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Cobalt in alluvial Egyptian soils as affected by industrial activities

Ensegam A.M. Zohny

(Physics Department, Faculty of Science, Cairo University, Beni-Swif Branch, Egypt)

Abstract: Twenty-five surface (0—20 cm) soil samples were collected from different locations in Egypt representing non-polluted, moderately and highly polluted soils. The aim of this study was to evaluate total Co content in alluvial soils of Delta in Egypt using the delayed neturen activation analysis technique (DNAA). The two prominent gamma ray lines at 1173.2 and 1332.5 keV was efficiently used for ^{60}Co determination. Co content in non-polluted soil samples ranged between 13.12 to 23.20 ppm Co with an average of 18.16 ± 4.38 ppm. Cobalt content in moderately polluted soils ranged between 26.5 to 30.00 ppm with an average of 28.3 ± 1.3 ppm. The highest Co levels (ranged from 36 to 64.69 ppm with an average of 51.9 ± 9.5); were observed in soil samples collected from, either highly polluted agricultural soils due to prolonged irrigation with industrial wastewater or surface soil samples from industrial sites.

Keywords: cobalt; neturen activation analysis technique (DNAA); surface soil sample; industrial activities

Introduction

In nature Co occurs in two oxidation states, Co^{2+} and Co^{3+}, and formation of the complex anion $Co(OH)^{-3}$ is also possible. During weathering Co is relatively mobile in oxidizing acid environment, but due to a high sorption by Fe and Mn oxides, as well as by clay minerals, this metal does not migrate in a soluble phase. Concentration of Co in soils in inherited from parent materials. Soils over mafic rocks and soils derived from clay deposits contain the highest amounts of this metal. Alloway (Alloway, 1995) in the same direction mentioned that naturally high Co contents are usually observed in soils over serpentine rock and ore deposits. Significant sources of Co pollution are related to nonferrous metal smelters whereas coal and other fuel combustion are of considerably less importance, however, roadside soils and street dusts are known to be enriched in Co.

Factors contributing to Co deficiency for grazing animals are mainly associated with alkaline or calcareous soils, slightly leached soils, and soils with high organic matter content. The Co content and distribution in soil profiles are also dependent on soil forming processes and therefore differ for soils of various climatic zones. Usually higher Co contents of surface soils are observed for arid and semiarid regions, whereas exceedingly low soil Co content has been reported for light soils of the Atlantic Coastal plain and for soils of the glaciated region of northeastern US.

The primary interest in Co as constituent of soils lies in its essential roles in ruminant animals and microorganisms, and because of deficiencies rather than excesses. Interest in Co in plant biology stems particularly from its essential role in biological N-fixation (Young, 1979).

Aubert and Pinta (Aubert, 1977) mentioned that total Co contents of soils vary widely from 0.05 to 300 ppm with an average content in the range of 10.0 – 15.0 ppm. Kobata-Pendias and Pendias (Kobata-Pendias, 1984) noticed higher Co content in the surface layer of soils in arid and semi arid regions. The contents of Co in soils vary mainly in relation to the parent materials from which they were derived, even though there are also differences with depth in the soil profile and between soil types derived from common parent materials due to pedological processes. Within a given soil profile, Co is generally concentrated in those horizons rich in organic materials and clays. The mobility of Co is strongly related to the kind of organic mater in soils. Organic chelates of Co are known to be easily mobile in soil profiles. Although soils rich in organic matter are known to have both a low Co content and low Co availability, Co organic chelates may also be readily available to plants. This is especially pronounced at higher pH and in freely drained soils.

The aim of this study was to evaluate total Co content in alluvial soils of Delta in Egypt using the delayed neturen activation analysis technique (DNAA).

1 Materials and methods

1.1 Soil sampling

Twenty five surface (0—20 cm) soil samples were collected from different locations in Egypt representing non-polluted, moderately and highly polluted soils. The non-polluted soil samples were collected from different sites not affected by any known sources of Co pollution. The moderately and highly polluted soils samples were collected from soils subjected to prolonged irrigation with either polluted industrial wastewater or samples collected from industrial sites e.g. meteorological workshops. The samples were air-dried, crushed pass a 2.0 mm sieve then the following analysis were conducted. Mechanical analysis was carried out by the pipette method also, soil pH and organic matter content was determined by standard method as described by Jackson (Jackson, 1967). Calcium carbonate content was determined volumetrically using Collin's Calcimeter.

1.2 Irradiation

Soil samples were sieved through 800 mesh sieve to obtain fine homogenous samples. About 0.1g of each sample was packed in pure aluminum foil and prepared for irradiation along with a capsule of standard reference materials (SL7). An empty aluminum foil of known weight was irradiated on the same conditions, for identifying and subtracting the background γ-ray lines due to the aluminum envelopes. Then all samples were sealed well in aluminum cans. The irradiation time was 48 hour at the Nuclear Research Center First Reactor 2MW (ET-RR-1). The neutron flux was 4.4×10^{12} n/(s·cm^2). After 72 hours (cooling time) samples were radio-assayed for gamma-ray spectra using high resolution Hyper Pure Ge detector connected to multi-channel analyzer through a suitable electronic system including the PCA computer program. The HP-Ge detector was model No. 15190 Coaxial type with a crystal of 76.11 cm^3 and FWHM of 1.72 keV at 1332.5 keV γ-ray line of Co with an efficiency of 15% and a peak to Compton ratio of 55. The calibration and detection efficiency was determined using Co and Cs standard sources.

1.3 Measurements

The samples were positioned individually at about 10 cm in front of the detector and the accumulating time were 2 hours for good statistics.

2 Results and discussion

Cobalt-60 was calculated by means of activities induced by ^{59}Co (n, γ) ^{60}Co reactions, two peak net area were obtained electronically with PCA program. This program automatically searches for significant peaks from the digital data of gamma spectra, and calculates the peaks, which represents the natural background and the comption continue from the more energetic peaks in the spectra. The two prominent gamma ray lines at 1173.2 and 1332.5 keV was efficiently used for ^{60}Co determination. Cobalt concentrations in soil samples were determined using the equation of comparative standard method (Ehman, 1991).

$$X_s = X_{st} \frac{CPM_s \times Wt_{st}}{CPM_{st} \times Wt_s},$$

where X_s is the concentration of Co/g in soil samples; X_{st} is the concentration of Co/g in standard samples; Wt_s is the weight of soil sample (g); Wt_{st} is the weight of soil standard sample (g); CPM_s is the counts/min of ^{60}Co in soil sample; CPM_{st} is the counts/min of ^{60}Co in standard sample.

Fig.1 shows partial γ-ray spectra for Co in selected soil samples from the industrial sites as an example for the high soil Co levels.

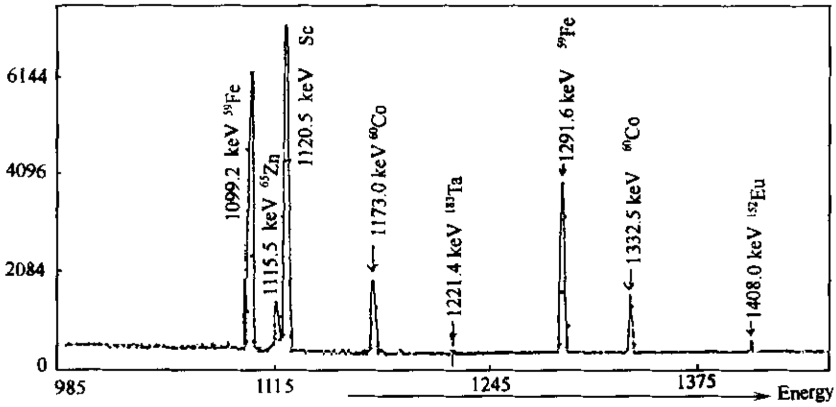

Fig. 1 Partial gamma-ray spectrum of the polluted soil samples

Table 1 shows some selected soil characteristics along with total Co concentrations determined by DNAA technique. Co content in non-polluted soil samples ranged between 13.12 to 23.20 ppm Co with an average of 16.9 ± 4.38 ppm. These values are relatively higher than reported by Rashad *et al*. (Rashad, 1995). They reported that normal levels of Co in the alluvial soils of Nile Delta ranged between 3.7 and 5.5 ppm with an average of 4.7 ppm. The normal Co content of surface soils usually ranges from 1.0 to 40.0 ppm, with the highest frequency in the range of 3.0 to 15.0 ppm. The grand mean Co concentration for world-wide soils is 8.5 ppm and for the soils of the US is 8.2 ppm. Usually higher Co contents of surface soils are observed for arid and semiarid regions (Kapata-Pendias, 1984).

Cobalt content in moderately polluted soils ranged between 26.5 to 30.00 ppm with an average of 28.3 ± 1.3 ppm. The highest Co levels; ranged from 36 to 64.69 ppm with an average of 51.9 ± 9.5; were observed in soil samples collected from, either highly polluted agricultural soils (samples # 19—21) due to prolonged irrigation with industrial wastewater or surface soil samples from industrial sites (samples # 22—25) as shown in Table 1.

Concerning contaminated Egyptian alluvial soils little work was done on cobalt. El-Leithi (El-Leithi, 1986) studied the effect of industrial activities on the soils of Nile Delta. He found that total content of Co in these soils range between 11.2 and 36.1 ppm with an average of 23.7 ppm. El-Gamal (El-Gamal, 1980) found that total Co ranged from 30.36 to 41.40 ppm with an average of about 36.5 ppm in El-Asfar sandy soils irrigated with sewage sludge for several years. The surface layers containing higher amounts of Co than the subsurface ones. Similar results were obtained by El-Nasher (El-Nasher, 1985), Rashad (Rashad, 1986) and Khalil (Khalil, 1990).

The data were submitted to statistical analysis and the correlation coefficients (r) between total Co and soil pH, O.M.%, $CaCO_3$%, clay % and silt % obtained as shown in Table 2. The simple correlation coefficient are used to explain the relationship between soil elemental contents and soil factors that may effect their contents such as soil pH, organic matter content, $CaCO_3$%, clay %, and silt %. Soil organic matter was correlated positively with total Co in soils ($r = 0.529$). By taking logarithms of the two variables a higher r-value was obtained, but the increase was only marginal (0.632 compared to 0.529). Similar trend was obtained with soil $CaCO_3$% content (Table 2). A negative correlation coefficient was obtained with soil pH and silt %.

Linear regression analysis of the obtained data could be summarized as follows:

Total soil Co = 182 − 19.2 (soil pH) $r = -0.348$,

Total soil Co = 17.04 + 5.11 (O.M., %) $r = 0.529$,

$$\text{Total soil Co} = 17.78 + 3.43\ (CaCO_3,\ \%) \quad r = 0.405,$$
$$\text{Total soil Co} = 21.99 + 0.23\ (\text{clay},\ \%) \quad r = 0.167,$$
$$\text{Total soil Co} = 41.07 + 0.33\ (\text{silt},\ \%) \quad r = -0.134.$$

Table 1 Cobalt concentrations in alluvial soil samples collected from different Delta sites (non-polluted and polluted) as determined by DNAA technique

Location	pH	O.M., %	$CaCO_3$, %	Clay, %	Silt, %	Total Co, ppm
Non polluted sites						
Bahtim # 1	7.8	2.40	2.15	45.80	31.50	13.20
# 2	8.1	2.15	1.80	43.80	35.50	14.10
# 3	8.2	1.15	0.85	39.90	41.20	13.12
Kaluob # 1	8.1	1.25	0.72	43.55	40.85	13.80
# 2	8.1	1.51	3.34	34.78	32.00	14.00
# 3	8.2	1.30	3.06	33.03	35.50	15.00
El-Qanater A	8.2	0.59	3.15	47.03	41.20	14.00
B	8.3	0.71	2.50	54.13	40.85	15.00
Qena	7.9	1.44	6.44	30.90	25.55	20.60
Giza	7.9	2.80	3.87	26.65	28.05	25.20
Tanta	7.7	3.37	3.40	38.50	19.15	21.30
Mansora	7.7	1.32	3.07	3.04	42.06	23.20
Moderately polluted sites						
Idfu	7.79	1.74	8.85	31.75	26.25	26.50
Zagazig	8.03	2.65	3.24	30.05	31.15	27.90
Minya	8.50	2.28	3.71	10.75	39.15	28.60
Damietta	7.65	3.00	3.26	43.00	20.95	28.50
Disuq	7.73	7.73	3.56	36.60	24.70	30.00
Highly polluted sites						
Mostord (A)	8.00	2.70	4.20	55.60	23.50	62.50
(B)	8.10	2.40	5.20	62.20	29.30	49.50
Shubra El-Kima	7.20	2.26	2.70	33.15	33.73	47.00
Balaks	7.50	1.76	1.74	34.70	31.50	36.00
Industrial sites # 1	7.90	5.94	3.94	35.20	31.80	44.99
# 2	8.20	6.33	4.35	42.50	35.60	64.69
# 3	7.50	3.70	3.70	39.90	42.80	56.83
# 4	7.50	3.82	3.82	34.20	33.90	53.83

Fig.2 shows the effect of either soil O.M. % or $CaCO_3$ % on soil total Co content in tested soils. It should be mentioned that the high variations in total Co at the same levels of either O.M. % or $CaCO_3$ % could be explained by the differences in soil pollution sources and type of soil usage.

Table 2 Simple correlation coefficient (r) between cobalt and selected soil properties

Soil factors	Total Co	Transformed data (log-values)
pH	-0.348*	-0.351
O.M., %	0.529**	0.632**
$CaCO_3$, %	0.405**	0.408**
Clay, %	0.167	0.131
Silt, %	-0.134	-0.117

* significant at 5% level; ** significant at 1% level

3 Conclusions

Total cobalt contents of alluvial delta soil of Egypt show considerable variation ranging from 13.1 to 64.7 ppm. The impact of either wastewater irrigation or industrial activities on soil total Co was obvious due to accumulation of organic matter and solid waste in the soil profile.

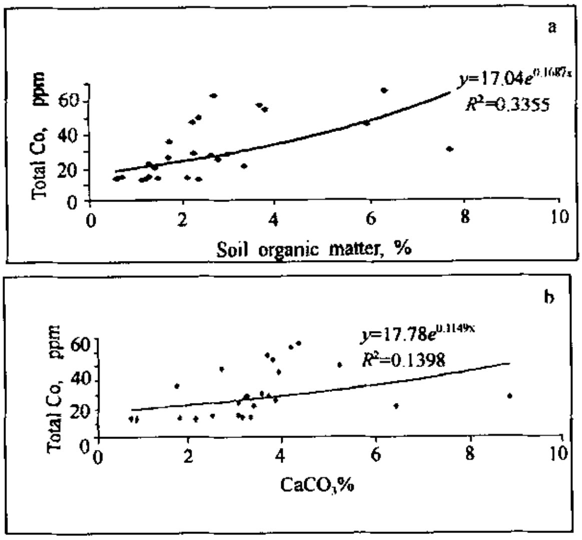

Fig.2 Relationships between (a) soil organic matter and Co content; (b) $CaCO_3$ % and Co content

It is noteworthy that DNAA technique could be used successfully for heavy metals determination due to its high sensitivity.

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