

SOIL CONTAMINATION THROUGH ATMOSPHERIC DEPOSITION IN AN URBAN AREA

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Abstract

Pollutants emitted to the atmosphere in urban areas have indirect effects through deposition on 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 over a 200km² 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, some sites in exceedance of current international soil guidelines. The results confirm the significant contribution of anthropogenic deposition from former and actual 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: surface soil contamination, urban site, atmosphere, deposition.

1. Location and methodology

1.1. Study location

1.1.1. Location

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).

1.1.2. Meteorological conditions

Due to its location between two mountain ranges, winds coming from either direction are often deflected. In Alsace, weather conditions are temperate (continental humid climate, classified as

a Cfb Climate, as in New Zealand according to the Koeppen-Geiger classification updated by Peel *et al.* in 2007).

The average annual precipitation is low (632 mm/year) and mainly occurs in the form of snow (30 days/year) or violent storms (29 days/year) 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 (2.9 m/s in average 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/year). The number of sunshine hours is below the national average around 1640 h/year (Meteo France 2008).

1.1.3. Geochemistry and geology of the area

The CUS area geology (BRGM 1971) comprises the main Rhine riverbed (mainly constituted of sands and gravels from the Rhine covered by overflowing silts), a layer of loess in the NW and

the riverbed of the Bruche (made of gravels and silts from the Vosges).

However, the surface soils mainly consist of modified and mixed soils with some anthropogenic residues.

1.2. 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 2011) as having a significant discharge of contaminants to air are: thermal power stations, printing industries, paper mill industries, petroleum refineries, petrol storage depots, beer breweries, industrial and domestic waste incinerators, metal treatment and manufacturing, wastewater treatment. The main heavy industries are located adjacent to the Rhine. A few former significant thermal power stations are also reported (MCC 2011). On the German (east) bank of the Rhine, the main industries are steelworks plants and a biomass power plant. Solid fuel home heating is carried out which also contributes to air pollution in the area. The location of key sites is shown in Appendix A.

1.3. Soil contamination assessment

1.3.1. Location and use of the sites

Twenty sites were sampled: 9 vegetable gardens (labelled JF) and 11 public parks (labelled PA). Within these sites, the sampling locations selected were in areas covered with grass, under normal rainfall (not below a tree) and without any treatment or modification based on historical assessment. The locations of the sites are shown in Appendix A.

1.3.2. Soil sampling methods

Soils were sampled using a hand core drill after removing the surface grass (light scratching). Sampling methodologies were adapted according to the applicable standards (AFNOR 1992, Laperche & Mossmann 2004) and the analytical specifications for the different elements. The main aspects are:

- 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 (only for 10 sites): 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.

1.3.3. Laboratory analysis and standards

Testing of the samples was carried out by French Committee of Accreditation accredited laboratories, using applicable analytical methods (ICP-AES, CV-AAS, ET-AAS, and HRGC-HRMS).

1.3.4. X-Ray Fluorescence (XRF) analysis and calibration

Semi quantitative evaluation was carried out with portable X-Ray Fluorescence (Niton® XL-723S). After a specific calibration (Laperche 2005), and a cross comparison with the analytical results, only a few elements (Zr, Sr, Pb, Zn, Fe) were considered to have a reliable quantification to justify statistical analysis. For these elements, analysis was carried out to compare the difference between the concentrations observed in the surface of the soil (top of the core) and at depth (side of the core between 0-5 cm).

2. Results and analysis

2.1. Metals

2.1.1. Total concentration

For a few elements (As, Co, Cr, Ni), statistical analysis indicates that the coefficient of variation (CV) is low and therefore the concentrations follow a normalized distribution. Previous geochemical investigations in the area (Elsass P. & Kramers E. 2003) confirm that the observed concentrations are close to the geochemical background.

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

Pb is a contaminant of concern due to historic diffuse emissions of fuel containing Tetraethyllead (between 1980 and 2000). However, a link between the main roads and the highest Pb concentrations was not established (JF_03: 405 mg/kg dry wt, JF_09: 328 mg/kg dry wt and PA_09: 196 mg/kg dry wt are located away from the major highways).

2.1.2. Depth profiling

Correlation graphs for XRF analysis indicate that there is a significant increase in concentration with the depth compared to the surface for Fe (Figure 1)

and locally for Pb (Figure 2), a lower tendency for Sr and Zr. Cu and Zn results show no clear trend.

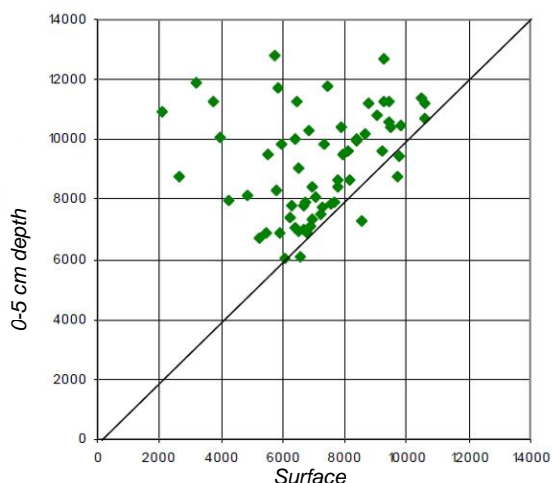


Figure 1. Enrichment of Iron with depth

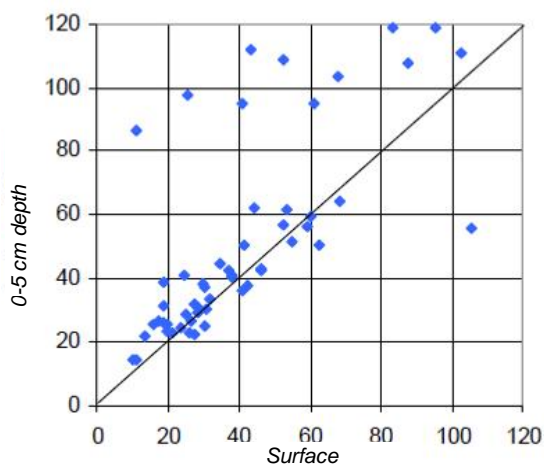


Figure 2. Enrichment of Lead with depth at a few locations

Rainfall analysis over the city indicates mainly acid pH (Herckes *et al.* 2001). The enrichment of Fe with the depth could therefore be linked to the higher mobility of that element in the soil with acid rain. This observation is consistent with lower mobilizable 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 is not explained, apart for JF_07 which is located below a major road traffic area (A35 and A351).

Nevertheless, the concentration on the surface is not higher than the one at depth which confirms that the Pb contribution from air deposition is not as strong as it was in the past.

2.2. Polycyclic Aromatic Hydrocarbons (PAHs)

Six different PAHs were analysed (Fluoranthene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indepyrrene, Benzo[g,h,i]perylene) One or more of PAHs were detected at 18 of the 20 sites. The concentration range is wide with significantly high concentrations observed on some sites for B[a]P (JF_05 : 6720 µg/kg dry wt, JF_07 : 2070 µg/kg dry wt, JF_01 : 1200 µg/kg dry wt).

The analysis of the proportion of the different substances over the total PAHs concentrations highlights a constant distribution over all the sites' concentration. Fluoranthene is, on average, 32% of the total PAHs, while Benzo[b]fluoranthene counts for 19% and B[a]P for 18%. This is consistent with concentrations observed in ambient air monitoring (ASPA 2010), indicating the PAHs may have a common origin.

In order to evaluate the potential road traffic contribution to PAHs, correlation between the total concentration and the vicinity of the sites has been carried out (refer Table 1).

| Total PAHs µg/kg dry wt | Predominant activity in the vicinity of the site | | | |
|-------------------------------|--|---------|---------|-----------|
| | Road traffic | Indust. | Natural | Resident. |
| Minimum | 287 | <5 | 6.3 | 310 |
| Maximum | 42000 | 2530 | 2880 | 4560 |
| Average | 10979 | 885 | 1011 | 1786 |
| Stand Dev | 16028 | 1426 | 1276 | 1682 |
| CV | 1.5 | 1.6 | 1.3 | 0.9 |
| Median | 5744 | 124 | 579 | 772 |

Table 1. Statistics of the PAHs per type of activities around the sites

The results confirm that the sites located around heavily trafficked roads have significantly higher concentrations (around one order of magnitude) than in other environments. Calculation of PAHs relative to distribution in soils (Yunker *et al.* 2002) confirms the origin from mixed source of wood based and petroleum based combustion fuels, as already observed in Christchurch, New Zealand (Environment Canterbury 2007).

In addition, the average concentrations are higher around residential areas. This is consistent with the observation that 95% of the ambient B[a]P in air comes from residential wood burning (ASPA 2009).

2.3. Volatile Organic Compounds (VOCs)

A range of 50 other VOCs were analysed on all the sites including among others: BTEX, chloroform, styrene, naphthalene. However, the Limit of Quantification (LQ) between 20 and 100 µg/kg dry wt depending on the product, was too high to allow these substances to be quantified. Therefore, these compounds were not considered further in the study.

2.4. Agrochemical products

Pesticides and insecticides are randomly detected on the sites. However, considering the substances detected, and their location, it can be noted:

- JF_03 showed 26.7 µg/kg dry wt of Dieldrine even though its use has been banned since 1994 (INERIS 2007). Other substances (including Aldrine) are all below the LQ, indicating the usage of Dieldrine at that particular location.
- JF_06 showed 2.6 µg/kg dry wt of 1,2,3-TCB and 5.5 µg/kg dry wt of 1,2,4-TCB. These products have been detected only at this location which is likely to be due to the application of pesticides on the fields nearby (fields located 300m W of the site).
- Hexachlorocyclohexanes (HCH) were always below the LQ (between 2 and 5 µg/kg dry wt) despite previous investigations indicating that some of these pesticides are present in the atmosphere of Strasbourg at a concentration between 345 and 3940 pg/m³ of total g-HCH (Sanusi A. *et al.* 1998).
- On seven sites (JF_02, JF_07, JF_08, PA_02, PA_03, PA_09, PA_10), Dichloro-diphenyl-trichloroethane (DDT), Dichloro-diphenyl-dichloroethylene (DDE) and dichloro-diphenyl-dichloroethane (DDD) have been identified. Only the p,p' isomers of these products have been quantified, corresponding to the technical grade DDT (ATSDR 1994). Despite DDT having been banned as a pesticide in Europe for over 30 years, DDT and its breakdown products, DDE and DDD (Pirnie E. *et al.* 2006) are still present in the soil. This is consistent with results found in New Zealand (Boul 1995).

The quantified elements confirm the persistency of the agrochemical products but also highlight contamination over the entire area, even some distance from the potential agricultural use of the compounds.

2.5. Non-Dioxin-Like PCBs (NDL-PCBs)

In evaluating the contamination situation, six congeners (# 28, 52, 101, 138, 153, and 180) were chosen as indicators for the occurrence of NDL-PCBs. NDL-PCBs were detected over 8 sites but the values are low for most of the sites. The maximum was observed in JF_03, (Σ PCBs of 112.7 µg/kg dry wt) but the origin of that concentration was not established.

The distribution of the different congeners over the sites is similar and shows that the LPCB (Σ cong. 28, 52, 101 = lower chlorinated PCBs) are less represented than the HPCB (Σ cong. 138, 153, 180

= higher chlorinated PCBs) as illustrated in the Figure 3.

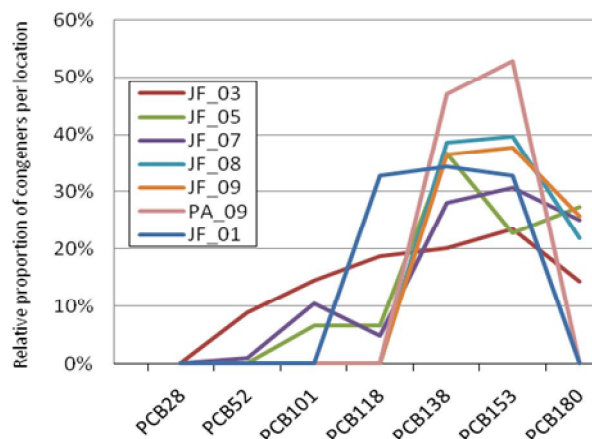


Figure 3. Relative proportion of the 6 congeners

The results are consistent with other results for vegetables (UBA 2007). This is likely to be due to the decreasing solubility in water of the higher chlorinated congeners (Shiu & Mackay 1986) which therefore have a lower tendency to leach than the lower chlorinated congeners (FAO 2000).

2.6. Dioxins and furans

Ten sites have been 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, show concentrations around 2 pg/g (sites JF_01, PA_02, PA_03, PA_04, PA_08 and PA_09 shown in Appendix A).

The highest concentrations observed are mainly located close to potential industrial emission sources of dioxins and furans:

- JF_04, 4.3 pg/g located in an heavy industrial area surrounded by an incinerator (700m NE), an oil depot and steel production plant (1000m E);
- PA_11, 6.14 pg/g is located in a heavy industrial area, 800m N of a waste incinerator;
- JF_03, 8 pg/g is located in a residential area but around 50m E from a municipal boiler;
- JF_09, 11 pg/g is located in an industrial area 300m E of a major paper mill industry.

In some vegetable gardens, the concentrations observed in PCDD/PCDF in the top soil exceed the German soil guideline value (above 5 pg/g I-TEQ, the cultivation of some plants should be avoided as described in UBA 2007). This geographical distribution confirms the contribution of the atmospheric pollutants from local sources and its tendency to have an impact in the direct vicinity of the emission source.

3. Conclusions

3.1. Results highlighted

The results of the study indicate the widespread contamination of soil through atmospheric deposition in the urban area.

The study has highlighted the contribution to the geochemical background over the entire area for some metals (Cu, Hg, Pb, Zn) and pesticides (DDT, slowly breaking down in DDE and DDD).

Higher concentrations of PAHs are 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 refineries and residential housing.

Agrochemical products are identified over the entire area even though the substance has been banned for many years, as is similarly found with substances in the air. The persistency in topsoil of some pesticides like DDT is significant and could therefore be reemitted to the atmosphere.

PCDD/PCDF also have significantly higher concentrations in the vicinity of the emission sources (incinerator, paper mill industry) even though the impact appears 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.

3.2. Identification of the source

The link between the concentration observed in the soils and the long term air discharges is difficult to establish especially because of the following aspects:

- Even if database and inventories are developed by the regulation authority (iREP), the ambient air quality predicted over that area does not take into account the emission from historical contributors or diffuse sources (agriculture). In some case, the contribution might be significant, as the former industrial practices, (coal thermal power stations), were not as 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 c 2011) for Strasbourg with likely associated emissions of PCDD/PCDF and other similar pollutants.

3.3. Health Risk Assessment considerations

3.3.1. Exposure to hazardous air pollutants

The study also demonstrated the importance of taking into account the concentration observed in soil through deposition as part of the health risk assessment process. To evaluate the potential health effect of an air discharge, practitioners often compare the predicted values with threshold values (MfE a 2010). However, 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 of France in relation to the geochemical background (As, Cr) and anthropogenic sources (Pb, B[a]P), which need to be considered in the exposure calculations as part of the evaluation process.

3.3.2. Exposure to contaminated land

Unlike the NZ approach (MfE b 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 difference between the background and the site observations. The results of the study give valuable information in the assessment of local geochemical background of soils which is significantly different to the national or regional background. It also demonstrates that atmospheric contribution needs to be taken into account during the contamination assessment, 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 the same usage.

3.4. Transposition to New Zealand

As in New Zealand, sources of discharge to air in Strasbourg are mainly related to industry, transport and residential wood fire 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,

New Zealand cities are made of houses with gardens, including vegetable gardens inside the city centre and sometime close to the 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 suggest that the results of that study are likely to be relevant to the situation in New Zealand.

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