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Atmospheric deposition in an urban area: implications for assessing the effects of hazardous air pollutants

A. Bouzonville, P. Elsass, F. Elsass and S. Atkins

Editor’s Note: Adrian Bouzonville was the winner of the Young Achievers Award at the CASANZ Conference in Auckland. This paper is an expanded version of his conference presentation.

ABSTRACT

Pollutants emitted to the atmosphere in urban areas have indirect effects through deposition onto the ground, which, over time, could negatively affect the quality of soil, plants, water and groundwater. In this baseline study, evaluation of topsoil contamination in an urban area of France has been carried out to correlate concentrations observed in the soil with the local air emission sources. The analytical program is an extensive study carried out over a 200 km² area and the results confirm pronounced anthropogenic contributions to the geochemical background for some metals (Cu, Zn, Pb, and Hg) over the entire area under assessment. In addition, PAH concentrations in topsoil have been noted to be significantly higher around heavily trafficked areas, confirming the contribution of road traffic. The contribution of domestic combustion and industrial sources has also been highlighted with elevated concentrations of dioxins and furans; with some sites in exceedance of current international soil guidelines. The results confirm the significant contribution of anthropogenic deposition from former and present-day industrial and road traffic sources to soil composition in an urban area. The high concentrations of trace metals and other hazardous pollutants in many urban soils in inner-city areas give rise to concerns about potential human health effects through ingestion of soil and vegetables grown locally.

Keywords: contamination, urban, topsoil, air pollutants, deposition

INTRODUCTION

It is widely recognised that precipitation scavenging, dry deposition, and re-suspension are significant mechanisms affecting the transport of hazardous air pollutants (Koester et al. 1992, Kaupp and McLachlan 1998). The concentration of trace elements in soils has been extensively investigated over rural and agricultural areas (Baize 1997; Baize 2010) whereas atmospheric aerosols composition and characterisation are mainly investigated in urban areas (Elssas et al. 2006). The contribution of atmospheric deposition to the soil is therefore of great scientific interest and has become a major environmental concern in the vicinity of industrial plants as well as at a global scale.

An assessment of soil quality has been carried out over the Urban Community of Strasbourg (CUS), France, which is a major industrial and transport node with poor air quality in a sensitive natural environment (aquifer around 2 m below ground level) extensively used for domestic and large scale agriculture. The study aims to provide data to evaluate potential risks to public health.

The study presented here relates to the analysis of soil samples from 20 sites for metallic trace elements, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), volatile organic compounds (VOCs), agrochemical products, dioxins and furans.

The results of this study are then discussed comparing the evolution of regulations in France with the applicable New Zealand regulations for assessing the effects of hazardous air pollutants or contaminated land.

ENVIRONMENTAL SETTINGS

Physical and climatic setting

Strasbourg is located in the Alsace province in the northeast corner of France. It is the eleventh largest city in France with a population of around 450,000. The Urban Community of Strasbourg (CUS) extends over a 300 km² area. Strasbourg is situated on the bank of the Rhine River, which forms the international border with Germany. The Rhine valley forms a natural and industrial corridor between the Vosges mountains (25 km West) and the Black Forest (20 km East).

Due to its location between two mountain ranges, winds are often deflected, particularly the predominant westerly winds. In Alsace, the climate is temperate (continental humid climate, classified as Cfb Climate) which is similar to the New Zealand climate according to the Köppen-Geiger classification updated by Peel et al. (2007).

The average annual precipitation is low (632 mm y⁻¹) and mainly occurs in the form of snow (30 days y⁻¹) or violent storms (29 days y⁻¹) typically in early and late summer. A significant temperature range (-15°C in winter and +35°C in summer) occurs over the year. Dominant winds (wind NNE-SSW) are not strong (average of 2.9 m s⁻¹ over 10 years measured at the airport, located out of the city) and pollution does not disperse well, especially during winter foggy days (56 days y⁻¹) when a relatively low inversion layer often exists. The number of sunshine hours is below the national average around 1640 h y⁻¹ (Météo France 2008).

Geochemistry and geology

The CUS area geology (BRGM 1971) comprises the main Rhine riverbed (mainly constituted of sands and gravels from the Rhine covered by overflow silts), a layer of loess in the North-West and the riverbed of the Bruche (composed of gravels and silts from the Vosges).

However, the surface soils in the city mainly consist of modified and mixed soils with some anthropogenic residues. Former and current industrial sites along with activities likely to have contaminated the soil are extensively identified and listed by the national government (BRGM 2011a, b).

Air pollutant emission sources

Strasbourg is an important centre for manufacturing and engineering, as well as road (A4, A35 and A351 motorways), rail and river transport. The port of Strasbourg is the second largest on the Rhine. The main industrial activities identified (MEDD 2011a,b) as having a significant discharge of contaminants to air are: thermal power stations, printing industries, paper mill industries, petroleum refineries, petrol storage depots, breweries, industrial and domestic waste incinerators, metal treatment and manufacturing, wastewater treatment. The main heavy industries are located adjacent to the Rhine. Two significant thermal power stations no longer operational are also reported (MCC 2011). On the German (east) bank of the Rhine, the main industries are steelworks and a biomass power plant. Solid fuel home heating is carried out in many homes which also contributes to air pollution in the area. The locations of the main air pollutant emission sources are presented in Figure 1.
ATMOSPHERIC DEPOSITION IN AN URBAN AREA

DESIGN OF THE STUDY

Twenty sites were sampled over the entire area without considering their proximity to the potential air pollutant emission sources: 9 vegetable gardens (labelled JF) and 11 public parks (labelled PA). The locations of key sites are shown in Figure 1. Within these sites, the sampling locations selected were in areas covered with grass, subjected to normal rainfall (i.e. not below a tree) and without any treatment or modification based on historical assessment prior to sampling.

Top soils were sampled using a hand core drill after removing the surface grass (light scraping). Sampling methodologies were adapted from relevant standards (AFNOR 1992; Laperche and Mossmann 2004; INVS 2005) and analytical specifications for the different elements. The main aspects included:

- **Metals**: creation of a composite sample (US EPA 2007) from 4 individual samples over a 2 x 2 m square;
- **Polycyclic aromatic hydrocarbons (PAHs)**, polychlorinated biphenyls (PCBs), volatile organic compounds (VOCs) and agrochemical products: extraction of 2 samples at 0-25 cm depth and storage in a glass bottle without breaking the core;
- **Dioxins and furans**: sampling at 0-10 cm depth and storage in a glass bottle without breaking the core.

All samples were kept in an icebox below 4°C and sent to the laboratories for analysis within 24 hours. Testing of the samples was carried out by laboratories accredited by the French Committee of Accreditation, using relevant analytical methods (inductively coupled plasma atomic emission spectroscopy (ICP-AES), cold vapour atomic absorption spectrometry (CV-AAS), electrothermal atomic absorption spectrometry (ET-AAS), high resolution gas chromatography (HRGC) and high resolution mass spectrometry (HRMS)).

On site, semi quantitative evaluation was carried out with a portable X-Ray Fluorescence apparatus (Niton® XL-723S). Following the specific calibration of the instrument (Laperche 2005), and a cross comparison with the analytical results, only a few elements (Zr, Sr, Pb, Zn, Fe) were considered to have sufficient precision and consistency to justify statistical analysis. For these elements, an analysis was carried out to compare the concentrations observed in the soil surface (top of the core) with concentrations at depth (side of the core at a depth of 5 cm).

RESULTS AND ANALYSIS

**Metals**

Metal concentrations observed in top soil are presented in Table 1. For a few elements (As, Co, Cr, Ni), statistical analysis indicated that the coefficient of variation (CV) was low and therefore the concentrations followed a normal distribution. Previous geochemical investigations in the area (Elsass and Kramers 2003) confirmed that the observed concentrations were close to the geochemical background and could be significant for some chemicals (median concentration for Cr is 61 mg kg⁻¹ dry wt compared to the median concentration in the top soil across France which is 38.3 mg kg⁻¹ dry wt, as described by Baize (2010)).

For other elements (Cu, Hg, Pb, Zn), the coefficient of variation was higher with a few high values above international guidelines. This is likely to be due to the geochemical background being affected by an anthropogenic contribution as similarly demonstrated in New Zealand (Kennedy 2008).

Pb is a contaminant of concern due to historic diffuse emissions of fuel containing tetraethyl lead (between 1980 and 2000). However, a link between the proximity to the main roads and the highest Pb concentrations was not established as three of the samples (JF_03, JF_09, PA_09) with the highest lead concentrations were from sites located away from main roads.

Although the 0-25 cm layer is commonly used to assess the top soil contamination (Laperche and Mossmann 2004), evaluation of metal concentrations at different depths was carried out on site to provide a vertical profile. Correlation graphs for XRF analysis

![Figure 1. Location of the sampling sites based on layers from OpenStreetMap (2011)](image-url)
## Table 1: Metal concentrations observed in topsoil

<table>
<thead>
<tr>
<th>Elements</th>
<th>As</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Li</th>
<th>Ni</th>
<th>Pb</th>
<th>Sr</th>
<th>V</th>
<th>W</th>
<th>Zn</th>
<th>Zr</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limit of Quantification (LQ)</td>
<td>5</td>
<td>2</td>
<td>5</td>
<td>10</td>
<td>5</td>
<td>0.1</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>5</td>
<td>20</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sites (JF = Vegetable Garden / PA = Public Park)</th>
<th>JF 01 ML 1</th>
<th>JF 02 ML 1</th>
<th>JF 03 ML 1</th>
<th>JF 04 ML 2</th>
<th>JF 05 ML 1</th>
<th>JF 06 ML 2</th>
<th>JF 07 ML 1</th>
<th>JF 08 ML 2</th>
<th>JF 09 ML 2</th>
<th>PA 01 ML 2</th>
<th>PA 02 ML 1</th>
<th>PA 03 ML 2</th>
<th>PA 04 ML 2</th>
<th>PA 05 ML 2</th>
<th>PA 06 ML 1</th>
<th>PA 07 ML 1</th>
<th>PA 08 ML 1</th>
<th>PA 09 ML 2</th>
<th>PA 10 ML 1</th>
<th>PA 11 ML 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals concentrations in the soil samples [mg kg⁻¹ dry wt]</td>
<td>8</td>
<td>&lt; LQ</td>
<td>12</td>
<td>72</td>
<td>36</td>
<td>&lt; LQ</td>
<td>42</td>
<td>30</td>
<td>58</td>
<td>193</td>
<td>30</td>
<td>252</td>
<td>196</td>
<td>234</td>
<td>274</td>
<td>7.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of quantification</td>
<td>20</td>
<td>3</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
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<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Minimum</td>
<td>6</td>
<td>&lt; LQ</td>
<td>9</td>
<td>46</td>
<td>18</td>
<td>&lt; LQ</td>
<td>26</td>
<td>15</td>
<td>16</td>
<td>83</td>
<td>29</td>
<td>22</td>
<td>65</td>
<td>105</td>
<td>7.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum</td>
<td>20</td>
<td>2</td>
<td>15</td>
<td>132</td>
<td>111</td>
<td>0.9</td>
<td>44</td>
<td>35</td>
<td>405</td>
<td>274</td>
<td>57</td>
<td>38</td>
<td>330</td>
<td>411</td>
<td>8.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Arithmetic mean (μ)</td>
<td>11.2</td>
<td>&lt; LQ</td>
<td>11.7</td>
<td>68.3</td>
<td>45.4</td>
<td>0.3</td>
<td>34.7</td>
<td>26.1</td>
<td>125.3</td>
<td>177.3</td>
<td>45.7</td>
<td>30.1</td>
<td>152.5</td>
<td>223.2</td>
<td>7.9</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Standard deviation(σ)</td>
<td>3.4</td>
<td>-</td>
<td>1.7</td>
<td>19.4</td>
<td>26.9</td>
<td>0.2</td>
<td>4.5</td>
<td>5.2</td>
<td>101.6</td>
<td>50.2</td>
<td>7.9</td>
<td>4.6</td>
<td>86.3</td>
<td>96.4</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Coefficient of variation (CV)</td>
<td>0.3</td>
<td>-</td>
<td>0.1</td>
<td>0.3</td>
<td>0.6</td>
<td>0.7</td>
<td>0.1</td>
<td>0.2</td>
<td>0.8</td>
<td>0.3</td>
<td>0.2</td>
<td>0.6</td>
<td>0.4</td>
<td>0.0</td>
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NZ NES SCVs (health) | As (pH 5) | Cd (pH 5) | Cr(VI) | Inorganic Hg comp. | Inorg. Pb | from MfE (2011) |
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<tbody>
<tr>
<td>Rural residential / lifestyle block 25% produce</td>
<td>17</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
<td>- 160</td>
<td>-</td>
</tr>
<tr>
<td>Residential 10% produce</td>
<td>20</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>- 210</td>
<td>-</td>
</tr>
<tr>
<td>High-density residential</td>
<td>45</td>
<td>230</td>
<td>-</td>
<td>-</td>
<td>- 500</td>
<td>-</td>
</tr>
<tr>
<td>Recreational</td>
<td>80</td>
<td>400</td>
<td>-</td>
<td>-</td>
<td>- 880</td>
<td>-</td>
</tr>
</tbody>
</table>

Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health

### Agricultural

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### Residential / parkland

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</table>
indicated that for Fe there was an increase in concentration with depth in some samples (Figure 2) and in a small number of localised areas distributed over the entire area for Pb (Figure 3), with a lower tendency for Sr and Zr. Cu and Zn results showed no clear trend. Uncertainties on the XRF analysis were not calculated in that study but are generally within ±20% for these elements in soil as already investigated by Lapereche and Mossmann (2004) and Bouzonville et al. (2008).

The leaching of metals is hard to quantify over such a wide area as the mobility of chemical elements is also affected by other parameters (pH of the soil and the rain, partition coefficient as described in US EPA (2005)). Rainfall analysis over the city indicates a mainly acidic pH (Herckes et al. 2001), although the sites sampled were slightly basic. The enrichment of Fe with depth could therefore be linked to the higher mobility of that element in the soil with acidic rain. This observation was consistent with less mobile elements (Cu, Zn, Pb) remaining longer in the topsoil.

On some sites (JF_07, PA_07, JF_03), the obvious increase of the Pb concentration with depth was not easy to explain, apart for JF_07 which was located near a major intersection of highways A35 and A351.

**Polycyclic Aromatic Hydrocarbons (PAHs)**

Six different PAHs were analysed (fluoranthene, benzo[a]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indenoepyrone, benzo[g,h,i]perylene). One or more PAHs were detected at 18 of the 20 sites. PAH concentrations observed in top soil are presented in Table 3. The concentration range was wide with high concentrations observed on some sites for BaP (JF_05 : 2070 µg kg\(^{-1}\) dry wt, JF_07 : 1200 µg kg\(^{-1}\) dry wt) but the origin of that concentration was not established.

In order to evaluate the potential road traffic contribution to PAHs, correlation between the total concentration and the proximity to the source was carried out (refer Table 2). The results confirmed that the sites located around heavily trafficked roads had significantly higher concentrations (around one order of magnitude) than in other environments. Calculation of PAHs relative to distribution in soils (Yunker et al. 2002) confirmed the origin from a mixed source of wood based and petroleum based combustion fuels, results similar to those observed in Christchurch, New Zealand (Environment Canterbury 2007).

In addition, the average BaP concentrations were higher around residential areas. This is consistent with the observation that 95% of the ambient BaP in air in this area comes from wood burning for residential heating (ASPA 2010).

**Volatile Organic Compounds (VOCs)**

A range of 50 other VOCs were analysed (VOCs). A few of these compounds have been quantified, DDE and DDT (Pirnie et al. 2006) were still present in the soil. This is also consistent with results found in New Zealand (Boul 1995).

**Non-Dioxin-Like PCBs (NDL-PCBs)**

In evaluating the contamination situation, seven congeners (# 28, 52, 101, 118, 153, and 180) were chosen as indicators for the occurrence of NDL-PCBs. NDL-PCBs were detected over 8 sites but the values were low for most of the sites. The maximum was observed in JF_03 (ΣPCBs of 112.7 µg kg\(^{-1}\) dry wt) but the origin of that concentration was not established.

The distribution of the different congeners over the sites was similar and showed that the Lpcb (Σ cong. 28, 52, 101 = lower chlorinated PCBs) were less represented than the HPCB (Σ cong. 118, 138, 153, 180 = higher chlorinated PCBs) as illustrated in the Figure 4. The relative distribution of the congeners was consistent with other studies on soils in urban areas (UBA 2007). This is likely to be due to the decreasing solubility in water of the higher chlorinated congeners (Shiu and Mackay 1986) which therefore have a lower tendency to leach than the lower chlorinated congeners (FAO 2000).

**Dioxins and furans**

Ten sites were sampled and analysed for polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF). The concentrations are reported in grams of toxic equivalents (TEQ). This method accounts for the differences among the 17 selected compounds by estimating toxicity of the individual dioxin compounds using a toxic equivalency factor (TEF). The 1997 WHO-TEF was used in the study (Van den Berg et al. 1998).

The sites located in a residential area, without any industrial sites in the vicinity.
showed concentrations around 2 pg I-TEQ g⁻¹ which is consistent with the mean values across France which range between 1.9 and 2.2 pg I-TEQ g⁻¹ as described by Bodénan and Michel (2008).

The highest concentrations observed were mainly located close to potential industrial emission sources of dioxins and furans:
- JF_04, 4.3 pg I-TEQ g⁻¹ located in a heavy industrial area surrounded by an incinerator (700m north-east), an oil depot and steel production plant (1000m east);
- PA_11, 6.14 pg I-TEQ g⁻¹ located in a heavy industrial area, 800m north of a waste incinerator;
- JF_03, 8 pg I-TEQ g⁻¹ located in a residential area but around 50m east from a municipal boiler;
- JF_09, 11 pg I-TEQ g⁻¹ located in an industrial area 300m east from a major paper mill.

In some vegetable gardens, the concentrations of PCDD/PCDF observed in the top soil exceeded the international soil guideline values (British Soil Guideline Value: 8 pg I-TEQ g⁻¹ for a residential use based on UK Environment Agency (2009), the German Soil Guideline Value: 5 pg I-TEQ g⁻¹ as described in BLAG (1992) and the Canadian Soil Quality Guideline for the Protection of Environmental and Human Health: 4 pg I-TEQ g⁻¹ for a residential or agricultural use as described in CCME (2007)). This geographical distribution confirmed the contribution of the atmospheric pollutants from local sources and its tendency to have an impact in the direct vicinity of the emission source.

**Results summary**

The results of the study indicated widespread contamination of soil through atmospheric deposition in the urban area. The study highlighted the contribution of the geochemical background over the entire area for some metals (Cu, Hg, Pb, Zn) and pesticides (DDT, slowly breaking down to DDE and DDD).

Higher concentrations of PAHs were noted directly around the main motorways but also around the historical thermal power plants using coal and heavy fuel oil and in the northern part of the city around the oil

### Table 2. Statistics of the PAHs per type of activities around the sites.

<table>
<thead>
<tr>
<th>Total PAHs [µg kg⁻¹ dry w]</th>
<th>Predominant activity in the vicinity of the site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Road traffic</td>
</tr>
<tr>
<td>Minimum</td>
<td>287</td>
</tr>
<tr>
<td>Maximum</td>
<td>42,000</td>
</tr>
<tr>
<td>Average</td>
<td>10,979</td>
</tr>
<tr>
<td>Median</td>
<td>5,744</td>
</tr>
<tr>
<td>Standard deviation(σ)</td>
<td>16,028</td>
</tr>
<tr>
<td>Coefficient of variation (CV)</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### Table 3. Statistics of the PAHs and PCDD/PCDF.

<table>
<thead>
<tr>
<th>Chemical compounds analysed</th>
<th>Unit</th>
<th>Number of detection</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Arithmetic mean</th>
<th>Median</th>
<th>Coefficient of variation (CV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry matter content</td>
<td>%</td>
<td></td>
<td>78</td>
<td>91</td>
<td>85</td>
<td>84</td>
<td>-</td>
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<tr>
<td>Non-Dioxin-Like PCBs (NDL-PCBs)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCB 28</td>
<td>µg kg⁻¹</td>
<td>0</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PCB 52</td>
<td>µg kg⁻¹</td>
<td>2</td>
<td>&lt;2</td>
<td>29</td>
<td>2</td>
<td>-</td>
<td>3.5</td>
</tr>
<tr>
<td>PCB 101</td>
<td>µg kg⁻¹</td>
<td>3</td>
<td>&lt;2</td>
<td>303</td>
<td>16</td>
<td>-</td>
<td>4.2</td>
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<tr>
<td>PCB 118</td>
<td>µg kg⁻¹</td>
<td>4</td>
<td>&lt;2</td>
<td>138</td>
<td>8</td>
<td>-</td>
<td>3.8</td>
</tr>
<tr>
<td>PCB 138</td>
<td>µg kg⁻¹</td>
<td>7</td>
<td>&lt;2</td>
<td>809</td>
<td>43</td>
<td>-</td>
<td>4.2</td>
</tr>
<tr>
<td>PCB 153</td>
<td>µg kg⁻¹</td>
<td>8</td>
<td>&lt;2</td>
<td>887</td>
<td>47</td>
<td>-</td>
<td>4.2</td>
</tr>
<tr>
<td>PCB 180</td>
<td>µg kg⁻¹</td>
<td>5</td>
<td>&lt;2</td>
<td>722</td>
<td>38</td>
<td>-</td>
<td>4.3</td>
</tr>
<tr>
<td>PCB totaux</td>
<td>µg kg⁻¹</td>
<td>8</td>
<td>&lt;2</td>
<td>2,888</td>
<td>154</td>
<td>-</td>
<td>4.2</td>
</tr>
<tr>
<td>Total hydrocarbons and polycyclic aromatic hydrocarbons (PAHs)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FLUORANTHENE</td>
<td>µg kg⁻¹</td>
<td>19</td>
<td>&lt;5</td>
<td>12,900</td>
<td>1,399</td>
<td>247</td>
<td>2.1</td>
</tr>
<tr>
<td>BENZO(B)FLUORANTHENE</td>
<td>µg kg⁻¹</td>
<td>18</td>
<td>&lt;5</td>
<td>10,000</td>
<td>850</td>
<td>140</td>
<td>2.6</td>
</tr>
<tr>
<td>BENZO(K)FLUORANTHENE</td>
<td>µg kg⁻¹</td>
<td>18</td>
<td>&lt;5</td>
<td>3,830</td>
<td>419</td>
<td>72</td>
<td>2.1</td>
</tr>
<tr>
<td>BENZO(A)PYRENE</td>
<td>µg kg⁻¹</td>
<td>18</td>
<td>&lt;5</td>
<td>6,720</td>
<td>699</td>
<td>146</td>
<td>2.2</td>
</tr>
<tr>
<td>INDENOPYRENE</td>
<td>µg kg⁻¹</td>
<td>18</td>
<td>&lt;5</td>
<td>4,350</td>
<td>447</td>
<td>81</td>
<td>2.2</td>
</tr>
<tr>
<td>BENZO(GH)PERYLENE</td>
<td>µg kg⁻¹</td>
<td>18</td>
<td>&lt;5</td>
<td>4,100</td>
<td>437</td>
<td>80</td>
<td>2.1</td>
</tr>
<tr>
<td>Total PAHs</td>
<td>µg kg⁻¹</td>
<td>19</td>
<td>&lt;5</td>
<td>41,900</td>
<td>4,254</td>
<td>750</td>
<td>2.2</td>
</tr>
<tr>
<td>Total Hydrocarbons</td>
<td>mg kg⁻¹</td>
<td>20</td>
<td>3</td>
<td>573</td>
<td>54</td>
<td>21</td>
<td>2.3</td>
</tr>
<tr>
<td>Polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCDD/PCDF (pg I-TEQ/g WHO 1997)</td>
<td></td>
<td>10</td>
<td>1.6</td>
<td>11.0</td>
<td>4.2</td>
<td>2.5</td>
<td>0.8</td>
</tr>
</tbody>
</table>
refineries and residential housing using wood fired heating.

Agrochemical products that had been banned for many years were identified over the entire area, similar to the situation for some of these substances in the air. The persistence in topsoil of some pesticides like DDT is significant and therefore has the potential to be reemitted to the atmosphere.

PCDD/PCDF also had significantly higher concentrations in the vicinity of the emission sources (incinerator, paper mill) even though the impact appeared to be restricted to the immediate area surrounding the source. Locating vegetable gardens in the vicinity of these areas should therefore be considered in the light of these results.

**DISCUSSION**

**Uncertainties**
The link between concentrations observed in the soils and long term air discharges is difficult to establish due to the following:
- Databases and emission inventories that have been developed by the regulatory authority (MEDD 2011(a,b)) to assess ambient air quality and long term soil contamination (from dry and wet depositions), do not take into account the emissions from historical contributors or diffuse sources (agriculture, domestic heating). In some cases, the contribution might be significant, as the former industrial practices (coal thermal power stations) were not as well regulated as they are now.
- Industrial accidents should also be taken into account as gas releases or fire smoke may have a significant impact on air quality. Over 71 accidental industrial fires are listed in the ARIA Database (MEDD 2011(c)) for Strasbourg with likely associated emissions of heavy metals, PCDD/PCDF and other similar pollutants.
- Topsoil is an appropriate medium to quantify the deposition of air contaminants (Durif 2004) over a long term exposure. However, the integrity of the topsoil (absence of modification or local contamination) is difficult to guarantee, so historical review of the site and observations made while sampling are critical to ensure appropriate samples are collected.

**Transposition to New Zealand**
As in New Zealand, sources of discharge to air in Strasbourg are mainly related to industry, transport and residential wood burning (winter). The general climate observed in New Zealand is similar to the one observed in Alsace and therefore, the transport of pollutants into the atmosphere is ruled by the same mechanisms and phenomena (winter fog, low inversion layer). Whereas vegetable gardens are often grouped together in Strasbourg in community allotments, New Zealand tends to have more individual housing with gardens, including vegetable gardens, within the city boundaries and sometimes these are close to industrial areas or heavily trafficked highways.

Similarities in the sources of emissions, the transfer (transport and deposition) of pollutants, the population distribution and the use of land in Strasbourg suggests that the results of this study are likely to be relevant to the situation in New Zealand.

**Health risk assessment considerations**
The study also demonstrated the importance of taking into account concentrations observed in soil through deposition as part of the health risk assessment process. To evaluate the potential health effects of an air discharge, practitioners often compare the predicted values with threshold ambient air values (MFE 2011)). This study indicated that deposition of air contaminants is significant over time and therefore the ingestion of various contaminants from the soil or from vegetables grown locally needs to be taken into account.

Furthermore, the measured concentrations have highlighted local characteristics of soils in this particular area in relation to the geochemical background (As, Cr) and anthropogenic sources (Pb, B[a]P, dioxins and furans), which need to be considered in the exposure calculations as part of the evaluation process.

Since 2003, Environmental Impact Assessment is required in France to quantify human health risk (INERIS 2003), taking into account the toxicological effects of different substances as well as relevant exposure pathways. The assessment of effects from air discharges is no longer restricted to the contaminants discharged to air by the activity but should encompass:
- the deposition of contaminants onto the soil and vegetables; as well as
- the wide range of contaminants present in the urban environment, whose chronic effects are likely to be cumulative.

Unlike the NZ approach (MFE 2010), the French regulation on contaminated land changed in 2007 from the comparison of results with guidelines and threshold values related to the use of land to a case by case approach that takes into account the local geochemical background together with a focus on the differences between the background and the site observations (MEDD 2007).

The results of this study provide valuable information in the assessment of the local geochemical background of soils which is significantly different from the national or regional background. It also demonstrates that atmospheric contributions need to be taken into account during contamination assessments, as the products observed in soils are made from a wide range of elements which might be persistent in the topsoil. These results could also be transposed to other cities with similar land uses.

Over the last ten years, the French regulations changed significantly to require a uniform approach when quantifying human health effects of emissions from industry requiring consent and from contaminated land. That change of approach is the result of the acknowledgement that in several locations, and especially in urban areas, people are exposed over time to multiple substances through multiple exposure pathways and that the effects are often cumulative.

Therefore to assess the effects and quantify the health risk for a population (whatever the situation) a specific conceptual scheme needs to be developed justifying the prevalence of the different pathways for the different substances. An example of a conceptual scheme showing the significant exposure pathways highlighted by this study is presented in Figure 5.

Guideline values, threshold values or standards are therefore no longer applicable as these are developed for specific and non exhaustive exposure pathways (as detailed in MFE 2010, TCEQ 2006 and CCME 1999) which often differ from local situations.

Building a site specific conceptual scheme allows consideration to the contribution of the assessed source of contamination or discharge to air, as well as the existing local background (ambient air and concentration in the soil, vegetables,
ground water...) and the local use of the site. Exclusion of an exposure pathway should then be discussed along with the uncertainty and potential impact on the quantification of human health risk.

CONCLUSION

The results of the investigations indicated widespread contamination of soil through atmospheric deposition in the urban area of a wide range of chemicals. The results confirmed the presence of significant concentrations of chemicals in the vicinity of the emissions sources, in addition to the contribution from diffuse sources over a wider area. The persistency of some chemicals (lead, agrochemical products) in soil has also been highlighted.

Populations in urban areas are increasingly exposed to multiple hazardous substances through multiple pathways. It is therefore necessary to review guidelines and policies to take into account that fact and reduce potential health risks for the people living in these areas.

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Figure 5. Example of a conceptual scheme to assess the exposure in an urban area


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