DISTRIBUTION OF HEAVY METALS CONCENTRATIONS IN SOILS AROUND THE INTERNATIONAL ATHENS AIRPORT (GREECE). AN ASSESSMENT ON PRELIMINARY DATA

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DISTRIBUTION OF HEAVY METALS CONCENTRATIONS IN SOILS AROUND THE INTERNATIONAL ATHENS AIRPORT (GREECE). AN ASSESSMENT ON PRELIMINARY DATA

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Abstract

Soils are receptors of atmospheric metal depositions and hence reliable indicators of pollution phenomena, especially for cases that potential site specific pollution sources are detected in terrestrial ecosystems. The purpose of this study was to assess the distribution of Cu, Zn, Fe, Mn, Ni, Cr, Pb, and Ba concentrations in soils nearby the International Athens Airport “El. Venizelos”, in Attica, Greece. Total metal concentrations were determined in 86 topsoil aqua regia extracts and the median values for Cu, Zn, Fe, Mn, Ni, Cr, Pb, and Ba concentrations were 23, 81, 22x10⁻³, 497, 87, 74, 75, and 423 mg kg⁻¹ respectively. Though median values are not considered as high, the 90th percentile concentration values for some metals are high, indicating possible soil enrichment by these metals. A tendency for increased concentrations of Zn and Cr along the north-south axis and of Pb, Cu and Ni at the northern part of the studied area was also observed. As a first approach to discriminate between natural and anthropogenic metal contributions in the soils of the area, the obtained preliminary data were subjected to cluster analysis and to the evaluation of metals Enrichment Factors (EFs). Both EF values and cluster analysis results suggested secondary Pb, Cu and Zn site specific accumulation in the soils of the studied area.

Keywords: Soil Characteristics, Heavy metals, Airport, Enrichment Factor, Cluster Analysis.

Περίληψη

Τα εδάφη, ως αποδέκτες της ατμοσφαιρικής απόθεσης μετάλλων, αποτελούν αξιόπιστους δείκτες ρύπανσης, ιδιαίτερα στις περιπτώσεις που εντοπίζονται πιθανές σημειώμενες πηγές ρύπανσης σε χερσαία οικοσυστήματα. Η παρούσα μελέτη ακολουθούσε τον εκτιμητικό τρόπο της κατανόησης των συγκεντρώσεων του Cu, Zn, Fe, Mn, Ni, Cr και Ba σε εδάφη κοντά στο Διεθνές Αεροδρόμιο Αθηνών “Ελ. Βενιζέλος”, στην Αττική. Σε 86 επιφανειακά δείγματα προσδιορίστηκαν οι ολικές συγκεντρώσεις μετάλλων, στο εκχύλισμα που προέκυψε μετά από κατεργασία με «aqua regia». Οι διάμεσες τιμές των συγκεντρώσεων του Cu, Zn, Fe, Mn, Ni, Cr και Ba ήταν 23, 81, 22x10⁻³, 497, 87, 74, 75 και 423 mg kg⁻¹ αντίστοιχα. Από τις διάμεσες τιμές δύο οι αυτές μεταδίδονται στο εδάφος με τα μέταλλα αυτά. Επίσης,
1. Introduction

Heavy metals occur naturally as chemical elements in the earth’s crust and surface soils in varying concentrations (Alloway and Ayres, 1997). Total metal contents in soils are directly related to the nature of the parent material they are derived from (Swaine and Mitchell, 1960). Soils in urban and rural areas may become contaminated by accumulation of heavy metals through natural processes and/or human practices that may be high enough to pose risk to human health, plants, animals, and ecosystems (D’amore et al., 2005). In terrestrial ecosystems many kinds of interactions between solids, liquids, gases and the biota take place as geochemical and biological processes (Giannakopoulou et al., 2012) that evolved and affected by anthropogenic factors such as agricultural practices, industrial activities, waste treatments etc. (Kabata-Pendias, 2001).

Increased heavy metal concentrations in soils have been recorded for many industrial, urban, rural, and mixed land uses areas (Srinivasa Gowd et al., 2010; Bretzel and Calderisi, 2006; Massas et al., 2009; Koulourasis et al., 2009). Considering that soils are not a renewable resource and that heavy metals do not biodegrade but accumulate in soils, it is necessary to monitor soil metal concentrations to prevent pollution situations and to propose remediation actions if necessary.

There are only few reports on the distribution of heavy metals in soils in the vicinity of international airports (Table 1). Thus, the purpose of this study was: (1) to determine the actual total concentration of Cr, Ni, Zn, Pb, Cu, Co, Mn, Ba, and Fe in soils around the International Athens airport area (2) to assess the spatial distribution of metals and (3) to discuss on possible relations between metals concentrations and soil properties.

2. Materials and Methods

2.1. Study area and sampling

The study area and the sampling sites are presented in Figure 1. Athens International Airport “El. Venizelos”, is located in Mesogaia region, Eastern Attica, Greece, approximately 25 kilometers northeast of Athens. The climate of the area is typical subtropical Mediterranean, with prolonged hot and dry summers succeeded by considerably mild and wet winters. The mean annual precipitation is approximately 400 mm, while snowfall is rare. The drought period usually begins in May and lasts until October. The daily mean temperature ranges between 27°C during the summer months and 11°C during the winter months (Papathanasiou et al., 2013a, b). Geologically, the study area is part of the Attico-Cycladic Massif. It is generally flat with low hills and consists of alluvial and diluvial deposits.

El. Venizelos airport operates since March 2001 and according to air traffic statistical data of the year 2013 has been ranked as the 35th airport in Europe. In 2014 the airport handled 154,530 aircraft movements, 15,196,369 passengers and 77,337,956 tons of cargo (http://www.aia.gr). The Municipalities of Spata, Koropi, Artemis and Markopoulo are located nearby. The airport facilities and infrastructure occupy an area of approximately 10 km² surrounded by agricultural land. Most of this land is covered by vineyards, but vegetable, olive and fruit tree cultivations are also present.
Topsoil samples (0-10 cm depth) were collected from the region around El. Venizelos airport during the summer of 2013. In order to obtain a distribution pattern of heavy metals concentrations in the soils of the area, a grid-type sampling scheme (cell size 1000x1000 m or 500x500 m in some cases) was followed, oriented by the presence of the airport. At every sampling site, three subsamples from 100 x 100 cm surface area were obtained and mixed to make each of the 86 bulk soil samples.

![Studied area and sampling sites](image)

**Figure 1 - Studied area and sampling sites.**

### 2.2. Sample preparation and analysis

The soil samples were transferred to the laboratory in polyethylene bags, air-dried and sieved through a 2-mm sieve. The mechanical composition of the samples was determined by the Bouyoucos hydrometer method (Bouyoucos, 1951), while the organic matter content by the Walkley-Black procedure (Nelson and Sommers, 1982). Soil pH was determined in 1:1 v/w soil-water ratio slurries by the use of standard glass/calomel electrodes. The CaCO$_3$ equivalent percentage was estimated by measuring the evolved CO$_2$ following HCl dilution.

To obtain “pseudo-total” metal concentrations, the soil samples were digested with aqua regia (Gasparatos and Haidouti, 2001). “Pseudo-total” expression accurately describes the metal concentrations determined in aqua-regia extracts, because aqua-regia digestion does not completely destroy silicates (Facchinelli *et al.*, 2001). However, in the text of this study, the term “total” is used for simplicity.

All metal concentrations were determined by atomic adsorption spectrophotometer Varian spectra A300. The calibration standards were prepared in aqua-regia matrix which was used for the soil
samples. A control sample was analyzed for every ten samples, and reproducibility was tested by reanalyzing 30% of the samples. Analytical precision, estimated as relative standard deviation, ranged from 3% to 5% depending on the metal.

2.3. Enrichment factor (EF)

Table 1 - Total metal concentrations in soils close to international airports.

Heavy metal enrichment factors (EFs) for the soil samples were calculated as described by Massas et al. (2010) and the following equation was used:

\[
EF = \frac{C_{it}}{A_{it}}
\]

where \(C_{it}\) is the total metal concentration in the ith sampling site and \(A_{it}\) is the target metal A value of the Dutch guidelines system (Netherlands Ministry of Housing, Physical Planning and Environment (Netherlands M.H.P.P.E., 2000), obtained by adjusting the standard \(A_{tv}\) value of the system for the ith sampling site according to the equation:

\[
A_{i} = A_{tv} \times \left[\frac{\{a + (b \times \% \text{clay}) + (c \times \% \text{organic matter})\}}{\{a + (b \times 25) + (c \times 10)\}}\right]
\]

where:

\(A_{tv}\) = standard A value of the metal in the Dutch guidelines system (Netherlands M.H.P.P.E., 2000)
% clay = percentage clay (grain size<2 mm) in the soil to be assessed
% organic matter = organic matter percentage (w/w) in the soil to be assessed
a, b, c = metal dependent constants for each metal

EF values > 1 may be considered as possible soil enrichment.

2.4. Statistical Analysis and GIS

The descriptive statistical parameters, correlation analysis and cluster analysis were carried out by using the statistical software STATISTICA for Windows (StatSoft, Inc., USA, 1995, Version 7).

Spatial distributions of total metal concentrations in the soils of the tested area were visualized on maps produced by the ArcMap V9.3 software. The Geostatistical Analyst extension was used to
interpolate values between the sampling sites and to create interpolated surfaces by the Inverse Distance Weighted method.

3. Results

3.1 Soil properties

The soils of the studied area were developed mainly on alluvial deposits and their physicochemical key characteristics are presented in Table 2. The soils show light to medium texture as sand content ranged from 28.00 - 85.40 % and clay content ranged from 8.00 to 42.60 %. The pH does not vary much and is slightly basic (mean value=7.95) suggesting sub alkaline conditions and low metal mobility in the tested soils. Calcium carbonate equivalent ranges from 2.7 to 54.4 %, with an average value of 19%. High percentages of carbonates in soils are usually related to low bio-availability of heavy metals. Organic matter content highly fluctuated between traces and 21.06%, but most of the samples are poorly or moderately supplied by organic matter. These properties point to soils of adequate drainage that secure sufficient soil aeration and oxidizing conditions. Sand, clay, silt, organic matter, calcium carbonate equivalent content values and pH values are normally distributed, pointing to minimal site specific system disturbance.

Table 2 - Descriptive statistics of selected physicochemical properties of the studied soils (N=86).

<table>
<thead>
<tr>
<th></th>
<th>Sand (%)</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
<th>Org. matter (%)</th>
<th>CaCO(_3) eq. (%)</th>
<th>pH (1:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>52.6</td>
<td>22.7</td>
<td>24.7</td>
<td>2.53</td>
<td>19.0</td>
<td>7.95</td>
</tr>
<tr>
<td>Median</td>
<td>52.8</td>
<td>23.5</td>
<td>24.3</td>
<td>2.24</td>
<td>19.8</td>
<td>7.96</td>
</tr>
<tr>
<td>Min.</td>
<td>28.0</td>
<td>2.6</td>
<td>8.0</td>
<td>traces</td>
<td>0.4</td>
<td>7.02</td>
</tr>
<tr>
<td>Max.</td>
<td>85.4</td>
<td>34.8</td>
<td>42.6</td>
<td>21.06</td>
<td>54.4</td>
<td>8.69</td>
</tr>
<tr>
<td>10(^{th}) percentile</td>
<td>40.0</td>
<td>14.0</td>
<td>15.5</td>
<td>1.01</td>
<td>2.7</td>
<td>7.64</td>
</tr>
<tr>
<td>90(^{th}) percentile</td>
<td>63.4</td>
<td>30.6</td>
<td>32.9</td>
<td>3.47</td>
<td>33.2</td>
<td>8.25</td>
</tr>
<tr>
<td>SD</td>
<td>9.6</td>
<td>6.5</td>
<td>6.7</td>
<td>2.38</td>
<td>11.8</td>
<td>0.26</td>
</tr>
<tr>
<td>CV%</td>
<td>18.2</td>
<td>28.6</td>
<td>27.0</td>
<td>94.12</td>
<td>61.8</td>
<td>3.30</td>
</tr>
</tbody>
</table>

3.2. Total metal concentrations

The descriptive statistics of the total Cu, Zn, Fe, Mn, Ni, Cr, Pb, and Ba concentrations are presented in Table 3. Though the mean total metal concentrations fall within the normal range for natural soils or for soils of low metal enrichment, the 90\(^{th}\) percentile and maximum values indicate that in some sampling sites (not necessary the same for all metals) concentration values exceed the reference “A values” or even the test “B values” of the Dutch System (Netherlands M.H.P.P.E., 2000). These increased metal concentrations, especially of Pb, Cu and Zn, point to secondary metal accumulation in the soils of the area, other than the presence of metals in soils due to soil formation processes. The observed high Ni mean total concentration is commonly detected in Greek soils and attributed to the soils’ parent material. However, some soil samples showed clear indications of Ni enrichment.
Table 3 - Descriptive statistics for the total concentrations of the studied metals of the soils all around El. Venizelos airport (N=86).

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Zn</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Pb</th>
<th>Ba</th>
<th>Fe*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg kg⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>27.02</td>
<td>95.21</td>
<td>562.72</td>
<td>92.13</td>
<td>79.77</td>
<td>78.96</td>
<td>442.53</td>
<td>22.39</td>
</tr>
<tr>
<td>Median</td>
<td>23.25</td>
<td>81.00</td>
<td>497.00</td>
<td>86.90</td>
<td>74.18</td>
<td>74.90</td>
<td>422.75</td>
<td>21.71</td>
</tr>
<tr>
<td>Min.</td>
<td>7.95</td>
<td>33.50</td>
<td>223.00</td>
<td>34.60</td>
<td>31.00</td>
<td>53.30</td>
<td>72.00</td>
<td>78.45</td>
</tr>
<tr>
<td>Max.</td>
<td>129.05</td>
<td>518.00</td>
<td>1491.00</td>
<td>177.10</td>
<td>154.35</td>
<td>271.20</td>
<td>1171.00</td>
<td>44.82</td>
</tr>
<tr>
<td>10th percentile</td>
<td>17.70</td>
<td>61.50</td>
<td>363.00</td>
<td>60.35</td>
<td>52.90</td>
<td>62.35</td>
<td>257.50</td>
<td>15.45</td>
</tr>
<tr>
<td>90th percentile</td>
<td>33.70</td>
<td>130.50</td>
<td>860.00</td>
<td>133.10</td>
<td>108.80</td>
<td>96.15</td>
<td>649.50</td>
<td>29.30</td>
</tr>
<tr>
<td>SD</td>
<td>16.66</td>
<td>56.59</td>
<td>232.17</td>
<td>28.75</td>
<td>24.35</td>
<td>26.24</td>
<td>174.15</td>
<td>62.00</td>
</tr>
<tr>
<td>CV%</td>
<td>61.66</td>
<td>59.43</td>
<td>41.26</td>
<td>31.20</td>
<td>30.53</td>
<td>33.23</td>
<td>39.35</td>
<td>27.69</td>
</tr>
</tbody>
</table>

*: Fe concentration in mg g⁻¹

4. Discussion

4.1. Distribution of metals

The interpolated studied area covered a land of 48 km² (including the airport). In Figures 2 and 3, the distribution of Pb, Ni, Cr, Ba, Cu, Zn, Mn and Fe total concentrations around the airport is presented. Not a clear unique pattern for the distribution of all metals can be detected. Spots of higher Pb and Cu concentrations are observed in the northern part of the studied area. Ni also shows a distribution pattern similar to that of Pb and Cu, while for Zn a south to north accumulation in the soils appears. Increased Cr, Ba and Mn concentrations observed in the western part though for Cr a north to south distribution is also apparent. Finally, the higher Fe concentration is clearly present in the south-west of the area. The interpolated maps that visualize the distribution of total metal concentrations in the soils around the El. Venizelos airport, can serve to relate the distribution pattern of each metal to specific potential metal sources. However, any discussion on the potential sources of the studied metals based on their distribution patterns in soils around the airport is beyond the scope of this preliminary assessment.

4.2 Enrichment Factors

Enrichment Factor (E.F.), as a soil pollution index that is calculated by metal concentration values normalized for clay and organic matter content of the soils, may provide a more precise approach to the data. The mean EF values for Pb, Cu, Zn, Ni, Cr and Ba are 1.03, 0.86, 0.75, 2.68, 0.80 and 2.29 respectively, indicating no or minor or moderate soil pollution, depending on the metal. Mean EF values suggest Ni and Ba accumulation in the soils of the area. However, the reference “A values” of the Dutch system (Netherlands M.H.P.P.E., 2000) that were used for the calculation of Ni and Ba EFs are lower than Ni and Ba background concentrations in most Greek soils, and this is probably the main reason for the high Ni and Ba EFs observed in the soils of the studied area (Geochemical Atlas of Europe, 2005). In Figure 4 the median, the 10th and 90th percentiles and the minimum and maximum EF values of the six metals are presented. Though median EF values are low (with the exception of the high Ni and Ba EF median values for reasons discussed earlier) the 90th percentile and the maximum EF values for Pb, Cu and Zn indicate site specific soil enrichment by these metals. This argument is further supported by the fact that Pb, Cu and Zn EF values do not follow a normal distribution pattern (Kolmogorov-Smirnov & Lilliefors test for normality).
4.3. Cluster Analysis and Correlations

As it is presented in Figure 5, two main clusters were distinguished. The metals included in the first main cluster are Cr, Ni, Ba, Mn, Fe and Zn while the second main cluster consists of Pb and Cu. Within the first main cluster two clear sub-clusters observed indicating a strong relation between Cr and Ni and Mn and Ba, respectively. A weak connection of Fe with the second sub-cluster is also noticed and a very weak association of Zn with the metals of the first main cluster is apparent. Considering that the smaller the linkage distance the stronger the relation between metals, it can be supported that the metals in each of the following Cr-Ni, Ba-Mn and Pb-Cu groups originated from the same source. The significant but weak correlations between the clay content and Cr, Ni and Mn total concentrations (r values 0.34, 0.36 and 0.34 respectively, p<0.05) indicate that to some extent these metals derived from the soil’s parent material. Clay content of the soils showed a significant correlation to the Fe total concentration (r=0.60, p<0.05) that strongly supports the geogenic origin of Fe. The physicochemical characteristics of the studied soils did not correlate to Ba, Cu, Zn and Pb total concentrations, pointing to secondary soil enrichment by these metals probably due to atmospheric depositions. However, to robustly support any assumptions relative to the origin of the metals in the studied soils the bioavailable / exchangeable forms of the metals must be determined and soil samples must be subjected to fractionation schemes, since heavy metals from anthropogenic sources could be more mobile than from geogenic sources (Burt et al., 2003; Gasparatos et al., 2015).

Figure 2 - Interpolated maps of the Pb, Ni, Cr, and Ba total concentrations in the soils around the El. Venizelos airport.
Figure 3 - Interpolated maps of Cu, Zn, Mn, and Fe total concentrations in the soils around the El. Venizelos airport.

Figure 4 - Presentation of Enrichment Factors (EFs) statistics.
5. Conclusions

This study attempted to record the levels of Pb, Cu, Zn, Ni, Cr, Ba, Mn and Fe in the soils around Athens International Airport after 13 years of airport operation. The mean metal concentrations were generally low but increased site specific Pb, Cu and Zn and to a lesser extent Ni concentrations were determined. Cluster and correlation analyses results and Enrichment Factor values support the assumption of secondary accumulation of the above metals in the soils of the studied area due to aerial depositions. The dense airplane landing and taking off, the maintenance of the aircrafts and the traffic burden within and nearby the airport area may contribute to the observed site specific soil enrichment by Pb, Cu and Zn. Considering that this study is an assessment on preliminary data, more scientific research is needed to clearly distinguish between the sources of the metals present in the studied soils.

6. References


