VERTICAL DISTRIBUTION OF HEAVY METALS IN SOILS UNDER THE APPLICATION OF INDUSTRIAL SLUDGE FROM PAINT AND PRINT INDUSTRY

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Abstract

Investigated were soil profiles (0-200 cm) under industrial sludge from a waste water treatment facility of a textile painting plant near Elin Pelin, Bulgaria. Morphogenetic and heavy metal analysis was carried out and relation was established with heavy metals and organic contaminants in soils. The soils (Profile 1 and Profile 2) were classified as Technosols and characterized by the presence of differentiated $B_u(1,2)$ horizons. The two soil profiles have neutral to alkaline soil reaction (pH 7-8) which correlates with the carbonate content. In the soil profile under sludge application Cu, Cr, Ni, Zn and Co distribution indicates anthropogenic source. Pb, Mn and Fe come from a different industrial source as their contents are elevated in the technogenic $B_u$ horizons of the soil profile. The sludge contained heavy metals are not likely to have been transported down the soil profiles. In the soil profile with no sludge addition the heavy metal distribution, again indicates anthropogenic sources with Zn, Cu, Mn and Pb showing elevated contents in the middle part of the soil profile. In the control soil ($Gleyic Luvisol$), chromium, nickel, cobalt and Fe are generally of lithogenic origin, while Cu, Zn, Mn have bio(pedo)genic sources. The anthropogenic-technogenic character of heavy metal sources was confirmed by some contaminant compounds (metabolites) detected in the $B_u$ horizons of the Technosols.

Key words: heavy metals, industrial sludge, sources, soil profile, Technosols

Introduction

Sewage sludge from waste water treatment has been considered to increase soil fertility due to the higher organic matter and macronutrient content. However, due to the presence of higher concentrations of heavy metals and organic pollutants, sewage sludge may pose a threat to human health (European Communities, 2001). The current trends in sewage sludge disposal relate to its recycling through agricultural utilization and incineration at the expense of land filling. The effects of sludge addition to soils on soil properties, the speciation of heavy metals and their bioavailability are widely investigated (Alloway and Jackson, 1991). Sewage sludge (SS) in Bulgaria is increasing its agronomic utilization, because of the need to lower disposal costs, recycle nutrient elements and counteract the decreasing fertility of arable soils (Tsa-dilas et al., 2000; Marinova, 2002; 2008). According to the Reports of the Ministry of Environment & Water in Bulgaria (2011a, b), the total amount of sludge generated by 31.12.2014 is estimated at 95 075 t DM/year.

There have been numerous reports so far on SS land disposal dealing with fertility and pollution aspects, such as (Williams et al., 1987; Campbell and Beckett, 1988; Wild et al., 1991; Giusquiani et al., 1992, 1995; Kasatikov and Runik, 1994; Giusquiani et al., 1992; 1995; Bacon et al., 2001; Petersen et al., 2003; Chen et al., 2003; Laturnus et al., 2007; Atanassova et al., 2005; Atanassova et al., 2006). In our former study (Atanassova et al., 2011) some anthropogenic contaminants (xenobiotics) were detected in the lower soil depths. The sludge layer contained dyes, steroids, etc. A couple of studies were carried out on leaching of sludge-contained heavy metals. According to their ability to leach from a light loam soil amended with sludge heavy metals are arranged in the decreasing order: Zn > Cr > Ni > Pb > Cu > Cd (Antanai-

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Soil samples and study site

Sanchez-Martin et al. (2005) found that concentrations of Zn and Pb were highest in the surface (0-10 cm) of soils amended with the highest dose of sludge and underwent a decrease with the increase in soil depth (0-50 cm). Their results reveal that almost no redistribution of the metals present in the sludge in the soil profile of the amended soils had taken place, indicating that under the experimental conditions used and for the two sludges metals were localized in the sludge layer.

The consequences of the application of sewage sludge to agricultural soils with regard to the long-term bioavailability and movement of metals deep into the soil profile are incompletely understood. Our aim is to address the heavy metals distribution and their sources in a deep technogenic soil profile (0-200 cm) affected by hydromorphic conditions, as related to soil genesis. In addition, our study is aimed at characterizing the present status and sources of metals in a past sewage sludge (SS) treated soils with implications on soil profile pollution, inheritance from the parent material and relation with organic pollutants and metabolites present.

Materials and Methods

Soil samples and study site

The study site was chosen in the area of “Mirolio” paint and print textile factory near Elin Pelin, Bulgaria where processed sludge from the waste water treatment plant (WWTP) was deposited in 2006. The sludge consisted of waste products from the painting manufacture with minor contribution from household waste water. The main analyzed parameters, i.e. heavy metals and organic pollutants (xenobiotics) are below the predicted non-effect concentrations PNEC (European Community, 2001) and the National Standards (Directive № 338, 2004; Directive № 3, 2008). Below the sludge layer there are technogenic horizons B_2 of 0-86 cm depth with artefacts.

The soils were morphologically described by Atanasova et al. (2011). Soils were classified as Urbic Garbic Mollic Technosols Calcaric Humic Siltic (Profile 1), Urbic Mollic Technosols Calcaric Siltic (Profile 2) and the Control soil as Gleyic Luvisol (FAO, 2002; Teoharov, 2004) for Bulgarian soils and the World Reference Base of Soil Resources WRB-SR (2006). The soil forming materials were alluvial-delluvial deposits. Soil material from the surrounding area was deposited over the natural soil profile with the purpose to isolate the eventual transport of sludge contained toxic elements. The transported soil layers were morphologically differentiated into horizons containing some artefacts such as construction materials. Plant cover was Echium Vuiigare, Cirsium, Galium Aparine, etc. The methods for analysis of the physico-chemical and morphological soil properties were: 1) particle size composition according to the Kachinsky method; 2) organic carbon by the Tjurin’s method; 3) pH in water (1:2.5); 4) cation exchange capacity according to Ganev and Arsova (1980); 5) heavy metals by aqua regia digestion (ISO 11466), followed by AAS analysis.

Organic compounds, including lipids and contaminants were extracted by Soxtec extraction, followed by purification and GC/MS analysis (Atanasova et al., 2011). Here we present the structure of some of the identified compounds in the soil profiles and relate their presence with heavy metal sources in the soils studied.

Statistical analysis

Principal component analysis was carried out (SPSS 19 for Windows) in order to identify interrelations among the measured parameters; distinguish between groups of metals of different sources and origin. Factors with an eigenvalue > 1 were extracted in addition and Cluster analysis was done, as well.

Results and Discussion

Selected soil properties were presented in Table 1. Soils were classified into the classes of silt loam and silty clay loam according to Soil Taxonomy. The slightly alkaline soil reaction in the Technosols restricts downward movement of the metals but may contribute to formation of labile organic complexes.

Heavy metal distribution in the soil under sludge, soil with no sludge and the control soil are presented in Figure 1 a, b, c, d, e, f, g. Some of the pollutant elements such as Mn and Zn, whose concentrations were elevated in the technogenic soil horizons, are present simultaneously with some xenobiotics observed in the B horizons, (Figure 2). Heavy metals distribution based on total contents in the soil with sludge application is characterized by the following trends: Cu, Cr and Ni exhibit elevated concentrations in the sludge layer, followed by a decrease in the lower depths to the geogenic levels. Ni exhibits increased content in the technogenic B_2 horizon. Pb concentrations are elevated in the technogenic horizons, as well, and imply anthropogenic sources.

In the soil profile with no sludge addition Zn and Pb were elevated in the upper three layers slowly decreasing down the soil profile. Ni distribution implies contamination from an external non-pedogenic source. Heavy metal distribution in the control soil implies pedogenic and lithogenic sources, as all the elements show either no variation along the soil depth or increase along the soil profile.

Statistical analysis can assist in distinguishing between types of sources of the elements, either anthropogenic, pedo-
### Table 1a
Selected soil properties for the Technosols

<table>
<thead>
<tr>
<th>No</th>
<th>Horizon/depth, cm</th>
<th>pH</th>
<th>CEC pH, cmol/kg</th>
<th>OM, %</th>
<th>Clay &lt;0.001m, %</th>
<th>Carbonates, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sludge 0-14</td>
<td>7.0</td>
<td>59.30</td>
<td>30.1</td>
<td>5.50</td>
<td>8.25</td>
</tr>
<tr>
<td></td>
<td>Bu₁ 14-53</td>
<td>7.4</td>
<td>24.20</td>
<td>1.79</td>
<td>24.20</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>Bu₂ 53-93</td>
<td>8.5</td>
<td>22.80</td>
<td>2.17</td>
<td>9.10</td>
<td>3.60</td>
</tr>
<tr>
<td></td>
<td>Akb 93-123</td>
<td>8.0</td>
<td>24.90</td>
<td>3.40</td>
<td>15.30</td>
<td>3.58</td>
</tr>
<tr>
<td></td>
<td>Bgk 123-143</td>
<td>7.6</td>
<td>24.60</td>
<td>1.23</td>
<td>15.50</td>
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</tr>
<tr>
<td></td>
<td>Ck 143-168</td>
<td>7.5</td>
<td>24.40</td>
<td>0.85</td>
<td>12.00</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>G 168-200</td>
<td>7.2</td>
<td>25.00</td>
<td>1.89</td>
<td>26.50</td>
<td>0.11</td>
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<tr>
<td></td>
<td>A 0-28</td>
<td>8.1</td>
<td>23.90</td>
<td>3.12</td>
<td>14.40</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Bu₁ 28-69</td>
<td>7.9</td>
<td>25.40</td>
<td>1.51</td>
<td>20.60</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Bu₂ 69-79</td>
<td>8.2</td>
<td>20.20</td>
<td>19.65</td>
<td>8.50</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>Bu₃ 79-86</td>
<td>6.8</td>
<td>21.20</td>
<td>3.30</td>
<td>21.60</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>ABb 86-100</td>
<td>6.5</td>
<td>20.80</td>
<td>3.02</td>
<td>10.90</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Bg 100-118</td>
<td>7.2</td>
<td>20.50</td>
<td>1.42</td>
<td>12.60</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Cg 118-135</td>
<td>7.3</td>
<td>21.10</td>
<td>0.28</td>
<td>7.00</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>G 135-159</td>
<td>7.8</td>
<td>22.00</td>
<td>0.94</td>
<td>16.30</td>
<td>0.8</td>
</tr>
</tbody>
</table>

### Table 1b
Selected soil properties for the Control soil

<table>
<thead>
<tr>
<th>Horizon depth, cm</th>
<th>pH</th>
<th>CEC, cmol/kg</th>
<th>SOM</th>
<th>Clay (&lt;0.001 mm)</th>
<th>Hygroscopic moisture, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₉ 0-27</td>
<td>6.0</td>
<td>22.9</td>
<td>2.78</td>
<td>22.9</td>
<td>3.90</td>
</tr>
<tr>
<td>A 27-48</td>
<td>6.3</td>
<td>23.5</td>
<td>1.91</td>
<td>26.6</td>
<td>3.90</td>
</tr>
<tr>
<td>G 48-87</td>
<td>5.9</td>
<td>20.8</td>
<td>1.30</td>
<td>19.5</td>
<td>2.59</td>
</tr>
<tr>
<td>G 87-120</td>
<td>6.1</td>
<td>20.6</td>
<td>1.13</td>
<td>20.2</td>
<td>2.78</td>
</tr>
</tbody>
</table>

![Fig. 1a. Heavy metals in Soil Profile 1 under sludge deposition](image-url)
Vertical Distribution of Heavy Metals in Soils under The Application of Industrial Sludge ...

**Fig. 1b.** Heavy metals in soil profile 2 without sludge deposition

**Fig. 1c.** Heavy metals in the control soil profile

**Fig. 1d.** Fe contents in soil profiles 1 and 2
The correlation matrix, the component matrix and the dendrograms are presented in Tables 2, 3, 4, 5, 6 and 7 and Figure 3a, b, c for the Technosols and the control soil respectively.

Factor and cluster analyses were carried out giving us the possibility to: 1) reveal the structure in the data and 2) distinguish among groups of separate independent variables. The cluster analysis was carried out with the purpose to identify interactions between the measured parameters. Correlation analysis was conducted to assess relations among variables.

For soil profile 1 under sludge application two principal components were identified with eigenvalues > 1 explaining 75%, 20.2%, of total variance (95.2%). The component matrix and the correlation matrix are presented on Tables 2 and 3. The first component is loaded by Cu, Cr, Ni, Zn and Co. These elements have elevated contents in the sludge layer and decrease their concentrations along the soil profile. Similar trends were observed by Antanaitis (2004). The second component is loaded by Pb, Mn and Fe. These elements accumulate in the technogenic B horizons below the sludge layer and we suspect that they originate from another industrial source. Leaching of Pb, Mn and Fe is not possible due to the lower contents of these elements in the sludge layer and the neutral pH 7 (Figure 1a, d, e). It can be concluded that most of the metals in this soil profile originate from anthropogenic-technogenic sources to the depth of the Cgk horizon and uniformly increase to the G horizon due to their lithogenic sources. The hierarchical cluster analysis shows similar results. The dendrogram in Figure 3a represents two major groups. The first major group consists of Cu, Cr, Zn, Ni and Co and the second
Vertical Distribution of Heavy Metals in Soils under The Application of Industrial Sludge ...

Fig. 2. Detected compounds with their mass spectra in the technogenic horizons
Table 2
Correlation matrix of heavy metals for soil profile 1

<table>
<thead>
<tr>
<th></th>
<th>Cu = Var 1</th>
<th>Cr = Var 2</th>
<th>Ni = Var 3</th>
<th>Pb = Var 4</th>
<th>Zn = Var 5</th>
<th>Co = Var 6</th>
<th>Mn = Var 7</th>
<th>Fe = Var 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu = Var 1</td>
<td>1.000</td>
<td>.972</td>
<td>.634</td>
<td>-.131</td>
<td>.996</td>
<td>.958</td>
<td>-.227</td>
<td>-.609</td>
</tr>
<tr>
<td>Cr = Var 2</td>
<td>.972</td>
<td>1.000</td>
<td>.693</td>
<td>-.012</td>
<td>.985</td>
<td>.959</td>
<td>.004</td>
<td>-.485</td>
</tr>
<tr>
<td>Ni = Var 3</td>
<td>.634</td>
<td>.693</td>
<td>1.000</td>
<td>.005</td>
<td>.686</td>
<td>.823</td>
<td>.214</td>
<td>.215</td>
</tr>
<tr>
<td>Pb = Var 4</td>
<td>-.131</td>
<td>-.012</td>
<td>.005</td>
<td>1.000</td>
<td>-.088</td>
<td>-.137</td>
<td>.601</td>
<td>.226</td>
</tr>
<tr>
<td>Zn = Var 5</td>
<td>.996</td>
<td>.985</td>
<td>.686</td>
<td>-.088</td>
<td>1.000</td>
<td>.973</td>
<td>-.154</td>
<td>-.547</td>
</tr>
<tr>
<td>Co = Var 6</td>
<td>.958</td>
<td>.959</td>
<td>.823</td>
<td>-.137</td>
<td>.973</td>
<td>1.000</td>
<td>-.099</td>
<td>-.368</td>
</tr>
<tr>
<td>Mn = Var 7</td>
<td>-.227</td>
<td>.004</td>
<td>.214</td>
<td>.601</td>
<td>-.154</td>
<td>-.099</td>
<td>1.000</td>
<td>.621</td>
</tr>
<tr>
<td>Fe = Var 8</td>
<td>-.609</td>
<td>-.485</td>
<td>.215</td>
<td>.226</td>
<td>-.547</td>
<td>-.368</td>
<td>.621</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Consists of Pb, Mn and Fe. The farthest the elements are situated, the least relation between them exists.

In the soil profile 2 (Tables 4 and 5) without sludge addition the elements load two PC, again with component 1 consisting of Cu, Cr, Ni, Zn, Co, Fe and Pb. The second PC was loaded by Pb, Mn and to a certain extent Zn. All these elements have anthropogenic sources, as their concentrations decrease along the soil depth with some elements such as Zn, Cu, and especially Mn and Pb showing elevated contents in the middle part of the soil profile. It can be concluded that Pb is of different anthropogenic source, Mn is suspected to be of dual origin, both anthropogenic and biogenic, similarly to Cu and Zn. Cu, Zn, Pb and Fe exhibit elevated contents in the middle part of the soil profile, the Bs horizons. Due to the slightly alkaline soil reaction, leaching of organic complexes of Cu, Pb and Zn is possible. However, the concentrations that are measured in this study refer to total contents and it is unlikely that twice as high concentrations for Pb and Zn could be measured if only

Table 3
Component matrix of the metals for soil profile 1 with sludge deposition

<table>
<thead>
<tr>
<th>Component</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu = Var 1</td>
<td>.994</td>
<td>-.048</td>
</tr>
<tr>
<td>Cr = Var 2</td>
<td>.973</td>
<td>.152</td>
</tr>
<tr>
<td>Ni = Var 3</td>
<td>.705</td>
<td>.537</td>
</tr>
<tr>
<td>Pb = Var 4</td>
<td>-.161</td>
<td>.656</td>
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<tr>
<td>Zn = Var 5</td>
<td>.996</td>
<td>.034</td>
</tr>
<tr>
<td>Co = Var 6</td>
<td>.982</td>
<td>.140</td>
</tr>
<tr>
<td>Mn = Var 7</td>
<td>-.200</td>
<td>.896</td>
</tr>
<tr>
<td>Fe = Var 8</td>
<td>-.533</td>
<td>.683</td>
</tr>
</tbody>
</table>

Table 5
Component matrix for soil profile 2

<table>
<thead>
<tr>
<th>Component</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu = Var 1</td>
<td>.977</td>
<td>.118</td>
</tr>
<tr>
<td>Cr = Var 2</td>
<td>.960</td>
<td>-.270</td>
</tr>
<tr>
<td>Ni = Var 3</td>
<td>.964</td>
<td>-.222</td>
</tr>
<tr>
<td>Pb = Var 4</td>
<td>.701</td>
<td>.669</td>
</tr>
<tr>
<td>Zn = Var 5</td>
<td>.941</td>
<td>.302</td>
</tr>
<tr>
<td>Co = Var 6</td>
<td>.860</td>
<td>-.472</td>
</tr>
<tr>
<td>Mn = Var 7</td>
<td>.565</td>
<td>.717</td>
</tr>
<tr>
<td>Fe = Var 8</td>
<td>.872</td>
<td>-.453</td>
</tr>
</tbody>
</table>

Table 4
Correlation matrix of heavy metals for soil profile 2

<table>
<thead>
<tr>
<th></th>
<th>Cu = Var 1</th>
<th>Cr = Var 2</th>
<th>Ni = Var 3</th>
<th>Pb = Var 4</th>
<th>Zn = Var 5</th>
<th>Co = Var 6</th>
<th>Mn = Var 7</th>
<th>Fe = Var 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu = Var 1</td>
<td>1.000</td>
<td>.904</td>
<td>.910</td>
<td>.772</td>
<td>.968</td>
<td>.762</td>
<td>.602</td>
<td>.797</td>
</tr>
<tr>
<td>Cr = Var 2</td>
<td>.904</td>
<td>1.000</td>
<td>.990</td>
<td>.500</td>
<td>.816</td>
<td>.951</td>
<td>.344</td>
<td>.955</td>
</tr>
<tr>
<td>Ni = Var 3</td>
<td>.910</td>
<td>.990</td>
<td>1.000</td>
<td>.553</td>
<td>.845</td>
<td>.924</td>
<td>.353</td>
<td>.928</td>
</tr>
<tr>
<td>Pb = Var 4</td>
<td>.772</td>
<td>.500</td>
<td>.553</td>
<td>1.000</td>
<td>.884</td>
<td>.272</td>
<td>.782</td>
<td>.266</td>
</tr>
<tr>
<td>Zn = Var 5</td>
<td>.968</td>
<td>.816</td>
<td>.845</td>
<td>.884</td>
<td>1.000</td>
<td>.660</td>
<td>.701</td>
<td>.666</td>
</tr>
<tr>
<td>Co = Var 6</td>
<td>.762</td>
<td>.951</td>
<td>.924</td>
<td>.272</td>
<td>.660</td>
<td>1.000</td>
<td>.187</td>
<td>.962</td>
</tr>
<tr>
<td>Mn = Var 7</td>
<td>.602</td>
<td>.344</td>
<td>.353</td>
<td>.782</td>
<td>.701</td>
<td>.187</td>
<td>1.000</td>
<td>.231</td>
</tr>
<tr>
<td>Fe = Var 8</td>
<td>.797</td>
<td>.955</td>
<td>.928</td>
<td>.266</td>
<td>.666</td>
<td>.962</td>
<td>.231</td>
<td>1.000</td>
</tr>
</tbody>
</table>
labile forms of these elements have leached from the upper horizons. Therefore, we ascribe these concentrations to external source. The dendrogram (Figure 3b) can be subdivided into two clusters, again supporting the principal component analysis and the heavy metals depth distribution.

In the Gleyic Luvisol (Control soil profile – Figure 1c, Tables 6 and 7, Figure 3c) we observe different loadings, as compared with the technogenic soils. Again, the elements load two principal components with eigenvalues > 1 explaining 64.3% and 28.4% of the total variance 92.7%. Chromium, nickel, cobalt and iron load the 1 PC, similarly to other studies and are generally of lithogenic origin. Copper and zinc are most probably of both lithogenic and bio(pedo)genic origin, while Pb exhibits only a slight loading (a smaller correlation coefficient) of the second component implying influence of different factors on its distribution and can originate from both anthropogenic and lithogenic sources. Mn loads the first PC, however with an opposite sign, i.e. its concentration increases in the uppermost biogenic horizons, therefore implying a biogenic source. The cluster analysis supports the principal component analysis, as Mn occupies the farthest branch of the second group of elements comprising two subgroups: Cu, Zn, Pb (subgroup 1) and Mn (subgroup 2).

Source related organic compounds in the soil horizons
Some xenobiotics and source specific compounds were detected in our previous study (Atanassova et al., 2011) in the technogenic B horizons where anthropogenic sources were suspected for Fe, Mn, Pb (Figure 2):
• exo-tricyclo[5.2.1.0(2.6)]decane C_{10}H_{16} considered a component fuel for use in pulse-detonation engines PDEs.
• 1,2-dihydroxyacenaphthylene, a polycyclic aromatic hydrocarbon derivative was detected in B_u and B_{gu} horizons and might be a contaminant metabolite.
• 4-methyl-4-hydroxy-2-pentanone is released to the environment as a result of its use as a solvent, additive or synthetic intermediate for many materials. However, it can originate from natural sources, as well. It was also found to be a component of the antibiotic produced by a soil bacterium, \textit{Intrasporangium} strain N8, with antibacterial activity against both Gram-positive and Gram-negative bacteria. Bioassay results showed activity against both mammalian and plant pathogenic bacteria (Okudoh and Wallis, 2012).

Table 7
Component matrix for the control soil profile

```
<table>
<thead>
<tr>
<th>Component</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu = Var 1</td>
<td>-.197</td>
<td>.968</td>
</tr>
<tr>
<td>Cr = Var 2</td>
<td>.950</td>
<td>-.235</td>
</tr>
<tr>
<td>Ni = Var 3</td>
<td>.982</td>
<td>.156</td>
</tr>
<tr>
<td>Pb = Var 4</td>
<td>-.827</td>
<td>.279</td>
</tr>
<tr>
<td>Zn = Var 5</td>
<td>-.094</td>
<td>.990</td>
</tr>
<tr>
<td>Co = Var 6</td>
<td>.989</td>
<td>.145</td>
</tr>
<tr>
<td>Mn = Var 7</td>
<td>-.769</td>
<td>-.398</td>
</tr>
<tr>
<td>Fe = Var 8</td>
<td>.987</td>
<td>.136</td>
</tr>
</tbody>
</table>
```

Other source specific compounds
• iso-propyl myristate was attributed to plant sources but may also be of a fungal origin. It was observed to be a component of emitted VOCs by \textit{Lactobacillus plantarum}, wood-pathogenic fungi (El-Fouly et al., 2011). It was detected in all the horizons of the soils studied (Figure 2).

We observed that persistent organic pollutants were either biodegraded following nearly 5 years after sludge deposition or incorporated in bound residues in the soil profiles, therefore representing < 0.1 % of total peak area of analyzed components under the experimental conditions specified.

Table 6
Correlation matrix of heavy metals for the control soil

```
<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Cr</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>Co</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu = Var 1</td>
<td>1.000</td>
<td>-.447</td>
<td>-.026</td>
<td>.356</td>
<td>.993</td>
<td>-.049</td>
<td>-.154</td>
<td>-.049</td>
</tr>
<tr>
<td>Cr = Var 2</td>
<td>-.447</td>
<td>1.000</td>
<td>.875</td>
<td>-.750</td>
<td>-.344</td>
<td>.898</td>
<td>-.740</td>
<td>.888</td>
</tr>
<tr>
<td>Ni = Var 3</td>
<td>-.026</td>
<td>.875</td>
<td>1.000</td>
<td>-.819</td>
<td>.073</td>
<td>.998</td>
<td>-.765</td>
<td>1.000</td>
</tr>
<tr>
<td>Pb = Var 4</td>
<td>.356</td>
<td>-.750</td>
<td>-.819</td>
<td>1.000</td>
<td>.304</td>
<td>-.794</td>
<td>-.280</td>
<td>-.820</td>
</tr>
<tr>
<td>Zn = Var 5</td>
<td>.993</td>
<td>-.344</td>
<td>.073</td>
<td>.304</td>
<td>1.000</td>
<td>.054</td>
<td>-.270</td>
<td>.051</td>
</tr>
<tr>
<td>Co = Var 6</td>
<td>-.049</td>
<td>.898</td>
<td>.998</td>
<td>-.794</td>
<td>.054</td>
<td>1.000</td>
<td>-.801</td>
<td>.999</td>
</tr>
<tr>
<td>Mn = Var 7</td>
<td>-.154</td>
<td>-.740</td>
<td>-.765</td>
<td>.280</td>
<td>-.270</td>
<td>-.801</td>
<td>1.000</td>
<td>-.770</td>
</tr>
<tr>
<td>Fe = Var 8</td>
<td>-.049</td>
<td>.888</td>
<td>1.000</td>
<td>-.820</td>
<td>.051</td>
<td>.999</td>
<td>-.770</td>
<td>1.000</td>
</tr>
</tbody>
</table>
```
Studied were soil profiles (0-200 cm) from the area of a print and paint industrial plant near Elin Pelin, Bulgaria under processed sludge application. In the soil under sludge application most of the heavy metals have anthropogenic sources. The heavy metals Cu, Cr, Ni, Zn and Co originate from the sludge. Pb, Mn and Fe come from another industrial source as their contents are elevated in the technogenic B1 horizons of the soil profile. In the soil profile with no sludge addition all the elements have anthropogenic sources, as their concentrations decrease along the soil depth with some elements, such as Zn, Cu, and especially Mn and Pb showing elevated contents in the middle part of the soil profile. In the control soil, chromium, nickel, cobalt and iron are generally of lithogenic origin, while Cu, Zn, Mn have bio(pedo)genic sources. The anthropogenic-technogenic character of heavy metal sources is confirmed by some contaminant metabolites detected in the technogenic-technogenic horizons of the Technosols.

Conclusions

References


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