ESTIMATION OF HISTORIC POLLUTION SOURCES FROM AN OIL EXTRACTION AFFECTED SITE

Laura RUSAI (FERENȚ)[1], Maria-Ema FACIU[2], George GAMAN[3], Ioana ȘTEFĂNESCU[4], Iuliana – Mihaela LAZĂR[5]

The studied area is used as pasture and a pipeline and an extraction well are positioned on it. 46 samples were collected from two depths while pH and concentration of heavy metals were analyzed using principal component analysis (PCA) and geographic information systems. Results observed were clearly different between the two depths, for heavy metals, the increase was observed on the deeper layer. Distribution maps showed a spatial variation of all parameters except Mn, while PCA performed on the heavy metals confirmed the anthropic sources for Cd, Cu, Ni, Pb, and Zn, and the natural source for Mn.

Keywords: heavy metal, physico-chemical parameter, pollution, soil

1. Introduction

Soil pollution with oil implies major risks to the environment and the leaching of pollutants in food chains, directly affects human's health [1-6]. In terms of chemical composition, oil is made up of complex mixtures including the three classes of hydrocarbons of which alkanes may produce irritations, and the polycyclic aromatic hydrocarbons (PAH) occupies an alarming place due to their mutagenic, carcinogenic and teratogen characteron the population [2, 7, 8].

Oil extraction activity leads to a series of accidents (oil spills, damage in the distribution of oil) which modify the physical and chemical properties of soils. In some cases, oil infiltration in a clay soil changes its permeability, causing toxicity and destroying its quality because the chemicals remain in the soil for decades [4-6]. Furthermore, excessive soil concentrations of heavy metals and total petroleum hydrocarbons have been reported in oil-affected areas [9, 10]. The

[1] Doctoral School in Environmental Engineering,"Vasile Alecsandri" University of Bacau, Romania, e-mail: rusai.laura@yahoo.com
[2] "Al. Vlahuta" Technological School, Bacau, Romania, e-mail: emafaciu@yahoo.com
[3] Faculty of Geography, "Babes-Bolyai" Universityof Cluj-Napoca, Department of Human Geography and Tourism, Romania, e-mail: gaman.george07@gmail.com
[4] Faculty of Engineering, "Vasile Alecsandri" University of Bacau, Romania, e-mail: ioana.stefanescu@ub.ro
[5] University of Bucharest, Faculty of Psychology and Educational Sciences, Bucharest, Romania, e-mail: iulia48lazar@gmail.com

contamination with heavy metals has a serious impact on biodiversity and it may have devastating effects on humans, including cancers [11-15].

Oil exploitation that has occurred in Moinești since 1440 led in time to accidents, hence the possibility that soils have suffered a decline in quality due to soil degradation [16] and residual pollution. Regular reports of the Environmental Protection Agency from Bacau county contain references to environmental accidents [16], but it has not been found in the literature a comprehensive monitoring or an analysis of soil pollution with heavy metals and petroleum products in the area.

The aim of this article is to identify and document the extent of soil pollution with heavy metals (Cd, Cu, Mn, Ni, Pb and Zn), their distribution in the surface layer (0-30 cm), and to study their transfer in the deeper layer (30-60 cm).

2. Core-research

Moineşti is located in the NW of Bacau county on the border the Eastern Carpathians and the Basin of Tazlău River. The study area is located in the contact zone between Moldovian and Eastern Carpathians, on the northern slope of theOsoiu hill (at foothills of mountains Gosmanu) in the Drilling Rigs Moineşti area [17]. The soil belongs to the luvisol types (clay-alluvial), being characterized by the presence of a clay horizon (Bt) and eluvial horizon (E), and by a petrographic composition comprising conglomerates, sandstone, marl and coal [18].

The area is administrated by Moineşti town, it belongs to the sensitive type of usage [19] and it is used by local people for grazing.An active oil well and a transport pipe for the extracted oil (Fig. 1) are within the sampling area.

A part of the area located 10 m away from the transport pipe and following the relief to the base of the slope has been vegetation free and has shown oil traces. The soil type is modified, being mainly sandy. The sampling locations covered the identified area, as well as its close proximity to its left and right, and other remote locations where no environmental changes were noticed.

Soil samples were collected from the surface (0-30 cm) in 33 locations, 13 of them being under the immediate influence of pollution sources: oil well and pipeline of transport. For the 13 sites, the samples were taken also from the deep layer (30-60 cm) to analyze the degree of transfer of pollutants. The soil sampling was carried out according to STAS 7184/1-75 [20] and the storage and preparation for chemical analysis were performed according to ISO 11464/1994 [21]. For the determination of pH, a soil solution in a ratio of 5:1 distilled water: soil was used and the equipment and sensors were from WTW InoLab [22].

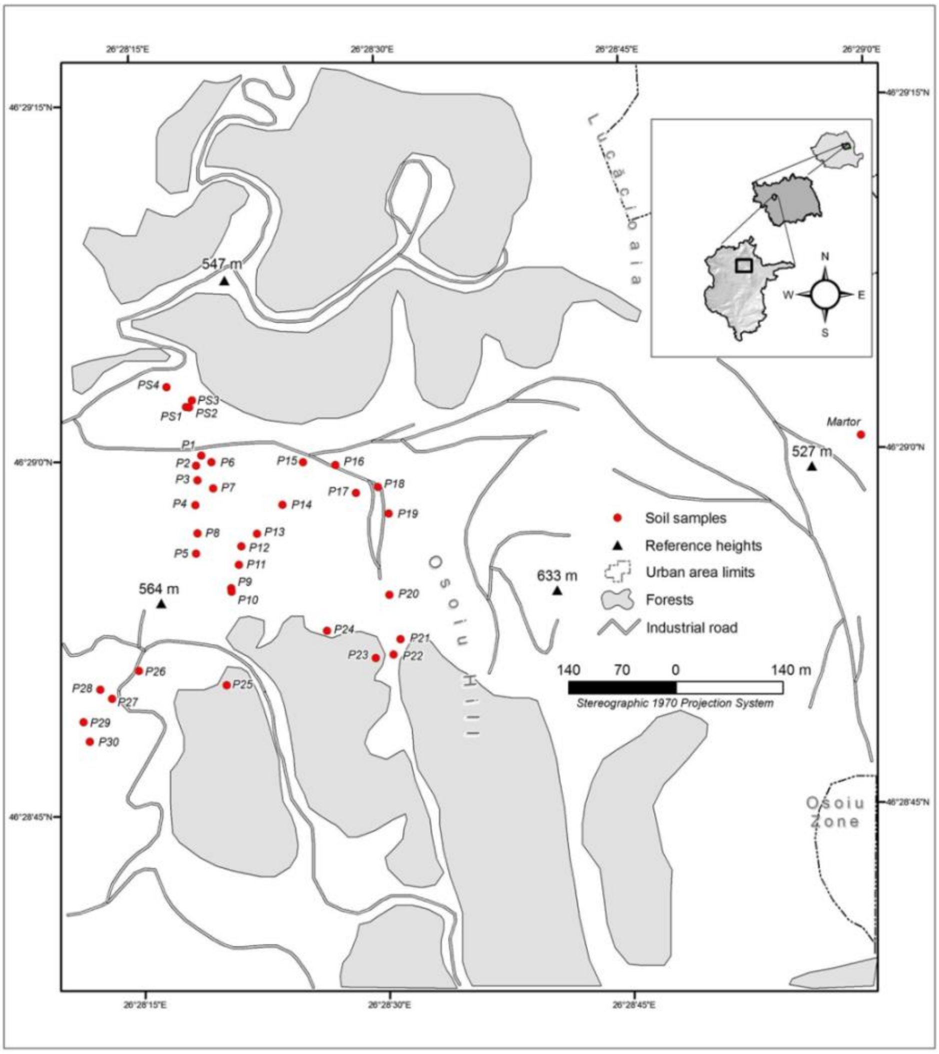

Fig.1. Representation of distribution of sampling points in Osoiu Hill area, Moinesti, Romania

Determination of heavy metal concentrations requires two steps: soil digestion (maceration of soil under the action of an acid) and reading of the solution resulting from digestion of soil at the atomic absorption spectrophotometer. The digestion of the soil for the determination of heavy metal concentration was performed according to the protocol for the characterization of the soil from the University of Vigo in Spain [23] using HNO_3 7M. In order to determine the concentrations of metals: Ni, Zn, Mn, Cd, Cu and Pb the atomic absorption spectrometry Varian was used according to ISO 11047/1998 [24] and the instruction manual [25]. The lamps used for the analyses were provided by the companies: Varian (Cd, Cu, Pb), • red (Ni), Agilent Technologies (Mn, Zn), and the standard solutions by Sigma - Aldrich.

Descriptive statistical analysis of data, the graphical representation, the standardization of values, Levene test and the principal component analysis (PCA) were performed using SPSS 20 software [26]. To represent the spatial distribution of parameters, the Ordinary Kriging interpolation method was used in ArcGIS 10 software [27].

The determined values for heavy metals concentration were compared with reference values in accordance with the national thresholds stated in OM 756/1997 [19]. For Mn, all values are below normal value, while for Ni all determined concentrations are in the range of normal value (NV) and the alert threshold (AT) (Table 1).

Table 1.

Exceeding threshold values according to OM 756/1997: Normal Value (NV), Alert Threshold (AT), Intervention Threshold (IT) as a percentage, for the heavy metals Cd, Cu, Mn, Ni, Pb, Zn analyzed on the two depths.

	Threshold values (mg/kg dried soil)			The percentage of the total number of locations which have exceed the threshold values					
				0-30 cm depth			30-60 cm depth		
	NV	AT	IT	Under NV	Between NV and AT	Between AT and IT	Under NV	Between NV and AT	Between AT and IT
Cd	1	3	5	0%	77.14%	22.86%	0%	71.43%	28.57%
Cu	20	100	200	28.57%	71.43%	0%	35.71%	64.29%	0%
Mn	900	1500	2500	100%	0%	0%	100%	0%	0%
Ni	20	75	150	0%	100%	0%	0%	100%	0%
Pb	20	50	100	0%	85.71%	14.29%	0%	78.57%	21.43%
Zn	100	300	600	85.71%	14.29%	0%	78.5%	21.43%	0%

For Cd, Pb and Zn it was recorded a higher percentage of exceedances of the higher threshold for the layer 30-60 cm. There were no exceeding of the intervention threshold (IT) for any of the analyzed heavy metals.

Comparison of the distribution parameters between the two depths

The analysis of variance of the pH and the heavy metals concentration between the two depths was carried out using Levene test and the Box Plot was used to represent graphically the results [26].

The coefficient of statistical significance test Levene confirms a significant difference between the average values of all parameters for the two depths (Sig.> 0.05).

The measured pH values for 0-30 cm depth range between 5.26 and 8.51 with an average of 7.24 (Fig. 2a). The high fluctuation of these values indicates that an ecological accident, probably, occurred and the area was mechanically decontaminated: removing the affected surface soil and replacing it with soil from other sources.

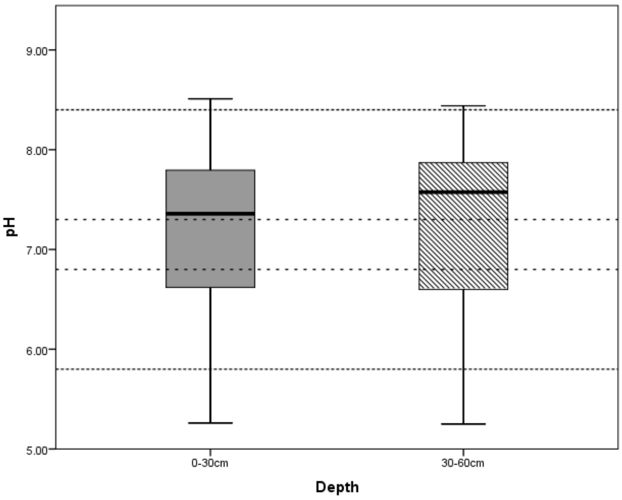

Fig. 2 a. Box Plot of recorded values for pH. The pH values range from strongly acid to strongly alkaline, in the identified area having acidic values. The high fluctuation of these values indicates that an ecological accident probably, occurred and the area was mechanically decontaminated.

From the Box Plot graphs (Fig. 2) it can be seen that the minimum values are higher for the depth layer (30-60 cm) for Cd (Fig. 2b), Cu (Fig. 2c), Mn (Fig. 2d), Ni (Fig. 2e), Pb (Fig. 2f), and Zn (Fig. 2g).

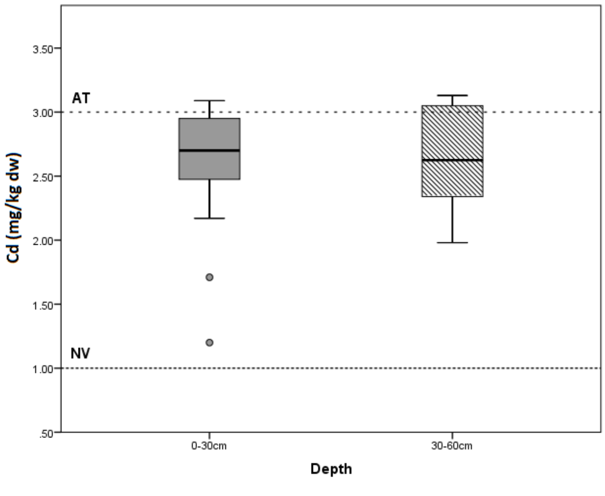

Fig. 2 b. Box Plot of recorded values for Cd concentrations from the soil. Exceedances of normal values were recorded at both depths, the alert threshold being exceeded in some locations

In the case of Cd, all samples including the control sample recorded values above the normal value (NV = 1 mg/kg dry soil). Some of the samples have exceeded the alert threshold for both depths (AT = 3 mg/kg dry soil).

In the case of Cu, exceedances of the normal value were registered for both depths in most locations. The control sample also exceeded the normal value (NV = 20 mg/kg dry soil).

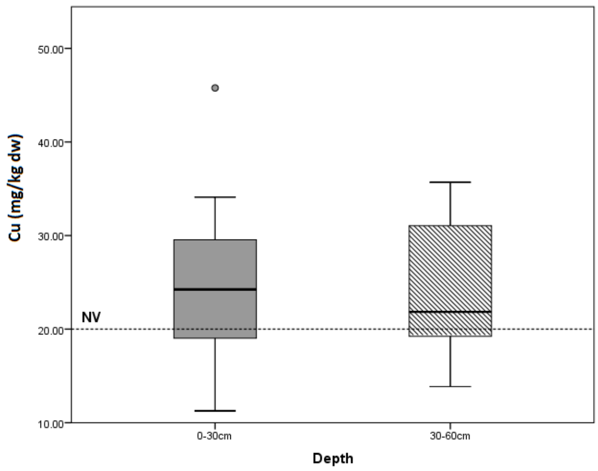

Fig. 2 c. Box Plot of recorded values for Cu concentrations from the soil. In both depths for most locations there were exceedances above normal value allowed

For Mn (Fig. 2d) and Ni (Fig. 2e), all values recorded for both depths, including the control sample, were below normal value (NV = 900 m/kg dry soil, NV for Ni = 20 mg/kg dry soil).

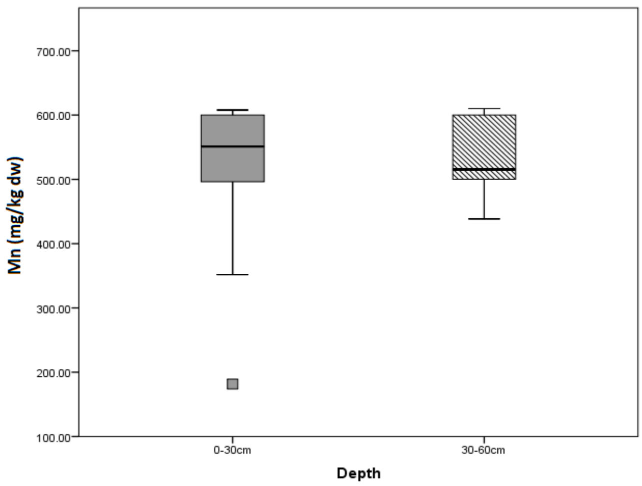

Fig. 2 d. Box Plot of recorded values for Mn concentrations from the soil. All values recorded for both depths, including the blank sample, were below normal value allowed

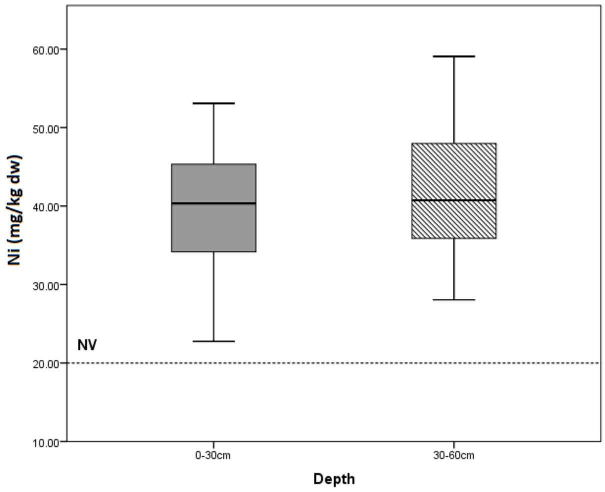

Fig. 2 e. Box Plot of recorded values for Ni concentrations from the soil. All values recorded for both dephts were below normal value allowed.

For Pb, all samples recorded values above the normal value (NV = 20 mg/kg dry soil). Some of the samples have exceeded the alert threshold for both depths (AT = 50 mg/kg dry soil). The value recorded by the control sample also exceeded the normal value allowed.

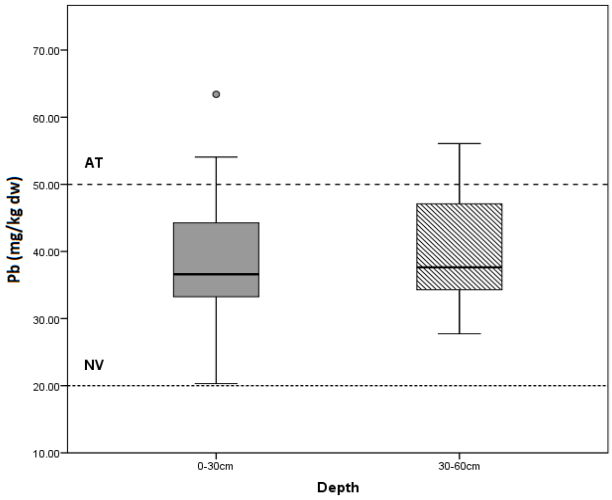

Fig. 2 f. Box Plot of recorded values for Pb concentrations from the soil. At both depths there were exceedances of normal values, in some locations being exceeded including the alert threshold

In the case of Zn, only 7 soil samples recorded exceedances above the normal value (NV = 100 mg / kg) but without reaching the alert threshold.

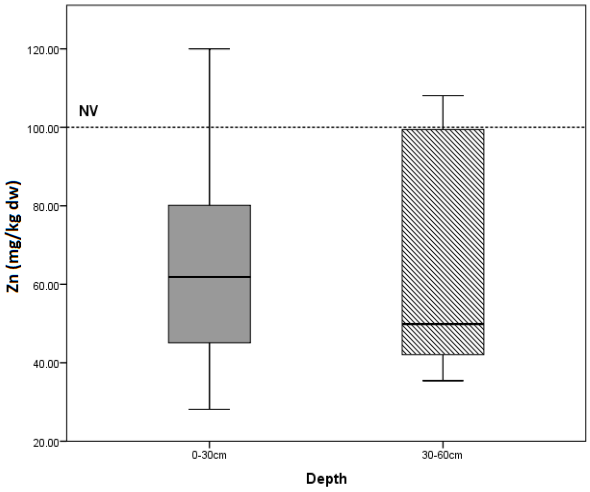

Fig. 2 g. Box Plot of recorded values for Zn concentrations from the soil. Only 7 soil samples recorded exceedances above the normal value

However, as regards its average value, the variation is low and the maximum value is lower for the deep soil, except for nickel. High outlier values were recorded for heavy metals concentrations in locations P24 and P25 for the top layer and location P5 in the deep layer. The high values recorded for the heavy metals concentrations, highlights a possible polluted area.

It was also observed a tendency of pollutant accumulation in the deep level marked by increased values for minimum and for quartiles 25 and 75. Berar and collaborators [28] obtained similar results in Baia Mare, Romania, where they found that pollutants (heavy metals) migrated to the deep soil layer. Babut and collaborators [29] in Zlatna Area, Romania, have found that by migrating into the deep profile soil, the limits of intervention used for sensitive soils have been surpassed by 8, 28, and 90 times for Cd, Zn and Pb respectively.

Analysis of the spatial distribution

To identify the sources of pollution, the analysis of the spatial distribution of recorded values for pH and heavy metals concentration was carried out (Fig. 3). It can be observed that Mn does not present spatial variation of concentrations (Fig. 3a) and given the low levels, much below NV (Table 1), it is possible that the recorded results represent its natural concentrations in the soil.

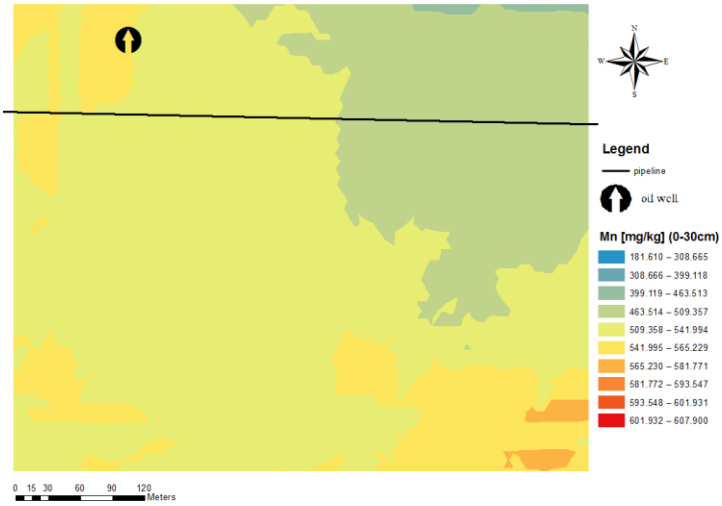

Fig. 3 a. The representation of the spatial distribution of Mn concentrations recorded in the soil at a depth of 0-30 cm. A slight spatial variation of the values can be observed, with a slight increase in the area of the extraction well.

For all the other heavy metals a maximum concentration in the oil well area was observed, marking its area of influence. At the south of the pipeline, spatial variation to lower values of Cd (Fig. 3b), Pb (Fig. 3c), Zn (Fig. 3d), Cu (Fig. 3e) and Ni (Fig. 3f) concentrations can be observed. It is possible that a leaching of the pipe has occurred in the area, and an intervention (removal of the contaminated soil) have been performed [30, 31].

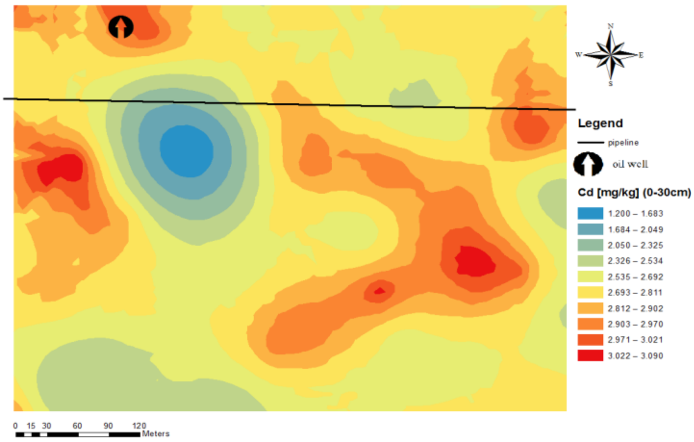

Fig. 3 b. The representation of the spatial distribution of Cd concentrations recorded in the soil at a depth of 0-30 cm. Several areas of maximum may be observed in the area affected by the extraction well and in two other areas adjacent to the transport pipeline. A minimum area can be seen overlapping the acidic pH range zone.

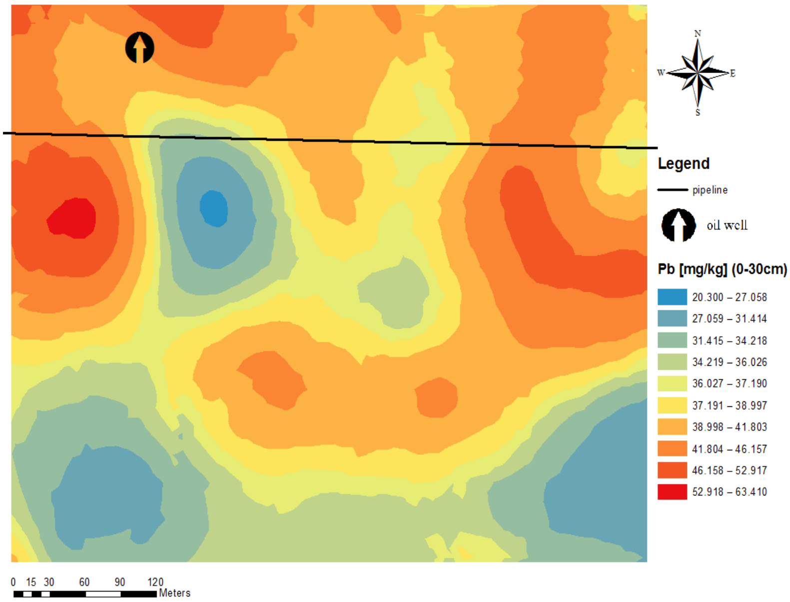

Fig. 3 c. The representation of the spatial distribution of Pb concentrations recorded in the soil at a depth of 0-30 cm. A minimum area can be noticed over lapping the identified area, the high concentrations being spread throughout the studied area.

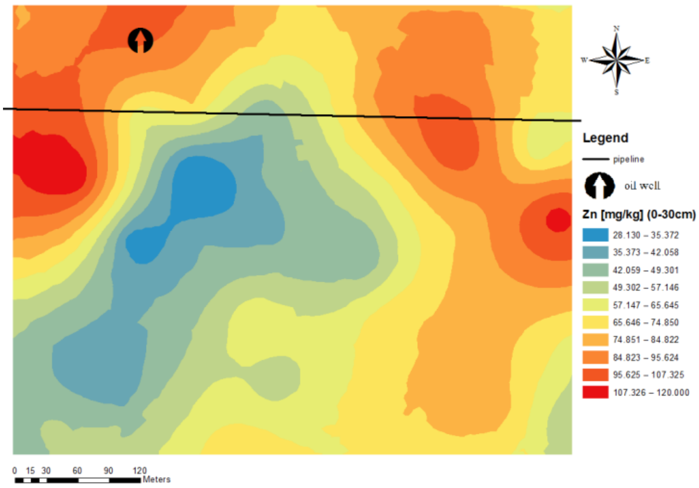

Fig. 3 d. The representation of the spatial distribution of Zn concentrations recorded in the soil at a depth of 0-30 cm. A minimum area can be noticed over lapping the identified area, as well as several maximum areas in the area influenced by the extraction well and in two other areas adjacent to the transport pipeline

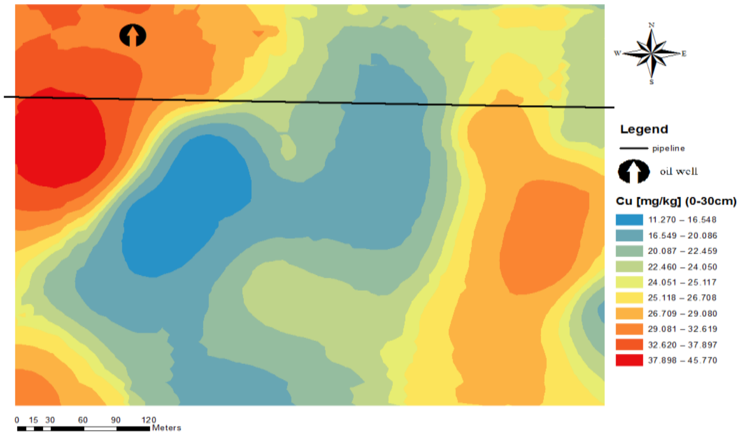

Fig. 3e. The representation of the spatial distribution of Cu concentrations recorded in the soil at a depth of 0-30 cm.A maximum area can be noticed in the area influenced by the extraction well and a minimum extended area can be seen overlapping the acidic pH range zone.

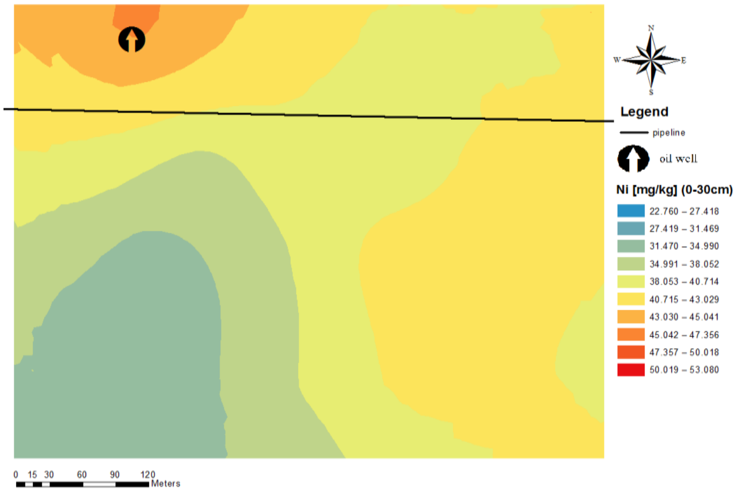

Fig. 3f. The representation of the spatial distribution of Ni concentrations recorded in the soil at a depth of 0-30 cm. It can be observed a slight variation with a maximum area in the area of the extraction well and a minimum of the extended area in the identified area

Analysing the spatial distribution map of pH values (Fig. 3g) it can be observed that in the same area the values are in the acidic range, where as in the rest of the study area, the pH is in the alkaline range.

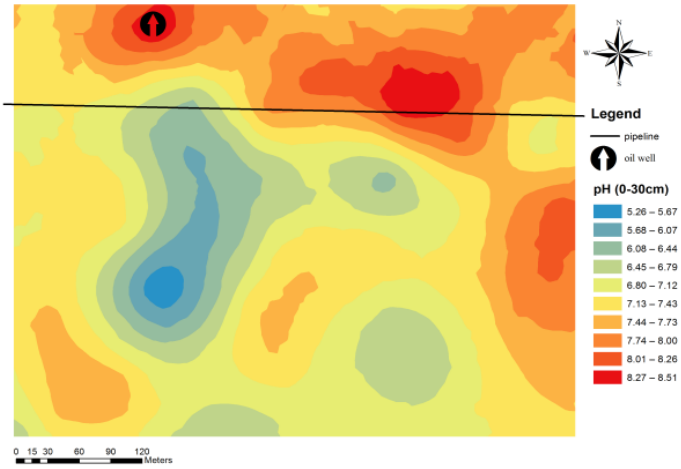

Fig. 3 g. Spatial distribution map of measured pH values for 0-30 cm depth. The values in the acidic range are grouped, while the values in the neutral-alkaline range are spread throughout the entire studied area.

In control location, pH registered a value of 8.04, confirming the alkaline character of the soil. Given the fact that the area where the difference in values is present, has a width of less than 300 m, we can conclude that the soil from 0-30 cm profile has other source and it was added during the correction process [30, 31].

Principal components analysis (PCA)

To verify if the analyzed heavy metals have different sources, principal component analysis (PCA) was run with Varimax rotation [26]. Values were standardized before running the analysis. Two distinct components were obtained, explaining 75.45% of the total variance. The first component comprised of Pb, Cu, Zn, Ni and Cd contributed 57.43% and the second component made up only of Mn contributed the remaining 18.01% of the variance (Table 2). The first component represents the anthropic soil pollution with heavy metals, while the second component is due to natural soil loading.

Table 2.

Summary of PCA results applied to heavy metals concentrations registered in Moinesti area, Romania. The first component represents the anthropic soil pollution with heavy metals, while the second component represents the natural soil loading.

Rotated Component Matrix[a]		
	Component	
	1	2
Zscore: Pb (mg/kg)	0.870	
Zscore: Cu (mg/kg)	0.858	

Zscore: Zn (mg/kg)	0.842	
Zscore: Ni (mg/kg)	0.825	
Zscore: Cd (mg/kg)	0.748	
Zscore: Mn (mg/kg)		0.971
Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.		
a. Rotation converged in 3 iterations.		

KMO test result was 0.738, confirming that the components were well defined.

PCA confirmed the conclusion of spatial distribution analysis: the anthropogenic sources influence the variation in Pb, Cu, Zn, Ni and Cd concentration, while Mn concentrations reflect the natural composition of the soil.

Similar results were obtained by the following researchers:

(1) Asia and collaborators [9]obtained exceeding in heavy metals concentrations over the permissible limits in the Niger Delta (Nigeria) in soil and water due to anthropogenic activities;

(2) Berar and collaborators [28] obtained similar results in Baia Mare, Romania, where they observed a migration of heavy metals in soil to a deeperlayer, in an area with historical pollution recorded;

(3) Liu and collaborators [2], in Yellow River Delta China, have noticed that the distribution of heavy metals in soil is influenced by the activities of oil exploration and restoration of humid areas.

(4) Akpoveta and Osakwe [32] analyzed the concentration of heavy metals contained in refined petroleum products in Agbor Delta, Nigeria, and reported high levels of lead and copper, which exceeded the permissible standard limits.

From the analysis of the literature, there was found a direct relationship between total petroleum hydrocarbons pollution and the existence of high concentrations of heavy metals in the soil [33-36].

6. Conclusions

Exceeding of the threshold values for both levels of soil have been identified for Cd, Cu, Ni, Pb and Zn. Cd and Pb concentrations exceeded the alert threshold(AT), without exceeding the intervention threshold (IT).

The succession of Cd>Pb>Ni>Cu>Zn>Mn was preserved on both levels.The percentage of samples for which exceedings have been recorded was slightly higher for the deep layer compared to the top layer, highlighting an accumulation of pollutants in the deep layer.

The only element for which there were no exceeding of thresholds is Mn. The distribution map and PCA indicated that the presence is due to natural sources.For the other elements analyzed the distribution maps showed spatial variation, with a maximum area in the vicinity of the oil well. PCA confirmed a common source for Cd, Cu, Ni, Pb and Zn. Further analysis including the total petroleum hydrocarbons is needed in order to confirm the anthropogenic source. The extraction activity influences the increase concentration of heavy metals in soil, in particular for Pb and Cd because heavy metals are common portions of petroleum and drilling fluid applied in oil exploitations.

Because the land is used for grazing, there is a need for careful monitoring and analysis of the degree of bio-accumulation of pollutants in vegetation.

R E F E R E N C E S

1. *M. Choura, S. Salhi, and F. Cherif*, Mechanical behaviour study of soil polluted by crude oil case of Sidi El Itayem oilfield, Sfax, Tunisia. Environ Earth Sci, 2009. **59**: p. 573–580.
2. *X. Liu et al.*,Compositional fractionation of polycyclic aromatic hydrocarbons (PAHs) in mosses (Hypnum plumaeformae WILS) from the northern slope of Nanling Mountains, South China. Atmospheric Environment, 2005. **39**: p. 5490-5499.
3. *B. Maliszewska-Kordybach et al.*, Monitoring of the total content of polycyclic aromatic hydrocarbons (PAHs) in arable soils in Poland. Chemosphere, 2008. **73**: p. 1284-1291.
4. *D. Placha, et al.*, The polycyclic aromatic hydrocarbon concentrations in soils in the Region of Valasske Mezirici, the Czech Republic. Geochemical Transactions, 2009. **10(12)**.
5. *M. Vila-Escale, T. Vegas-Vilarrubia, and N. Prat*, Release of polycyclic aromatic compoundsinto a Mediterranean creek (Catalonia, NE Spain) after a forest fire. Water Research, 2007. **41**: p. 2171-2179.
6. *Z. Wang et al.*, Distribution and sources of polycyclic aromatic hydrocarbons from urban to rural soils: A case study in Dalian, China. Chemosphere, 2007. **68**: p. 965-971.
7. *Falahudin, D., et al.*, Distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in coastal waters of the Timor Sea. Coastal Marine Science, 2012. **35**: p. 112-121.
8. *G. Jixiang, F. Jia, and C. Jingjing*,Characteristics of petroleum contaminants and their distribution in Lake Taihu, China. 2012.**6**(1).
9. *I.O. Asia et al*., The effects of petroleum exploration and production operations on the heavy metals contents of soil and groundwater in the Niger Delta. International Journal of Physical Sciences, 2007. **2**(10): p. 271-275.
10. *J.G. Lü et al.*,Primary investigation of the pollution status of polycyclic aromatic hydrocarbons (PAHs) in water and soil of Xuanwei and Fuyuan, Yunnan Province, China. Chinese Science Bulletin, 2009. **54**(19): p. 3528.
11. *S.J. Robertson et al.,* Petroleum hydrocarbon contamination in boreal forest soils: a mycorrhizal ecosystems perspective. Biological Reviews, 2007. **82**(2): p. 213-240.
12. *H.M. Fulekar, A. Singh, and M.A. Bhaduri*, Genetic engineering strategies for enhancing phytoremediation of heavy metals. African Journal of Biotechnology, 2009. **8**(4): p. 529–535.
13. *O. Dobre, A. Woinaroschy, and E. Panţuru*, Germinating seeds on contaminated soil U.P.B. Scientific Bulletin, 2016. **78**(1): p. 89-98.
14. *R.-E. Pătescu et al.*, Applicability of chitosan/hydroxyapatite composites for adsorptive removal of lead, copper, zinc and nickel from synthetic aqueous solutions, U.P.B. Scientific Bulletin, 2017. **79**(1): p. 119-134.

15. *D.R. Popoviciu and T. Negreanu-Pîrjol*, Copper, manganese and zinc bioaccumulation in three common woody species from black sea coastal area. U.P.B. Science Bulletin 2018. **80**(2): p. 49-56.
16. APM-Bc, Rapoarte anuale (Annual Reports). 2015: National Environment Agency, Bucharest.
17. *V.Anghel,* Moinesti: 565 de ani de la prima atestare documentară (565 years since the first documentary attestation. Bacau, 2002.
18. *ICPA*, Sistemul român de taxonomie (The Romanian System of Soil Taxonomy), A.a.E.P. National Institute of Research and Development for Soil Science, Editor. 2003.
19. *Romanian Government*., Ordinul nr. 756/3.11.1997 pentru aprobarea legislației privind evaluarea poluării mediului (Order no. 756/3.11.1997 to approve legislation on environmental pollution assessment), G. Document, Editor. 1997: Official Gazette no. 303 bis / November 6th.
20. *ASRO*, STAS 7184/1-75 Prelevarea probelor de sol pentru studiil pedologice și agrochimice (Soil sampling for pedological and agrochemicals soil studies). 2002: Standards Association from Romania.
21. *ISO*, I., Soil Quality – Pretreatment of samples for physico-chemical analysis. 1994: International Organization for Standardization Geneva, Switzerland.
22. *WTW,*WTW pHotoFlex/pHotoFlex Turb Photometry Analysis Manual. 2009, Weilheim, Germany: WTW GmbH.
23. DdIQ, Soil characterization protocols (in Spanish). 2012: Laboratorio Grupo de Bioprocesos, University of Vigo, Spain.
24. *International Organization for Standardization,*ISO, ISO 11047 Soil Quality – Determination of cadmium, chromium, cobalt, copper, lead, manganese nickel and zinc. Flame and electrothermal atomic absorption spectrometric methods. 1998, Geneva, Switzerland.
25. *Varian,* Varian AA 240FS Analysis Manual. 2007, Varian Inc.
26. *A. Field,*Discovering statistics using SPSS. 2006: SAGE Publications.
27. *L.M. Scott, and M.V. Janikas,* Spatial Statistics in ArcGIS, in Handbook of Applied Spatial Analysis. 2010, Springer. p. 27-41.
28. *I.M. Berar, et al.*, Studii și cercetări privind evaluarea calității solurilor în S.C. Romplumb S.A. Baia Mare pentru remedierea zonelor poluate (Studies and research on evaluation of quality of soils in the S.C. Romplumb S.A. Baia Mare to remedy polluted fields) ProEnvironment, 2010. **3**: p. 472 - 476.
29. *C.S. Babut et al.,*Analysis of heavy metals from a polluted site in order to rehabilitate it. A case study on the Zlatna area. ProEnvironment 2013. **6**: p. 432 - 437.
30. *D. Malschi and G. Stan,*Reconstrucția ecologică - principii, noi orientări, perspective(Ecological reconstruction - principles, new guidelines, perspective). Vol. 7. 2006, Environment&Progress.
31. *I. Voicu,* Method of removal of petroleum products in the event of shore contamination. in Proceedings of 14th International Conference "Professor Dorin Pavel - Founder of Romanian Hydropower". 2014. Sebes, Romania.
32. *A. Vincent*, and S.A. Osakwe, Determination of heavy metal contents in refined petroleum products. IOSR Journal of Applied Chemistry 2014. **7**(6): p. 01-02.
33. D.A. Mustafaet al., Oil spill related heavy metal: a review. Malaysian Journal of Analytical Sciences, 2015. **19**(6): p. 1348 - 1360.
34. *M.C. Onojake and O. Frank,*Assessment of heavy metals in a soil contaminated by oil spill: a case study in Nigeria. Chemistry and Ecology 2013. **29**(3): p. 246 – 254.

35. *J. Fu et al.*,Monitoring of non-destructive sampling strategies to assess the exposure of avian species in Jiangsu Province, China to heavy metals. Environmental Science and Pollution Research 2014. **21**(4): p. 2898 – 2906.
36. *E.I. Obiajunwa et al.*, Characterisation of heavy metal pollutants of soils and sediments around a crude-oil production terminal using EDXRF. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 2002. **194**(1): p. 61-64.