E-mail:aidasapcanin@bih.net.ba
Phone: 00-387-33-586187

Abstract: Models could be used to simulate target variable responses to changes in very complex systems such as soils polluted by heavy metals. Chemical properties of soil such as pH in H_2O, pH in 1 mol/L KCl, humus and $CaCO_3$ could influence metal mobility and can be used to assess impact of various antropogenic activities. The soil samples were collected from playgrounds located in different areas of Sarajevo. Heavy metals: Cd, Pb, Cu and Zn and basic chemical properties of soil were determined. Statistical analysis was conducted to obtain the correlation coefficient of two selected variables in a data sample, as a normalized measurement of how the two are linearly related. Determined content (mg/kg) for Cd, Pb, Cu and Zn in the spring season were in the ranges of: 0.91-2.15; 26.69-118.97; 19.14-80.21; 75.85-161.45 and in the autumn season were in the ranges of: 0.80-2.14; 41.07-152.71; 29.46-140.74; 71.77-199.04, respectively. The results showed that the highest correlation coefficient was 0.91, for the total content of Cu in the soils in regard to the content of Pb in the autumn season and this indicates a strong and positive correlation. Generally, our results could be used for prediction of heavy metal distribution in playground soil.

INTRODUCTION

Mathematical and computer modelling help us with understanding processes occurring in soils. A number of models are being developed now which can quantitatively predict movements and sorption of heavy metals in soil with good accuracy (Dube et al., 2001). In recent years, researchers have focused on modelling of multicomponent reactive transport and have developed models to study the mobility of potentially toxic heavy metals in the surface soils. The heavy metals are reactive and undergo various chemical transformations in the contaminated soil. Numerous studies have shown that the major sources of heavy metal pollution in urban soils include emissions from traffic (exhaust, tire wear debris particles, particles formed by weathering street), industrial wastes (from power plants, coal combustion, metallurgical industry, automobile repair plants, chemical plants), household garbage, building and weathered particles of sidewalk and precipitation in the atmosphere, etc (Hu et al., 2013; Su et al.. 2014). The content of heavy metals in soils can vary widely, even in uncontaminated soils (Qayyum et al., 2015). All inorganic pollutants are considered to be the most common and potentially harmful substances in urban soil in areas affected by anthropogenic pollution (EC, 2013). Due to the fact that children, the most vulnerable population, are in direct contact with surface soils, it has become clear that soils from children playgrounds should be examined with special care and attention. Polluted soils can directly affect children's health as pollutants and particles from playgrounds can enter their bodies through oral ingestion, inhalation, or in a dermal contact. That is why soil samples, and the soils generally, affect human health, have become a very good diagnostic tool for an assessment of the environmental status of the city (Sapcanin et al., 2016). In urban environments such as children playgrounds, polluted soils can have a direct influence on infants and children's health, because of heavy metals inherent toxicity.

Heavy metals once introduced to the environment by one particular method may spread to various environmental components, which may be caused by the nature of interactions occurring in this natural system. Heavy metals may chemically or physically interact with the natural compounds, which changes their forms of existence in the environment. In general, they may react with particular species, change oxidation states and precipitate (Dube et al., 2001.) Heavy metals are ecologically very important, they are not biodegradable and they move through the ecosystem.

Models could be used to simulate target variable responses to changes in very complex systems such as soils polluted by heavy metals. Determination of chemical properties of soil such as pH in H_2O, pH in 1M KCl, humus and $CaCO_3$ could influence metal mobility and can be used to assess impact of various antropogenic activities in soils of interest and to give the environmental buffering capacity and to model pathways in the polluted soils leading to the human health risk of exposure (Kabata-Pendis and Mukherjee, 2007). Every model is created by using the data received as an experimental result from natural or simplified (pseudo-natural) system, which must be accurately defined and in controlled conditions. Obtained results are transformed into a general formula. On the basis of this formula, the scientist chooses a suitable model (Altman, 1991; Armitage and Berry, 1994). The last step is checking the model in different physiochemical conditions to define where and when this model can be applied. There are two types of approach to modelling the system, the predictive and the descriptive ones. In the predictive modelling, the primary objective is to obtain the best possible fit to the available data, since in that way there will be the maximum possible confidence in the predictions made by the model in regions where there are no experimental data with which to compare it. In the descriptive modelling, on the other hand, the goal is to use the model to gain more information about the way in which the real system functions. Furthermore, the primary intent is not to obtain the best possible fit to experimental data, but rather to increase knowledge of the binding precess. In any case, one of the first stages in the modelling process is the correlational and regressional analysis. By using the regression and correlation, the correlation between two or more variables is analyzed. The correlation implies the analysis of the strength and direction of the correlation, while the regression implies the analysis of the shape and direction of the correlation, and the analysis in terms of independent/dependent (predictor/outcome) variables, with the intent of making prediction. (Altman, 1991; Armitage and Berry, 1994; Bland, 2005). In the regressional model, knowledge of values of independent variables enables predicting values of the dependent variables.

Whenever there is a significant correlation between the two variables, the value of one variable can be used for predicting the value of the other variable. (Nedunuri et al., 1995).

MATERIAL AND METHODS

For the purpose of this study, the soil samples were collected from selected public children playgrounds located in eight different urban areas of Sarajevo according to ISO 11047 protocol, in the spring and autumn seasons.

Ten sub-samples were collected from the top 10 cm layer of the soil and mixed to obtain a bulk composite sample. Samples were collected with a stainless trowel and transferred to the laboratory in plastic bags. Stones and foreign objects were hand-removed, and the samples were air-dried for seven days.

Furthermore, the samples were then ground in order to obtain a fine homogenous powder. Basic properties (pH in H_2O, pH in 1M KCl, humus and $CaCO_3$) of the examined soil samples were determined by standard methods of soil analysis (Sapcanin et al., 2016).

Samples for the determination of heavy metals Cd, Pb, Cu, and Zn were prepared by microwave – assisted acid digestion and determined by using an atomic absorption spectrophotometer, Shimadzu AA 6800, according to Environmental Protection Agency (EPA) protocols.

Mathematical-statistical analysis

Statistical analysis was conducted to obtain the correlation coefficient of two selected variables in a data sample, as a normalized measurement of how the two are linearly related. Estimation of dependence of the selected variables has been carried out according to the following criteria:

if the value of the correlation coefficient is ≥ 0.70, then correlation is strong;

if the value of the correlation coefficient between 0.30 – 0.69, then correlation is medium;

if the value of the correlation coefficient is < 0.30, then correlation is weak,

And if the value of the correlation coefficient is 0.0, then there is no lienar correlation (which does not exclude the possibility of having a non-linear form of correlation).

RESULTS AND DISCUSSION

The results of the determination of some basic properties of the examined samples from the public park and playground soils in the spring and autumn seasons are presented in Table 1.

Results of the pH values for the active acidity in the soil in the selected public children playground soils range from: 7.94 to 8.29, so that the examined soils are classified as alkaline ones. Results of the pH values for the substituted acidity in the soil on the selected public children playground soils range from: 7.26 to 7.68, so that the examined soils are classified as alkaline ones – in alkaline soils sorption of metals is lower, however, metals remain for longer periods in the soils. The content of humus in the soil in the selected public children playground soils ranges from: 2.94-11.75, and based on the humus content, the examined soils are classified as soils with weak or strong presence of humus.

Table 1. Basic chemical properties (pH in H_2O, pH in 1 mol dm^{-3} KCl, humus, and $CaCO_3$) of the soil samples from selected playgrounds in the spring and autumn seasons.

Playground	pH in H_2O		pH in 1M KCl-u		Humus (%)		$CaCO_3$ (%)	
	Spring	Autumn	Spring	Autumn	Spring	Autumn	Spring	Autumn
1	8.17	8.16	7.59	7.30	5.83	5.63	14.26	18.28
2	8.26	8.17	7.73	7.58	3.38	5.54	15.88	17.95
3	8.34	8.14	7.74	7.68	2.94	4.14	17.63	20.73
4	8.14	7.97	7.57	7.54	4.48	4.66	25.20	27.23
5	8.20	8.22	7.63	7.63	11.75	6.48	17.88	36.31
6	8.12	8.04	7.63	7.51	5.16	5.16	5.90	17.15
7	8.29	8.06	7.26	7.61	6.02	6.23	19.73	1.49
8	8.13	7.94	7.41	7.46	2.97	3.85	5.49	4.57

The content of $CaCO_3$ in the soil in the selected public children playground soils ranges from: 1.49-36.31, and based on the content of $CaCO_3$ in the soil, the examined soils are classified as soils with weak or strong carbon content.

Table 2 shows basic statistical parameters: mean value, standard deviation, median, variance, minimum and maximum value and the range of the content (mg/kg) of metals/metalloids, in the soil collected from the old children playground in the spring season in Sarajevo.

Table 2. Basic statistical parameters calculated for the content of metal (mg/kg) in public children playground areas in Sarajevo in the spring season

Heavy metal	Mean (mg/kg)	SD	Median	Variance	Min	Max	Range
Cd	1.42	0.56	1.49	0.32	0.48	2.1596	1.68
Pb	68.65	32.15	65.21	1033.71	26.7	118.9793	92.28
Cu	45.36	21.94	40.5	481.46	19.14	80.2156	61.07
Zn	129.94	35.99	137.66	1295.24	75.85	173.44	97.58

Results show that maximum values for the content of metals Cd, Pb, Cu i Zn are higher from the target value according to the Dutch legislation. Obtained maximum values have not exceeded the values which may require intervention in form of remediation, nevertheless, the obtained values do not exclude risks which may be posed to the ecosystem.

According to the results obtained for maximum values of the content of metals/metalloids, the order is as follows: Zn > Pb > Cu > Cd.

Table 3 shows basic statistical parameters: mean value, standard deviation, median, variance, minimum and maximum value and the range of the content (mg/kg) of metals/metalloids, in the soil collected from the old children playground in the autumn season in Sarajevo.

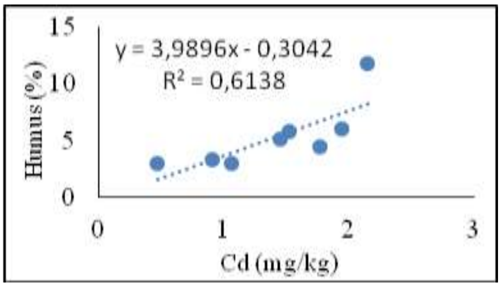
Table 3. Basic statistical parameters calculated for the content of metal (mg/kg) in public children playground areas in Sarajevo in the autumn season

Heavy metal	Mean (mg/kg)	SD	Median	Variance	Min	Max	Range
Cd	1.56	0.47	1.64	0.23	0.81	2.14	1.34
Pb	79.13	46.30	55.33	2144.12	41.07	152.72	111.65
Cu	54.54	39.72	40.73	1577.69	18.92	140.74	121.81
Zn	125.94	40.95	123.75	1677.18	71.76	199.04	127.27

Determined content (mg/kg) for Cd, Pb, Cu and Zn in the spring season were in the ranges of: 0.91-2.15; 26.69-118.97; 19.14-80.21; 75.85-161.45 and in the autumn season were in the ranges of: 0.80 - 2.14; 41.07-152.71; 29.46-140.74; 71.77-199.04, respectively. The results showed that the soils of public parks and playgrounds could be marked as slightly to medium contaminated by determined heavy metals.

Results show that maximum values for the content of metals Cd, Pb, Cu i Zn are higher from the target value according to the Dutch legislation (VROM, 2000). Obtained maximum values have not exceeded the values which may require intervention in form of remediation, nevertheless, the obtained values do not exclude risks which may be posed to the ecosystem.
According to the results obtained for maximum values of the content of metals/metalloids, seasonal variations have been noticed, ie. maximum values of the content of Pb and Cr were higher in autumn in respect to spring, while maximum values of the content of Ni, Cu, Zn, and Se, were higher in spring in respect to autumn. Based on the results obtained for maximum values of the content of metals/metalloids, the order is as follows: Zn > Pb > Cu > Cd.

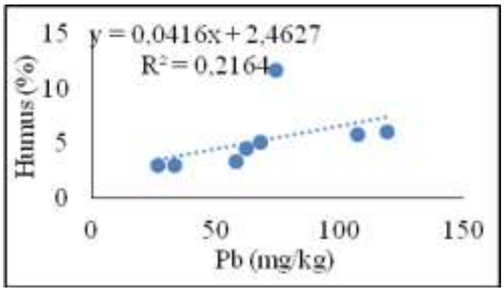
Results of the correlation of the total content of Cd in relation to the content of humus in the spring season are shown in Graph 1.



Graph 1. The total content of Cd in the soil in relation to the content of humus in the spring season

The results show that the highest correlation coefficient for the total content of Cd in the soils in relation to the content of humus in the spring season was 0.78, which indicates to a strong and positive correlation. That means that the increase of the content of humus affects the increase of the total content of Cd.

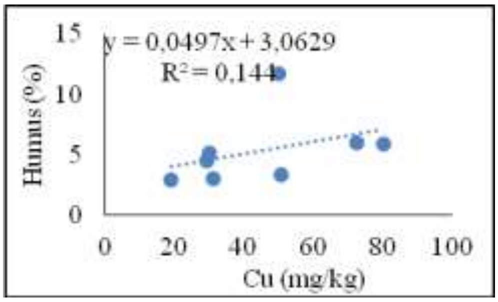
Results of the correlation of the total content of Pb in relation to the content of humus in the spring season are shown in Graph 2.



Graph 2. The total content of Pb in the soil in relation to the content of humus in the spring season

The results show that there is a correlation between the total content of Pb in the soil and the content of humus as the value of the correlation coefficient is 0,47, which indicates to a medium and positive correlation.

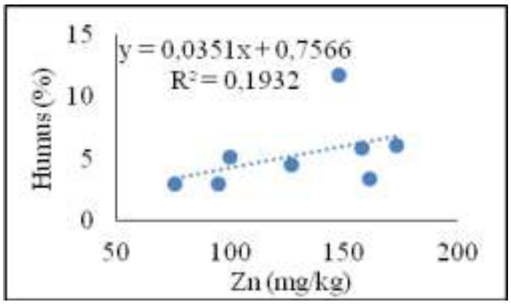
Results of the correlation of the total content of Cu in relation to the content of humus in the spring season are shown in Graph 3.



Graph 3. The total content of Cu in the soil in relation to the content of humus in the spring season

The results show that the correlation coefficient for the total content of Cu in relation to the content of humus is 0,38, which indicates to a medium and positive correlation of these two parametres.

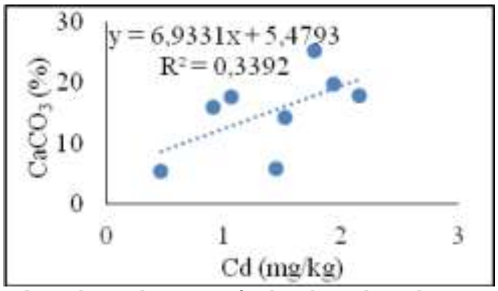
Results of the correlation of the total content of Zn in relation to the content of humus in the spring season are shown in Graph 4.



Graph 4. The total content of Zn in the soil in relation to the content of humus in the spring season

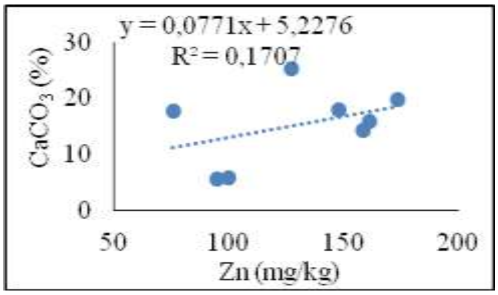
The results show that the correlation coefficient for the total content of Zn in relation to the content of humus is 0,44, which indicates to a medium and positive correlation of these two parametres.

Results of the correlation of the total content of Cd in relation to the content of $CaCO_3$ in the spring season are shown in Graph 5.



Graph 5. The total content of Cd in the soil in relation to the content of $CaCO_3$ in the spring season

The results show that the correlation coefficient for the total content of Cd in relation to the content of $CaCO_3$ is 0,58, which indicates to a medium and positive correlation of these two parametres.
Results of the correlation of the total content of Zn in relation to the content of $CaCO_3$ in the spring season are shown in Graph 6.

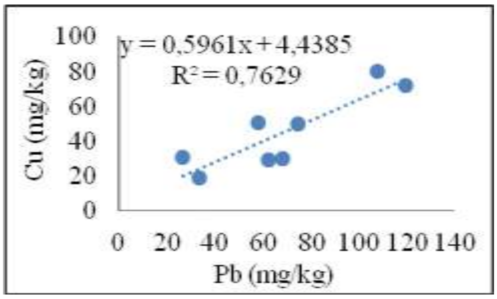


Graph 6. The total content of Zn in the soil in relation to the content of $CaCO_3$ in the spring season

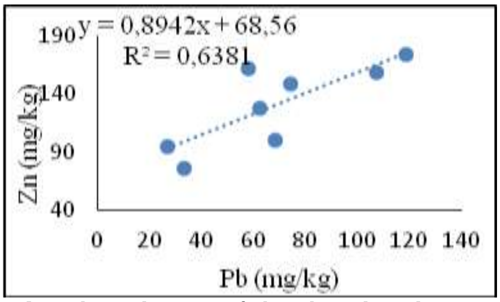
The results show that the correlation coefficient for the total content of Zn in relation to the content of $CaCO_3$ is 0,41, which indicates to a medium and positive correlation of these two parametres.

Basic chemical properties of soil such as pH in H_2O, pH in 1 mol dm^{-3} KCl, humus, and $CaCO_3$ could influence metal mobility and the determined values could be used to model pathways in the polluted soils.

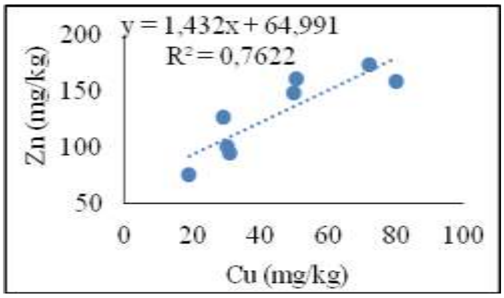
The correlations between the heavy metals studied are shown in the Graphs 7 to 11, as follows:



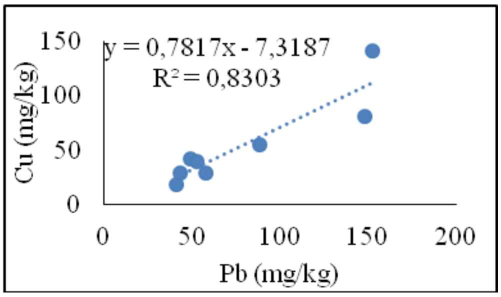
Graph 7. The total content of Pb in the soil in relation to the content of Cu in the spring season



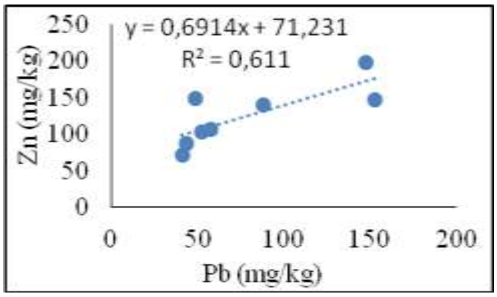
Graph 8. The total content of Pb in the soil in relation to the content of Zn in the spring season



Graph 9. The total content of Cu in the soil in relation to content of Zn in the spring season



Graph 10. The total content of Pb in the soil in relation to the content of Cu in the autumn season



Graph 11. The total content of Pb in the soil in relation to the content of Zn in the autumn season

Results of the correlation between the heavy metals studied offer remarkable information on the sources and pathways of the heavy metals. Pb was strongly correlated with Cu (r =0,87) and Zn (r =0,8) in the spring season. Cu was strongly correlated with Zn (r =0,87) in the spring season. Pb was strongly correlated with Cu (r =0,91) and Zn (r=0,78) in the autumn season.
The highly significant positive correlation between the heavy metals investigated indicates that their compounds occurred from various anthropogenic activities in the children playgrounds environment.

CONCLUSIONS

The presence of heavy metals in soils represents a significant environmental hazard, and one of the most difficult contamination problems to solve. There are two main reasons: firstly, due to the chemical character of heavy metals - they are not subjected to biodegradation processes, and they accumulate in the environment; and secondly, due to the complexity of the soil matrix. The unhomogeneity of soils is so high, that we cannot provide all the features of soil samples without employment of some approximations. Simplification of this matrix increases chances of recognition of basic soil processes. Another option which could enable us to understand better processes occurring in the soils is to employ a computer simulation. However, it seems most effective to apply computer methods with the simulation of natural physicochemical processes in a simplified soil matrix. It can be concluded that, generally speaking, the results obtained from this research can be used for predicting the distribution of content of heavy metals in the soil in the children playground areas.

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Summary/Sažetak

Modeli se mogu koristiti za simulaciju odgovora ciljnih varijabli na promjene u veoma kompleksnim sistemima kao što su zemljišta kontaminirana teškim metalima. Karakteristike zemljišta kao što su pH u void, pH u KCl-u, humus i $CaCO_3$ mogle bi utjecati na mobilnost metala i mogu biti upotrebljena za procjenu djelovanja raznolikih antropogenih aktivnosti. Uzorci tla prikupljeni su sa igrališta lociranih u različitim dijelovima Sarajeva. Teški metali: Cd, Pb, Cu i Zn kao i osnovne hemijske karakteristike tla su određeni. Statistička analiza je izvedena da se dobiju podaci o korelacijskim koeficijentima za dvije odabrane varijable u uzorku podataka kao normaliziranog mjerenja da li su varijable linearno povezane. Izmjereni sadržaj (mg/kg) za Cd, Pb, Cu i Zn u proljetnjoj sezoni kretali su se u rasponu od: 0.91-2.15; 26.69-118.97; 19.14-80.21; 75.85-161.45 i u jesenjoj sezoni kretali su se u rasponu od: 0.80-2.14; 41.07-152.71; 29.46-140.74; 71.77-199.04, respektivno. Rezultati pokazuju da je najveća vrijednost korelacijskog koeficijenta iznosila 0.91, za ukupni sadržaj Cu u

tlu, u odnosu na sadržaj Pb u jesenjoj sezoni i to indicira jaku i pozitivnu korelaciju. Generalno bi se naši rezultati mogli upotrijebiti za predviđanje raspodjele teških metala u tlu igrališta.