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Assessment of the Total Nickel Content and its Available Forms in the Soils Around Cement Plant Lafarge Poland

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ABSTRACT: Limestone, exploited near Bielawy, a town located in the kujawsko-pomorskie province of Poland, is the main raw material in the production process in a cement plant. The dust emitted by the factory is of alkaline pH and contains such heavy metals as: cadmium (Cd), lead (Pb), chromium (Cr) and nickel (Ni). The research aims at assessing the influence of cement dust on the total content and bioavailable forms of nickel in the soils adjacent to the *c*ement plant. The material comprised the samples of luvisols, taken at different distance from the pollution emmiter, in which the following parameters were determined: pH in 1M KCl, the content of $CaCO_3$, organic carbon and texture. The total content of nickel ranged between 1.40 and 8.70 mg/kg and as such it does not exceed the nickel content typical for non contaminated soils of the region. The content of phytoavailable forms of nickel ranged between 0.03 and 0.8 mg/kg and is considered as below-toxicity level, yet may cause allergies. Taking into consideration the texture of the examined soils, their low buffer capacity and vulnerability to pollution it is critical to control the content of nickel and the other metals in soils surrounding the cement plant.

Key words: Cement, Dust, Soil, Nickel, Environment

INTRODUCTION

The areas adjacent to the cement plant may be exposed to emission of polluting gases (nitrogen and sulphur oxides) and dust of alkaline reaction, containing heavy metals. Data from literature (Chang, 1996; Frias & Sanchez de Rojas, 2002) indicate that the emitted dust may contain cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu), zinc (Zn) and nickel (Ni). The content of nickel in the main raw materials ranged from 1.5-7.0 mg/kg in lime, 20-80 mg/kg in hard coal and 20-80 mg/kg in clay of different origin (Sprung, 1985). Additionally, in cement production wastes such as galvanic sludge, chromium or nickel sludge, are incorporated (Lawrence, 1998). As an alternative raw material, municipal solid waste was also recycled and used as a fuel in Portland cement technology (Kikuchi, 2001). The consequence of such activities is the presence of metals in the final product: cement and in cement - dust. Alkaline reaction may limit the phytoavailability of trace elements (Chang, 1996). Considering potential danger due to accumulation of metals in soils, it is essential to monitor the influence of emitted pollutants in the soils.

Alkaline reaction of the emitted dust causes excessive alkalisation of soil, and the dust is also the source of heavy metals, including nickel. The study of nickel content in soils adjacent to cement plant Lafarge S.A. was undertaken due to the reports of the development of allergy symptoms among people living in the region. Nickel and its salts are the commonest allergens (Christiansen, 1990). Nickel compounds were also classified as carcinogenic to humans (Denkhaus, Salnikov, 2002). Nickel is easily available for plants, and its toxicity, apart from influencing the nitrogen bonding processes in plants, may cause allergies and changes in bone marrow of people and animals (Tandon, 1993, Birmingham & McLaughlin, 2006).
The research was undertaken in order to asses the influence of cement dust on selected soil properties and the total content as well as bioavailable forms of nickel in the soils adjacent to *Lafarge* Cement Poland S.A. plant.

MATERIAL & METHODS

The research material comprised the samples of luvisols and podzolic soils, taken at different distance from the pollution emitter (Fig. 1). The research falls within the period between the years 1995 and 2008. The samples were taken once a year at two depths: 0 - 20 cm and 20 - 40 cm. The soil material, once dried and

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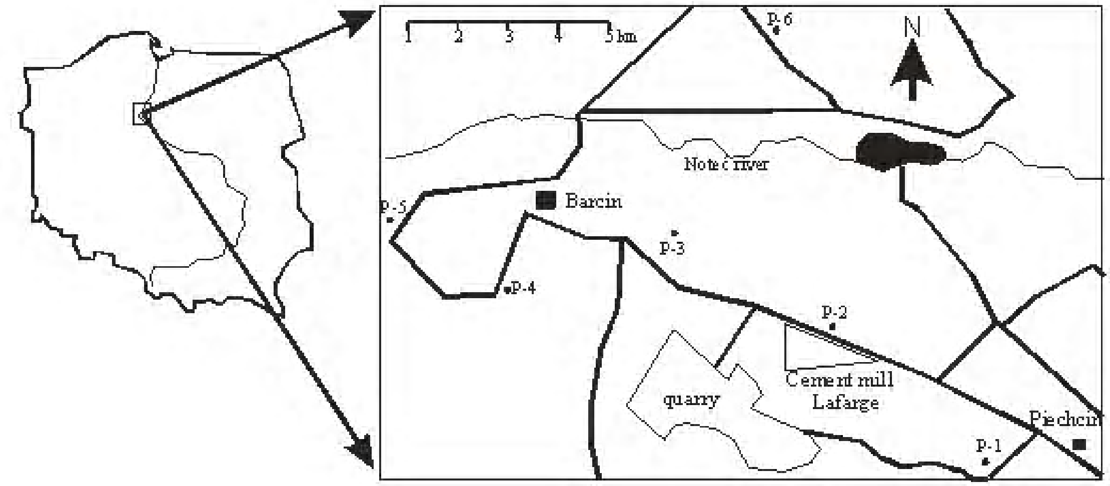

Fig. 1. Location of soil samples

sifted by a 2 mm sieve, was examined for: pH in 1M KCl, the content of $CaCO_3$, content of organic carbon using methods applied in soil science laboratories, and texture using areometric method by ISO11277:1998. The total content of nickel was determined after mineralization of soil in the mixture of acids (HF and $HClO_4$) using Crock and Severson's procedure (1980) and the content of available Ni - after extraction with DTPA solution according to Lindsay and Norvell method (1978). The concentration of nickel in solutions were determined using ASA method on SP – 2100 instrument. All analysis have been done in triplicate. In the tables mean values are presented.

RESULTS & DISCUSSION

The texture of examined soils varies little and the content of fine fraction (∅ < 0.02 mm) does not exceed 20 % (Table 1). The content of organic carbon (6-10 g/kg) indicated low level of organic matter in the analysed samples, characteristic for luvisols. The pH of the soils was different depending on the location of the sampling site and varied from 4.65 to 8.55 (Table 2). The alkaline pH was observed in surface (pH KCl 7.11 – 8.55) and subsurface samples (pH KCl 7.25 – 8.54) from site P2, located close to the emitter.

The pH of examined soils was different depending on the location of the research point and varied in subsequent years (Table 2). The elevated alkaline pH occurred in all the years of study (1995-2008).

Calcium carbonate occurred in surface and subsurface samples in all sites, only in the first years of study. In the year 1998 however, the presence of $CaCO_3$ was observed only in samples taken from the sites located closest to the plant (7.19% and 4.74%). Unchangeably since 1995, calcium carbonate was detected in samples from surface and subsurface horizons in the point P2, and its concentration equals 7.19% to 15.22% and 4.74% to 16.28% respectively, with a tendency to increase, which is due to the vicinity of the emitter. In the soil samples form site P5, the content of $CaCO_3$ ranges between 1.8% to 0.7% in surface samples and from 1,3% to 0,6% in subsurface samples. Its content in subsequent years decreases.

The total content of nickel ranged between 1.40 – 8.70 mg/kg(Table.2 , Fig.2, 3). Higher content of this element was found in surface horizons (0-20 cm). In the subsequent years of study, the highest amounts of nickel were found in the samples from the site P-2 (the point closest to the emitter). The total content of nickel in the analysed soil samples during the entire study period (1995-2008) around the Lafarge plant is close to the geochemical background (Kabata-Pendias & Pendias, 1999), and equals 4.50 mg/kg, which allows to classify these according to classification of pollution levels as soils with a natural nickel content – 0 degree (Kabata- Pendias et al., 1993). Soils containing more fine particles (below 0,02 mm) have a greater content of this element. The content of DTPA extracted forms of nickel ranged between 0.03 to 0.8 mg/kg(Table 2). The highest contents of available nickel in soils was observed in close vicinity of the factory (0.36 mg/kg) and in surface horizons of all research points.

The impact of the atmospheric pollution caused by cement industry on the ecosystems was reported previously (Dąbkowska-Naskręt *et al.,* 1997; Monski & Aasgarani, 1999). The cement factory is a source of alkaline dust and gasous contaminants, like nitrous oxides and sulfur oxides. The dust can be emitted at every stage of the manufacturing process: preparation of raw materials (lime, clay) pyroprocessing and

Table 1. Physicochemical properties of soils

Sample	Depth [cm]	Texture [%] [mm] 1-0.1	0.1-0.02	<0.02	C-org.* [g/kg]	$CaCO_3$* [%]
P-1	0-20	75	10	15	11.9	0.1
	20-40	73	11	16	8.5	0.1
P-2	0-20	82	13	5	14.1	5.7
	20-40	80	13	7	8.2	4.7
P-3	0-20	74	17	9	11.5	0.1
	20-40	70	19	11	10.0	0.1
P-4	0-20	59	24	17	10.7	0.1
	20-40	55	26	19	9.1	0.1
P-5	0-20	62	22	16	11.7	0.1
	20-40	62	23	15	10.2	0.1
P-6	0-20	79	23	8	8.5	0.1
	20-40	70	22	8	7.6	0.1

* mean values from 14 years (1995 – 2008)

Table 2. Total and DTPA extractable Ni in soils in the period 1995 – 2008 – (mean values)

Sample	Depth [cm]	Ni total [mg/kg]	Ni DTPA [mg/kg]	Ni_{DTPA}/Ni_{total} [%]	pH in 1 M KCl
P-1	0-20	3.30 – 7.30 / 5.10	0.060 – 0.660 / 0.290	1.5 – 7.6 / 4.2	6.12 – 7.40 / 6.96*
	20-40	2.60 – 6.30 / 4.65	0.110 – 0.370 / 0.238	2.7 – 9.5 / 5.7	6.33 – 7.58 / 7.01*
P-2	0-20	5.50 – 7.50 / 6.15	0.220 – 0.440 / 0.358	3.8 – 7.8 / 6.0	7.11 – 8.55 / 7.82*
	20-40	3.70 – 8.70 / 5.72	0.110 – 0.30 / 0.291	2.0 – 9.5 / 5.6	7.25 – 8.54 / 7.88*
P-3	0-20	2.60 – 8.20 / 4.23	0.120 – 0.570 / 0.325	3.3 – 21.8 / 9.5	5.62 – 6.33 / 5.99*
	20-40	1.40 – 8.40 / .39	0.100 – 0.390 / 0.244	2.4 – 17.5 / 7.5	5.65 – 6.54 / 6.14*
P-4	0-20	3.30 – 8.20 / 5.78	0.100 – 0.740 / 0.330	2.1 – 13.8 / 6.4	5.22 – 6.12 / 5.72*
	20-40	3.60 – 8.00 / 5.75	0.190 – 0.510 / 0.326	2.8 – 9.1 / 5.9	5.09 – 6.15 / 5.64*
P-5	0-20	2.40 – 8.70 / 5.15	0.120 – 0.720 / 0.306	3.3 – 10.4 / 6.3	5.05 – 7.11 / 6.48*
	20-40	3.00 – 8.10 / 5.47	0.070 – 0.800 / 0.302	2.3 – 10.5 / 5.4	4.65 – 7.76 / 6.48*
P-6	0-20	3.10 – 6.50 / 4.53	0.090 – 0.480 / 0.281	2.0 – 15.5 / 7.0	5.17 – 6.24 / 5.65*
	20-40	3.30 – 6.80 / 4.67	0.030 – 0.400 / 0.268	0.6 – 12.0 / 6.4	5.20 – 6.57 / 5.78*

* - geometric mean

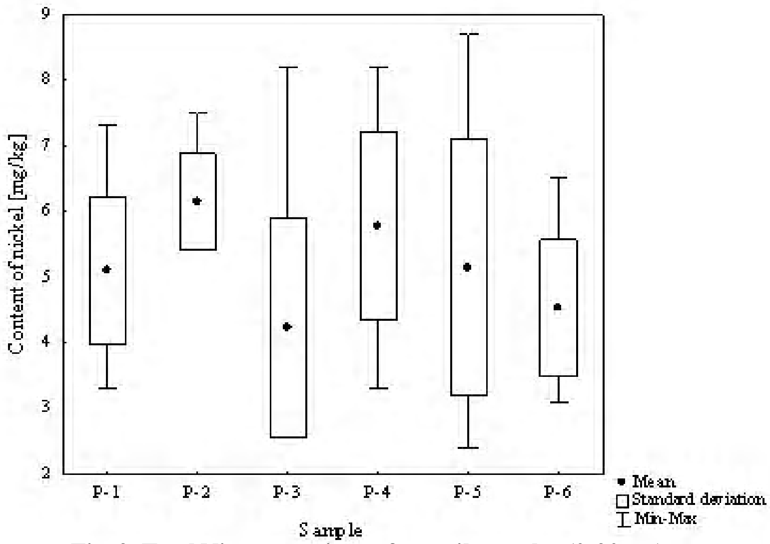

Fig. 2. Total Ni contents in surface soil samples (0-20 cm)

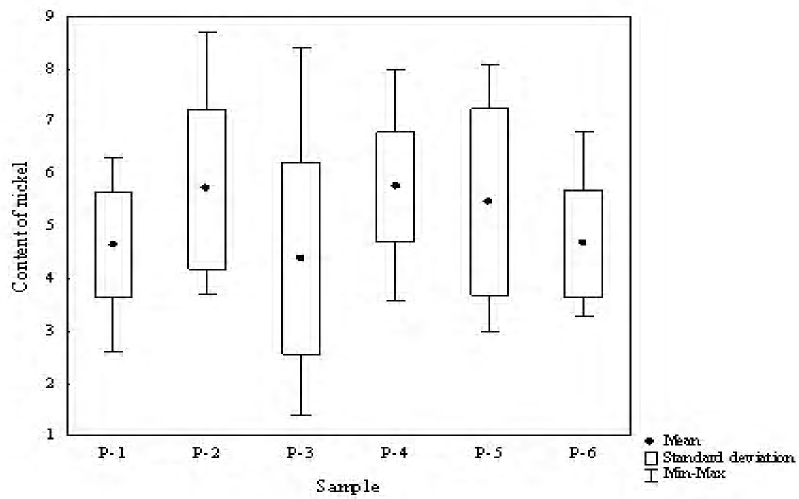

Fig. 3. Total Ni contents in subsurface soil samples (20-40 cm)

formation of cement clinker, packing and loading of the final product. Furthermore, the source of pollution can be alternative fuels used for clinker production like waste oil, sewage sludge, waste tyres, plastics, and other wastes. Combustible wastes of different origin like fly ash, ground slag from steel industry replace raw natural materials and often are source of metals to the environment.

Dust falling on the soil near the Bielawy cement plant caused a shift in soil pH to the alkaline side. Alkaline pH of soil from site P –2 is caused by a high level of lime in emitted cement dust (~ 40 % of CaO). The highest impact of cement industry was observed in the nearest zone of the cement plant – point P2. The sampled soil at this point had pH above 7.11 up to 8.55 (mean 7.82) in the surface horizon and 7.25 up to 8.54 (mean 7.88) in subsurface horizon every year (1995 – 2008). Soil pH values above 7.0 indicate evident anthropogenic effect of cement dust deposition on the soil surface. In unaffected soils of the region pH values were in the range 5.0 – 6.2. It should be stressed that calcium carbonate was detected in all samples only in the first year of the study (1995). The presence of $CaCO_3$ in studied soils is of anthropogenic origin, and the previous research on the soils in the vicinity of Lafarge Cement plant in Bielawy showed that parent material does not contain $CaCO_3$ (Cieśla *et al.,* 1994).

Calcium carbonate in acid soils being under the impact of industrial emission is described as the tracer of the pollution led by the cement industry (Zerrougi & Sbaa, 2008). The total content of nickel ranged between 1.40 and 8.70 mg/kg (Table 2, Fig. 4, 5). Higher content of this element was found in surface horizons (0-20 cm), compared to subsurface horizons. This might indicate partly anthropogenic origin of this metal. In the subsequent years of study, the highest amounts of nickel were found in the samples from the site P-2 (the point closest to the emitter). However, the total content of nickel in the analysed soil samples during the entire study period (1995-2008) around the Lafarge plant is close to the geochemical background for this metal and equals 4.50 mg/kg, which allows to classify studied soils as soils with a natural nickel content – 0 degree of contamination (Kabata- Pendias and Pendias, 1999).

Nickel is a mobile element, and its mobility is determined by the soil pH and its texture (Rogóż and Grudnik, 2004). Soils containing more particles below 0,02 mm present a greater content of this element which is confirmed by the analysed soil samples (Table 1, 2) (Kabata- Pendias and Pendias, 1999; Perlak, 2000). In alkaline and neutral soils, the solubility of nickel decreases.The content of DTPA extracted forms of nickel ranged between 0.03 and 0.8 mg/kg (Table 2). The highest content of available nickel in soils was observed in close vicinity of the factory (0.36 mg/kg) and in surface horizons of all sites. The ratio of phytoavailable DTPA – extractable nickel to total metal content is very low, particularly in alkaline plots and does not exceed 20 % of the total. Thus, cement dust changed the originally acidic podzolic soil and luvic soil to neutral. Its toxical influence on plants may be visible in disorders of photosynthetic process, and transpiration (Zerrougi and Sbaa, 2008).

Elevated pH of soils limits phytoavailability of nickel. In the examined soil samples affected by dust rich in lime, the contents of mobile Ni forms fall below the values regarded as toxic.

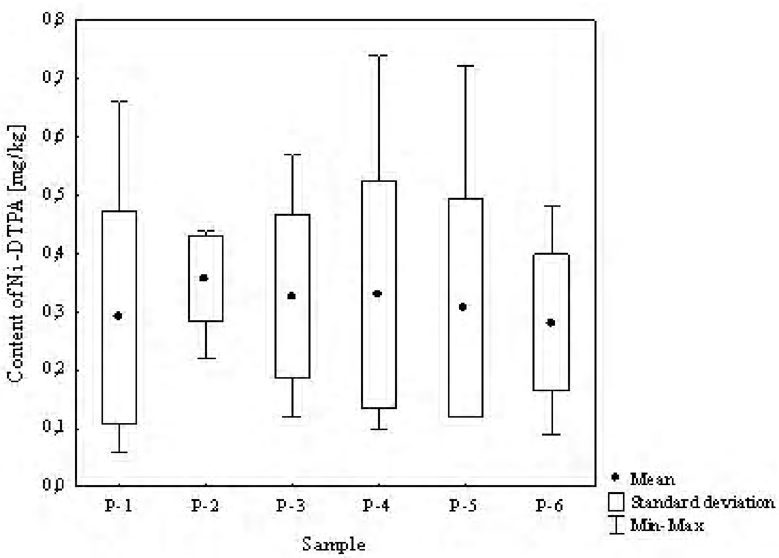

Fig. 4. DTPA extractable Ni in surface soil samples (0-20 cm)

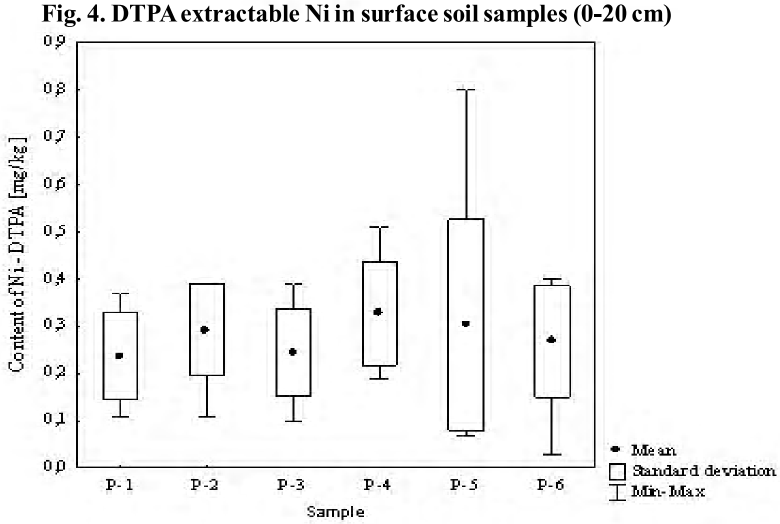

Fig. 5. DTPA – extractable Ni in subsurface soil samples (20-40 cm)

CONCLUSION

The texture of examined soils allows to categorise them to sandy soils, with low organic carbon content typical for the soils of this region. The pH of the soils varied depending on the location of the sampling point. Alkaline reaction was found in surface and subsurface samples from points located in direct vicinity of the factory and elevated pH in other studied soils under the impact of cement dust emission. The presence of $CaCO_3$ detected in some of the examined samples was of anthropogenic origin, and cause pH increase in soils in the subsequent years of research. The total contents of nickel in the analysed soil samples during the entire period of study (1995-2008) in the vicinity of Lafarge plant are close to the natural content. The content of DTPA-extracted nickel ranged between 0.03 and 0.8 mg/kg and as such is considered as below-toxicity level. Thus, allergy diseases observed among people living in the vicinity of cement plant are not caused by the excess of nickel. However, it is necessary to obey the 1994 European Union nickel directive (94/27/EC) regulating permissible level of nickel released to the environment.

In the subsequent years of study (1996 – 2008) increased soil pH value was observed only in one sampling point: P-2. Such a positive change in soil properties could be connected with a change in technology of cement production (from wet to dry) and reduction of emitted dust.

Cement industry emmisions as a potentially hazardous for the environment needs to be under periodical control, particularly in the case of very vulnerable soils in the vicinity of cement plant in Bielawy.

REFERENCES

Birmingham, B. and McLaughlin, D. (2006). Soil investigation and human health risk assessment for nickel in community soils near a former nickel refinery in Southern Ontario, Canada,. J. Toxicol. Environ. Health A, **69**, 845-892.

Chang, L., W. (1996). Toxicology of metals CRC. Lewis Publishers, Boca Raton, FL, USA.

Christiansen O.B. 1990. Nickel dermatisis, an update. Dermat. Clin., **8**, 37-40.

Cieśla, W., Zalewski, W. and Jaworska, H.(1994). Acidity and related properties in arable soils in the midst of KCW-KUJAWY lime and cement plant. Zesz. Probl. Post. Nauk Rol., **413**, 75-81.

Crock, J.G., and Severson, R.C.(1980). Four reference soil and rock samples for measuring element availability in the western energy regions. Geochem. Surv. Circ. ,**841,**1-16.

Denkhaus E. and Salnikov K. (2002). Nickel essentiality, toxicity and carcinogenity. Crit. Rev. Oncology, **42**, 35-56.

Dąbkowska- Naskręt, H., Jaworska, H. and Długosz, J. (1997). The influence of emited cement dust on properties of soils. Fertilization for Sustainable Plant Production and Soil Fertility, 11th World Fertilizer Congress of CIEC.

Frias, M. and Sanchez de Rojas, I. (2002). Total and soluble chromium, nickel and cobalt content in the main materials used in the manufacturing of commercial cement. Cem. Concrete Res., **32**, 435-440.

Kabata-Pendias A. and Pendias H. (2001). Biogeochemistry of trace elements. Lewis Publ. Boca Raton (FL. USA).

Kikuchi, R. (2001). Recycling of municipal solid waste for cement production: pilot scale test for transforming incineration ash of solid waste into cement clinker. Resour. Conserv. Recycl. , **31 (2)**, 137–147.

Lawrence, C. D. (1998). The constitution and specification of Portland cement in: P.C. Hewlett (ed.) Lea's Chemistry of Cement and Concrete.4 th Edition, Arnold Paus, UK.

Lindsay, W. L. and Norvell, W. A. (1978). Development of a DTPA soil test for Zn, Fe, Mn, and Cu. Soil Sci. Soc. Am. J., **42**, 421-428.

Monski, A. and Aasgarani, M. K. (1999). Producing Portland Cement from iron and steel slags and limestone. Cem. Concr. Res., **29 (9)**, 1373 – 1377.

Rogóż, A. and Grudnik, J. (2004). Assessment of trace element pollution of soil and root crops. Ecol. Chem. Eng., **11 (8)**, 775-785.

Perlak Z. (2000): Differentiation of heavy metal contents in the profiles of meadow soils in Odra river valley on Bytom Odrzański area, Zeszyty Problem. Post. Nauk Rol., **471**, 1099-1107.

Sprung, S. (1985). Technological problems in pyroprocessing cement clinker: cause and solution. (Dűsseldorf , Beton Verlag).

Tandon, R. and Aarts, B. (1993). Chromium, nickel and cobalt contents of Australian cements. Cont. Derm., **28**, 201 – 205.

Zerrougi Z. and Sbaa, M. (2008). Assesment of cement dust impact on the soil using principal component analysis and GIS. Int. J. Environ. Sci. Technol., **5 (1)**, 125 –134.