A STATISTICAL ANALYSIS OF REGIONAL OIL IMPACTS ON ENVIRONMENT

C. Oprea [a], M. V.Gustova [a], O. D. Maslov [a], I.A. Oprea [a], P. J. Szalansky [b]

[a] Joint Institute for Nuclear Research, Frank Laboratory of Neutron Physics, Departament of Experimental Nuclear Physics, Joliot-Curie 6 str. 6, 141980 Dubna, Russian Federation
[b] Lodz University, Faculty of Physics and Applied Informatics, Lodz, Poland

Abstract

The analytical work consisted of the measuring of the concentrations of 25 chemical elements (i. e. Ca, K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, As, Se, Br, Rb, Sr, Y, Zr, Nb, Sb, I, Cs, Ba, La, Ce) in soils and water river sediment from the region of oil refinery complex Vega in the town of Ploiesti, Romania. The analyses were carried out on the grain fractions < 2 mm by using the X-ray fluorescence method.

Further the results were used to develop an approach for incorporating information on chemical availability in soils and river into risk assessment and risk-based decision making.

Introduction

In terms of the amounts of substances released, the oil pollution may have harmful effects on soil-plant ecosystems, all of them being related to human health. The oil pollutants can originate from a single point source presenting a local character as well as they can be released by mixed diffuse or punctual sources. Furthermore, to the level of ecosystem pollution contribute both local pollutants and those transported over long distances.

Emission estimates have long been basic tools for soil quality assessment. Usually emission data from specific test sources as well as continuous emission monitors are used as input information for developing emission control strategies. The literature data on soil contamination surveys by different monitoring techniques encounter a substantial difference between the estimates derived using different methods. Several projects related to the long-range atmospheric transport of trace heavy metals are carried out by environmental international/national organizations.

One of the task forces in the fields of long-range transport and deposition of heavy metals is to perform integrated assessment model calculations on heavy metal emissions in the all regions.

Common aspects for local soil contamination

Several changes of soil quality occur when soil is exposed to different impact levels. The contaminated sites include sites at different levels of environmental and human health impacts, ranging from minor to relevant significant effects. Some common key aspects can be identified:- The contamination deriving from point sources, mainly waste disposal, industrial and military activities, and accidents.- The major local impacts of contaminated soil breed health problems due to direct contact with contaminated soil and use of contaminated groundwater, that imply the necessity to restrict some uses of the land.- The sustainable use of agriculture land supposes the mapping of soil parameters that result in regular network grid monitoring of the average extent of pollutant impacts on soil.

Indicators for oil pollution

In the past years a preliminary list of indicators for soil contamination from oil localized and diffuse sources was identified and reviewed using the comparable data sets availability and quality. The development of oil pollution indicators for diffuse soil contamination follows the general scheme from the Figure 1.

Data collection approach

The problem is the choice of the kind of sites (i.e. petrol stations) to be included.

The approach employed for data collection used in our researches implied an overall indicator to assess the number of sites that had been investigated to an acceptable standard for their use. More detailed stages of the process could introduce double counting of sites; depending on how often information was collected and updated.

Importance and data availability of this indicator were considered high. Some work has already been carried out in the monitored area. Unfortunately no clear distinction between different local sources of emission is possible.

The Ploiesti town region has been identified as one of oil contaminated zones. It is a highly industrialized town and also a petrochemical town, as presents several oil refineries.

To all samples collected in area of the Vega oil refinery (20x20 km^2), one to three locations has to be contributing to each sampling location. The spots were further categorized by groups in relation with the downwind distance from the oil smelter complex.

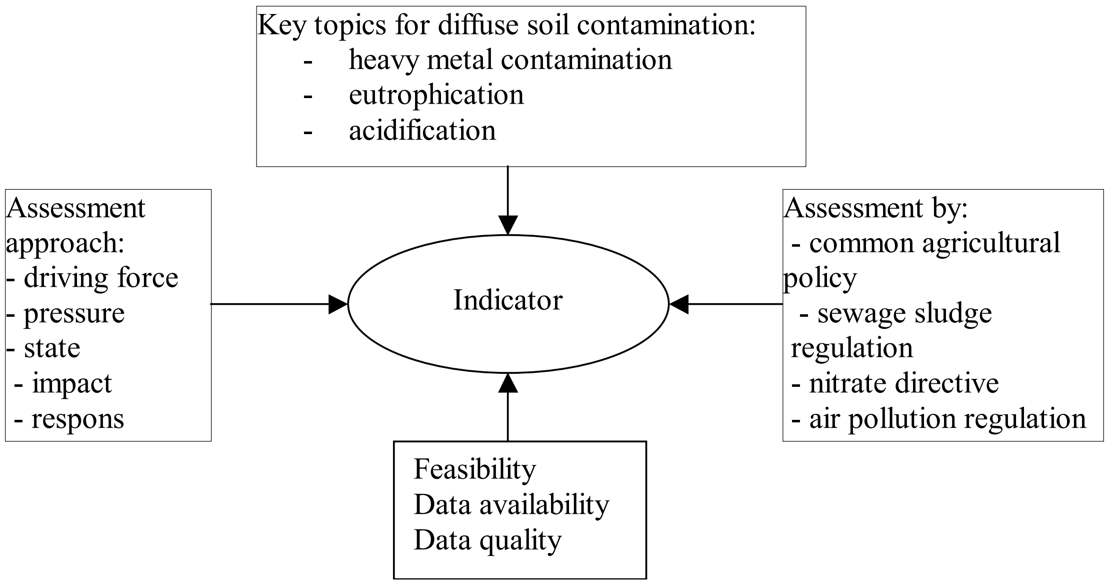

Figure 1. General scheme of the oil pollution indicators (EEA, 2002)

Results and discussion

The measured concentrations of 25 chemical elements (i. e. Ca, K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, As, Se, Br, Rb, Sr, Y, Zr, Nb, Sb, I, Cs, Ba, La, Ce) for 52 categorized locations sampled in the Vega oil refinery area were determined. The average values of heavy metals were found for each spot category (Table 1). Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Pb, As, Se, Sb and Ba decrease in the following order of the distance from the refinery location: 1 km > 10 km > 20 km. The heavy metals levels as determined in river sediments of the Teleajen river were lower than those found at 1 km from the plant, but higher than those recorded at 20 km far from the plant. Their distribution point for the oil refinery discharges as source of those elements in the river. Concentrations of other elements vary since of the natural variability of the environment (Table 1).

Table 1. The mean elemental concentrations (% at) for different categories of sampling locations

Element	Av. conc., %			
	Soil, 1km	Soil,10 km	Soil, 20 km	River sediment

K	7.3±1.0	3.9±1.2	0.99±0.15	≤0.85
Ca	0.7±0.2	2.1±0.5	4.2±0.5	3.1±0.4
Ti	0.99±0.15	0.68±0.12	≤0.15	0.42
V	≤0.19	≤0.12	≤0.05	≤0.07
Cr	0.25±0.01	0.08±0.02	≤0.06	0.1±0.03
Mn	0.12±0.04	≤0.03	≤0.014	≤0.05
Fe	3.17±0.03	2.19±0.03	1.78±0.03	2.51±0.03
Ni	0.033±0.010	0.027±0.009	≤0.009	0.015±0.004
Cu	0.061±0.009	0.037±0.006	0.017±0.004	0.048±0.009
Zn	0.039±0.006	0.019±0.006	0.013±0.006	0.015±0.006
Pb	0.024±0.003	0.015±0.003	0.0086±0.0029	≤0.004
As	0.016±0.003	≤0.003	≤0.003	0.009±0.001
Se	0.011±0.002	0.007±0.002	0.004±0.001	-
Br	0.007±0.002	0.006±0.002	0.006±0.002	0.013±0.002
Rb	0.0169±0.0012	0.0061±0.0013	0.0059±0.0012	0.013±0.008
Sr	0.0645±0.0009	0.0146±0.0010	0.0100±0.0008	0.02180±0.0011
Y	0.0055±0.0008	0.0067±0.0009	0.0021±0.0008	0.0066±0.0010
Zr	0.0255±0.0008	0.0256±0.0008	0.0235±0.0008	0.0019±0.0008
Nb	0.0019±0.0006	0.0025±0.0007	0.0009±0.0002	0.0021±0.0007
Sb	0.0036±0.0013	0.0034±0.0014	-	0.0050±0.0008
I	0.0043±0.0012	0.0032±0.0013	0.0048±0.0010	0.0015±0.0008
Cs	0.0038±0.0013	0.0022±0.0012	0.0018±0.0012	0.0031±0.0012
Ba	0.0588±0.0016	0.0517±0.0017	0.00762±0.0016	0.0685±0.0017
La	0.0036±0.0013	0.0035±0.0013	0.0020±0.0012	≤0.0013
Ce	0.0058±0.0016	0.0106±0.0015	0.0054±0.0012	0.0106±0.0014

R-mode factor analysis (Table 2), used to determine correlations among the measured elements, confirmed that elements Cu, Zn, As and Pb contribute to an overall pollution factor (F1). Concentrations V, Ni and Pb are strong correlated each other in the factor F2 assigned to petrol refining source. The factor F3 is mostly loaded with bedrock elements as Ca and Se.

The results for the all heavy metals, mainly for the three elements of major concern (V, Ni and Pb) show a proportional variation with the downwind distance approximated with a linear decrease of element concentration away from the source of pollution.

Table 2. R-mode factor analysis loadings

Metal	Factor 1	Factor 2	Factor 3

K	**0.75**	0.47	0.36
Ca	**-0.78**	0.39	**0.75**
Ti	**0.91**	0.30	-0.14
Cr	**0.90**	-0.17	0.07
Mn	**0.78**	0.25	-0.09
Fe	**0.88**	0.15	-0.02
Ni	**0.86**	**-0.84**	-0.08
V	0.47	**-0.73**	-0.03
Cu	0.45	-0.49	-0.20
Zn	0.54	-0.13	-0.06
As	-0.43	-0.47	-0.17
Se	**0.77**	0.38	**0.72**
Sb	**0.73**	0.07	0.04
Ba	0.49	0.25	-0.28
Pb	0.51	**-0.82**	0.19
Eigenvalue	4.17	2.35	0.48
Variance	0.44	1.81	0.16

Conclusions

It has been shown that the XRF analysis can be efficiently used for the screening of surface soil and river sediment elemental composition over local areas. The survey showed that in the monitored area bordering the Vega oil refinery complex there are zones with significantly elevated concentrations of Ni, Pb and V and other heavy metals as As, Cr, Cu, Fe, Sb and Zn linked to anthropogenic activities in the oil and hard industry.

Data for the indicator "progress in the management of contaminated sites" seems to be more accessible and it was further developed.

References

1. Cevik, U., S. Kaya, B. Ertugral, H. Balts, S. M. Karabidak. 2007. *K-shell X-ray fluorescence cross-sections and intensity ratios for some pure metals at 59.5 and 123.6 keV.* Nucl Instrum Methods B 262:165.

2. Gonzales-Fernandez, O., I. Queralt, M. L. Carvalho, G. Garcia. 2007. *Elemental analysis of mining wastes by energy dispersive X-ray fluorescence (EDXRF).* Nucl Instrum Methods B 262:81.

3. EEA, 2001a. *Proposal for a European soil monitoring and assessment framework*. Tech. rep. 61/2000.

4. European Commission, 2002. *Towards a strategy for soil protection*. COM 179 final.

5. Nedelcu M., C. Oprea, C. Podina, D. Cupsa, I. A. Oprea, A. Teusdea, I. Burca. *Impact of hazardous substances in/on soil*. *Research reports*. 37^{th} Annual meeting of ESNA, Sept. 10-14, 2007, JINR (in press).

6. Oluwole, A. F., O. Ajayi, J. O. Ojo, F. A. Balagun, I. B. Obioh, J. A. Adejumo, O. J. Ogunsola, A. Adepetu, H. B. Olaniyi, O. I. Asubiojo. 1994. *Characterization of pollutants around tin mining and smelting operations using EDXRF*. Nucl Instrum Methods A 353:499.

7. Oprea C., A. Mihul. 2007. *Oil pollution in relation with land use. Research reports*. 37^{th} Annual meeting of ESNA, Sept. 10-14, 2007, JINR (in press).

8. Orescanin, V., L. Mikelic, S. Lulic, G. Pavlovic, N. Coumbassa. 2007. *Seasonal variations in the concentrations of selected heavy metals and radionuclides in Sava River sediments upstream and downstream of NPP Krsko*. Nucl Instrum Methods B 263:85.

9. Randa, Z., J. Kucera, L. Soukal. 2001. *Possibilities of simultaneous determination of lead and thallium in environmental and biological samples by microtron photon activation analysis with radiochemical separation*. J Radioanal Nucl Chem 248 1:149.