

Short Communication

Identifying New ‘Hotspot’ Heavy Metal Contamination in Industrial Zone Soil

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Abstract

Concentrations of dangerous and harmful substances (PCB, TPH and heavy metals) were determined in soils in an industrial zone near the center of Banja Luka and the Vrbas River. PCB, TPH and heavy metals were found in the analysis location as a result of general anthropogenic factors. Contaminated soils have a negative impact on human health and the environment. The mean concentrations of Pb, TPH, Cu, PCB, Ni, Cd and Hg were 4874, 4105, 545.7, 282.1, 225.7, 12.15 and 5.896 mg/kg, respectively. Results show that concentrations were very high for all analyzed parameters, and these values indicated that the soil was highly polluted. Principal component analysis has shown that industrial factors and human activities are the cause of pollution. At the location it is necessary to determine the origin of pollution and recultivation and remediation activity of planned activity.

Keywords: hotspot, soils, heavy metals, TPH, PCB

Introduction

Identification and treatment of contaminated and unsafe locations (hotspots, hazard sites, blackspots, sites with promise, high-risk sites, and accident-prone sites) is the first major step in safety assessment [1, 2]. The former industrial complex Incel Banja Luka Cellulose Factory is categorized as a hotspot (waste from cellulose and viscose factory) [3, 4], and decontamination of soil contaminated by polychlorinated biphenyl (PCB) oils from transformer stations in the vicinity of the factory

has been suggested. The location was recognized as a hotspot from the aspect of PCB. Previous research was based on analysis of PCBs and organochlorine pesticides in air [5, 6], because chlorine liquefaction units (KREBS SWISS Technology) were installed on the site in 1971-1980 for chlorine drying and cooling 67 tpd, chlorine compression 35 tpd and chlorine liquefaction 50 tpd [7]. Previous studies indicate that the level of PCBs on several sampling sites in Banja Luka was as high as 400.000 ng/g (400 mg/kg) of the dry soil sample, which are two orders of magnitude higher than on any other investigated site performed by UMASA.RECETOX [8].

Analysis of total petroleum hydrocarbons (TPH) and heavy metals so far have not been performed in location.

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Inorganic pollutants (TPH, PCB and heavy metals Cd, Pb, Ni, Cu and Hg) can be strongly accumulated in soil, water and plants, and significant quantities of toxic metals are discharged into ecosystems [9]. TPH and PCB are ubiquitous class organic pollutants that are a human health risk [10]. Heavy metals (HMs) occur naturally in the environment; however, the concentration of some HMs has increased tremendously since the beginning of the industrial revolution due to many industrial activities [11]. Heavy metal pollution has attracted more attention because of its toxicity and mobility from polluted soil/water/air to living beings [12].

During the war of 1991-1995 a large number of industrial buildings were damaged, destroyed or devastated, including the Incel factory. Incel is a former company based in Banja Luka that originally manufactured cellulose, viscose and paper products. Established in 1954, it was a major industrial conglomerate in the field during the socialist era, employing up to 6,500 workers. Following a period of decline in the 1980s and the War in Bosnia and Herzegovina in the 1990s, the destroyed factory was subsequently split into several smaller enterprises. The result was the emission of various toxic substances into all components of the environment.

This research is focused on the presentation and discussion of the data related to contamination of soils by dangerous and harmful substances (PCB, TPH and heavy metals). The primary aim of this study was to determine soil pollution in the Incel industrial complex, Banja Luka, Republic of Srpska, Bosnia and Herzegovina, probable hotspot of heavy metals in Banja Luka, Republic of Srpska, Bosnia and Herzegovina.

Material and Methods

Location

The object of our research was to determine soil pollution at the Incel location (former cellulose factory, now industrial complex) 3 km from the center of Banja Luka – the second-largest city in Bosnia and Herzegovina with a population of 185,000. The city is situated in a basin 164 m above sea level. The average annual temperature reaches 10.7°C, the average January temperature is 0.8°C, and the average temperature in July reaches 21.3°C.

Sampling and Analysis

Samplings were performed in eight locations in the Incel industrial complex during April 2019. Sampling of the soil was carried out with Eijkelpamp agrisearch sampling equipment (Netherlands). Physical and chemical analyses were conducted on the samples' pH, organic matter, TPH, PCB (sum PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180), and

total forms of heavy metal pollution and existing pollution were monitored. Acidity (pH) was measured in deionized water, organic matter content by applying Tyurin's method, and TPH and PCB analysis was performed by gas chromatography. Heavy metal concentrations were processed based on the principles described in Standard Methods with disintegration techniques and analyzed according to national legislation [13].

Statistical Analysis

Statistical data processing while determining the relationship between TPH, PCB, and heavy metals was calculated with correlation analysis. A bivariate correlations study (Spearman's, Pearson's and Kendall rank correlation coefficient test) was performed, and a significance level of p value <0.05 , $p < 0.01$ and $p < 0.001$ was used. Descriptive statistical operations like mean, median, standard deviation (SD), variance, minimum (min), maximum (max), skewness and Kurtosis test were applied for analysing the measured data. Statistical analyses (Spearman's, Pearson's and Kendall's correlation coefficient tests) and factor analysis (principal component analysis for pollutants) were applied for getting the qualitative information of the source of the five types of heavy metals, TPH and PCB. We used Excel 2016 JASP 0.8.5.1 software for statistical data processing.

Results and Discussion

In the research, pollutants, TPH and PCB, and heavy metal concentrations (Cd, Pb, Ni, Cu and Hg) that originate from human activity were determined. In Table 1 all of the data were first processed for statistical analysis. As can be seen, Pb is the pollutant with the highest mean concentration (4874 mg/kg), followed by TPH, Cu, PCB, Ni, Cd and Hg, with mean concentrations of 4105, 545.7, 282.1, 225.7, 12.15 and 5.896 mg/kg, respectively.

Concentrations of PCB and heavy metals are greater than measured values during other surveys [14-19].

In small samples, skewness test values greater or less than 1.96 are sufficient to establish normality of the data (for PCB, Pb, Ni and Hg) [20]. Skewness tests for TPH, Cd and Cu show that data distribution is not normal, which is confirmed by the Kurtosis test. Coefficient of variation (CV) is an index showing the extent of variability in relation to the mean of the samples. It can be used for identifying the anthropogenic contribution degree for pollution in environmental studies. If $CV < 0.10$ and > 0.90 are mean, low and high anthropogenic contributions, respectively [21]. Analyzing pollutants have $CV > 0.90$ (except Hg). Values for PCB, Ni, Pb, Cu, Cd and TPH, are 0.94, 1.03, 1.41, 1.57, 2.19 and 2.66, respectively. These values indicate high anthropogenic contribution, and concentrations of

Table 1. Statistical summary of pollutants (TPH, PCB and heavy metals).

	TPH	PCB	Cd	Pb	Ni	Cu	Hg
Valid	8	8	8	8	8	8	8
Min	20	25	0.42	158	78.9	44.6	0.94
Max	31090	600	77.3	18138	706	2488	11.6
Mean	4105	282.1	12.15	4874	225.7	545.7	5.896
Median	107.0	196.0	1.400	605.0	112.0	152.0	5.950
Std. Deviation	1.091e+4	264.3	26.55	6883	232.8	855.6	4.586
Coefficient of Variation	2.66	0.94	2.19	1.41	1.03	1.57	0.78
Variance	1.191e+8	6.984e+4	704.7	4.738e+7	5.418e+4	7.320e+5	21.03
Skewness	2.820	0.3879	2.739	1.332	1.726	2.129	0.1222
Kurtosis	7.963	-2.169	7.598	0.5662	1.895	4.395	-2.044

pollutants in the soil samples varied significantly from location to location.

The results correlation analysis are shown in Table 2. The results of the correlation analysis Cd and

Table 2. Correlation between pollutants (TPH, PCB and heavy metals).

	Pearson		Spearman		Kendall	
	r	p	rho	p	tau B	p
TPH - PCB	0.510	0.197	0.877**	0.004	0.784**	0.010
TPH - Cd	-0.111	0.793	0.184	0.663	0.231	0.442
TPH - Pb	-0.253	0.545	0.024	0.954	0.038	0.899
TPH - Ni	-0.204	0.628	-0.220	0.601	-0.113	0.702
TPH - Cu	0.243	0.561	0.268	0.520	0.189	0.524
TPH - Hg	0.159	0.707	-0.220	0.601	-0.189	0.524
PCB - Cd	-0.035	0.934	0.576	0.135	0.415	0.164
PCB - Pb	-0.021	0.961	0.374	0.362	0.222	0.451
PCB - Ni	-0.214	0.610	0.096	0.820	0.074	0.802
PCB - Cu	0.167	0.693	0.602	0.114	0.371	0.209
PCB - Hg	0.090	0.833	-0.096	0.820	-0.074	0.802
Cd - Pb	0.832*	0.010	0.766*	0.027	0.618*	0.034
Cd - Ni	0.524	0.183	0.587	0.126	0.473	0.105
Cd - Cu	0.936***	< .001	0.946***	< .001	0.837**	0.004
Cd - Hg	0.499	0.208	0.419	0.301	0.255	0.383
Pb - Ni	0.819*	0.013	0.714	0.058	0.571	0.061
Pb - Cu	0.719*	0.044	0.810*	0.022	0.643*	0.031
Pb - Hg	0.435	0.281	0.405	0.327	0.357	0.275
Ni - Cu	0.415	0.306	0.500	0.216	0.357	0.275
Ni - Hg	0.093	0.827	-0.048	0.935	-0.071	0.905
Cu - Hg	0.563	0.146	0.571	0.151	0.429	0.179

* p < .05, ** p < .01, *** p < .001



Fig. 1. Sampling locations (1-8).

Cu is positive for the level of significance $p < 0.001$ (Pearson's and Spearman's Correlation Coefficient test). Correlation TPH and PCB are shown for the level of significance $p < 0.01$ (Spearman's Correlation Coefficient test). The results for Cd and Pb and Pb and Cu are shown for the level of significance $p < 0.05$ (Spearman's, Pearson's and Kendall's correlation coefficient tests).

Correlation Cd and Cu and correlation Cd and Pb and correlation Pb and Ni are a strong positive, which means that high Cd/Pb variable scores go with high Cu/Pb/Ni variable scores (and vice versa). Correlation TPH and PCB, correlation Pb and Cu and correlation Cu and Hg are moderately positive, which means there is a tendency for high TPH/Pb/Cu variable scores to

Table 3. Component loading for pollutants (TPH, PCB and heavy metals), according to factor analysis.

	RC 1	RC 2	RC 3	Uniqueness
Cd	0.614	0.492	.	0.101
Cu	0.507	0.541	.	0.089
Hg	.	1.025	.	0.150
Ni	1.032	.	.	0.133
PCB	.	.	0.916	0.224
Pb	0.897	.	.	0.049
TPH	.	.	0.817	0.241

go with high PCB/Cu/Hg variable scores (and vice versa). Variables are not normally distributed, and more important is the Spearman rank correlation method. By normal standards, according to Spearman's correlation, the association between the two variables (Cd and Cu; Cd and Pb; Pb and Ni; TPH and PCB; Pb and Cu and Cu and Hg) would be considered statistically significant. Such results suggest that these pollutant pairs might have similar sources or have been affected by similar factors. Values of correlation analysis for other pollutants is not relevant.

The research was applied factor analysis (FA), whose results determine the effective variable factors. The aim FA is to create fewer factors by combining two or more variables. These fields may easily hypothesize too many variables, so factor analysis helps to find essentials of a theory [22]. Principal component analysis (PCA) was used. The primary output for PCA shows the correlation between each variable of a principal component and the variable factors (RC1, RC2 and RC3) (Table 3).

PCA, which attempts to explain the variance of a large dataset of intercorrelated variables with a smaller set of independent variables, is a powerful pattern recognition tool [9]. PCA's approach to data reduction is to create one or more index variables (components) from a set of measured variables. Fig. 2a) shows what PCA is doing to combine seven measured variables into three components: RC1, RC2 and RC3. The direction of the arrows shows how the variables (TPH, PCB, Cd, Pb, Ni, Cu and Hg) contribute to the variable factors. The weights to emphasize Ni and Pb (for RC1), Hg (for RC2) and TPH and PCB (for RC3) variables more than others. Using PCA we obtained three factors that clarify the grouping of pollutants: factor RC1 represents the heavy metals Ni, Pb, Cd and Cu; factor RC2 represents the heavy metals Hg, Cu and Cd; and RC3 represents PCB and TPH.

The RC1 factor is an industrial factor in location (Ni, Pb, Cd and Cu) and explained 48.94% of total variance. Pb and Ni were strong positively loaded (>0.75). Cd and Cu were moderately loaded ($0.75-0.50$) [23] (Table 4). Ni, which occurs naturally in the Earth's crust, may enter the environment as a

Table 4. Eigenvalue and percentage variance for factors.

RC	Eigenvalue	% variance
1	3.42582	48.94
2	1.78048	25.435
3	0.805846	11.512
4	0.53209	7.6013
5	0.431051	6.1579
6	0.0247031	0.3529

result of natural processes and mostly by human activities [13]. Other heavy metals are from industrial activities.

The RC2 factor is in relation with the accumulator recycling factory in location and explained 25.435% of total variance. Hg was strong positively loaded (>0.75). Cu was moderately loaded ($0.75-0.50$) and Cd was weakly loaded ($0.50-0.30$) (Table 4). Hg is not essential at low levels for all living organisms.

The RC3 factor is exclusively related to waste from transformers in location. The source of PCB and

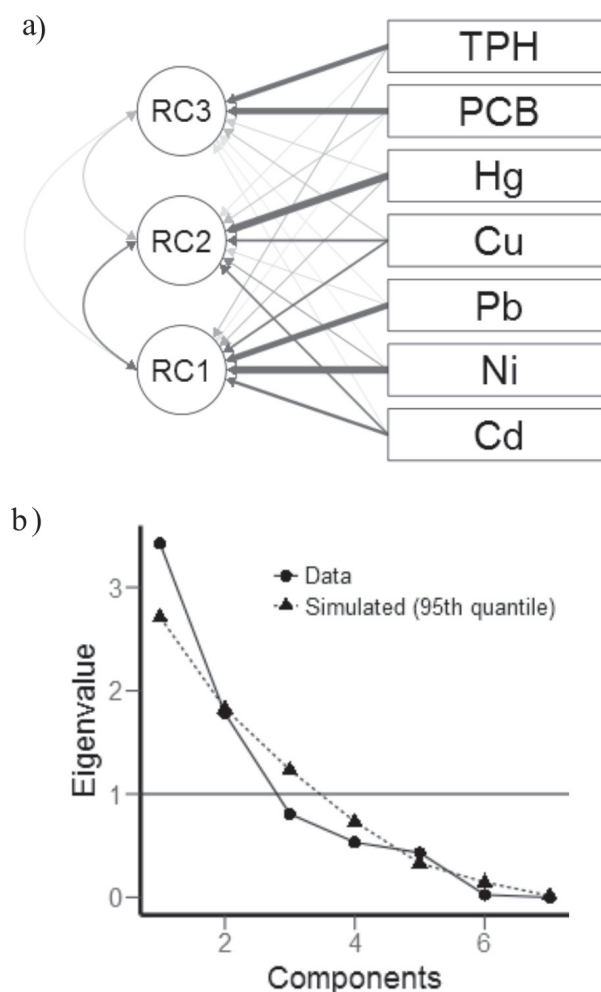


Fig. 2. Path diagram a) and scree plot b).

Table 5. Degree of soil load.

Location	Type of soil	pH (H ₂ O)	Organic matter (%)	Degree of soil load (%)				
				Cd	Pb	Ni	Cu	Hg
1.	Clay	4.8	3.0	537	775	230	897	526
2.	Clay	6.9	3.2	94	278	145	123	63
3.	Clay	6.6	2.8	510	8112	941	348	401
4.	Clay	6.7	3.3	3865	12092	627	2073	535
5.	Clay	7.9	6.8	46	4400	129	130	581
6.	Clay	7.4	4.7	21	199	136	37	10
7.	Clay	7.3	3.6	21	290	170	45	100
8.	Clay	7.5	3.1	33	105	105	70	767
Average values:				641	3281	310	465	373

TPF pollution is related to damaged and destroyed transformers and barrels at the Incel factory in the waste storage area. This factor explained 11.512% of total variance (Table 4).

Fig. 2b) shows the PCA scree plot. Eigen values higher than one were taken as criterion for evaluating the principal components required to explain the sources of variance in the data. According to rotated oblique percentage variance, three factors explained 85.89% of the total variance.

The degree of soil load is calculated according to the Rulebook [18] (Table 5). Average values degree of soil load show that V class is a land of very high load, with degree of soil more than 200%. Locations 3 and 4 are very load, especially lead. Ecological investigation levels and health investigation levels (commercial/industrial includes premises such as shops and offices as well as factories and industrial sites) [24] are exceeded for all tested parameters.

Conclusions

Results indicate that the soils in the research area suffer different levels of dangerous and harmful substances (PAH, TPH and heavy metals), and the pollution status of the different pollutants varies among sampling locations. Results show that concentrations were very high for all analyzed parameters. These values indicate that the soil was highly polluted. Principal component analysis shows that they are industrial factors and human activities caused the pollution.

The higher content of TPH, PCB and heavy metals suggest that it is necessary to provide additional investigation other than heavy metals and a larger number of samples on location. In regards to these results, it is possible to estimate their influence in the examined area. Since several sites are close to the aquatic environment, sediment and biota samples

should be analyzed as well. It is necessary to determine the origin of pollution, to perform the analysis of plant material and on the basis of the obtained results. Risk should be evaluated and recultivation and remediation activity planned.

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Conflict of Interest

The authors declare no conflict of interest.

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