CHARACTERISATION OF A HYDROCARBON POLLUTED SOIL BY AN INTENSIVE MULTI-SCALE SAMPLING

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ABSTRACT

The Pollut-Eval® is a new on-site analyser of hydrocarbon pollution, which was developed as a complementary measurement tool for industrial polluted soils. The main goal of this study is the validation of this new gauge. This is achieved through the comparison with a standard method (Gas Phase Chromatography) leading to a first effective validation. Another interest of this project is the study of short-distance variability of the hydrocarbon concentrations which is made possible by the Pollut-Eval® gauge. A multi-scale sampling is performed using nested grids, from centimetric to decametric scales. The geostatistical analysis highlights the very high spatial variability at short distances. At last, we complete the study with a comparison between Pollut-Eval® and a geophysical methodology which is less convincing, with some practical problems (relativity of a geophysical analysis for example).

INTRODUCTION

During the diagnosis of a polluted site one is faced with the problem of sampling scheme costs (de Fouquet, 2006). As a result, a number of faster or on-site measurement methodologies (Jeannée and de Fouquet, 2003) have been developed, such as the Pollut-Eval® gauge (Benoit et al., 2008).

LOQUAS (*LO*calisation and *QUA*ntification of organic pollutant in *S*oil) research project includes a multi-scale and multi-method sampling. The sampled areas and measurement methods are first presented. The correlation between the Pollut-Eval® analyses and the standard Gas Phase Chromatography (GPC) method is then examined in order to evaluate the new gauge. Thanks to the simplicity of Pollut-Eval® measurements and their low cost, an intensive sampling is made, which enables a detailed study of the spatial variability of hydrocarbon concentrations, from centimetric to decametric scale. Finally, these measurements are compared with an electrical resistivity survey.

MATERIAL AND METHODS

The Studied Areas

Various sampling phases are performed on two contiguous areas named A and B, belonging to a disused industrial zone polluted by jet fuel hydrocarbons. Figure 1 presents Area B, which is the most intensively sampled. Pollut-Eval® and GPC analyses have been carried out on a surface of 12 x 12 m (named 12m-square) whereas electrical resistivity has been measured on a surface of 26 x 24 m (named 25m-square) and on a larger zone, the "profiles".

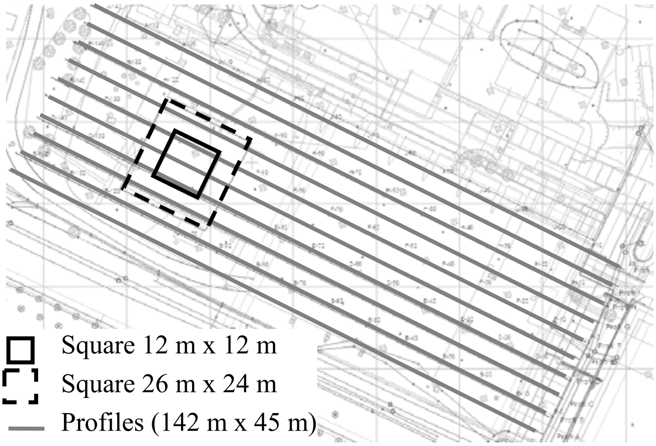

Figure 1: Presentation of Area B.

On Area A, a 30 m side square, Pollut-Eval® and GPC data were measured in order to study the correlation between these two measurement methods.

Measurement Methods and Associated Variables

Gas Phase Chromatographic Analysis

Gas Phase Chromatography is the most widely used physico-chemical method to diagnose hydrocarbon polluted soils and is recommended by the AFNOR (French standards association). It includes a solvent extraction phase and therefore cannot be used on-site. The GPC separates the different volatile pollutants of a 40 g soil sample. The detected hydrocarbons go from seven atoms of carbon (C_7) to forty atoms (C_{40}); the heavier hydrocarbons are not detected. The sum of these hydrocarbons concentrations is named Q_t. On Area B, all these measurements belong to the 12m-square.

Pollut-Eval® Analysis

Unlike traditional methods the new gauge can be used on-site to quantify the hydrocarbon soil pollution because it does not require any pre-treatment. The analysis consists of a pyrolysis of a 100 mg sample. The soil sample is heated from 50°C to 650°C with a 50°C/min gradient. The various organic compounds are then identified according to their boiling points and quantified with a pre-calibrated flame ionisation detector; the analysed "hydrocarbon cut" (also called Q_t) goes from C_7 to more than C_{40}. The measurements are made on Area A (from two different gauges, belonging to IFP and ARCADIS) and on the 12m-square of Area B.

Electrical Resistivity Survey

The electrical resistivity method is based on the variation of the electrical potential measured between two electrodes. It characterises the flow of free electric charge in the soil (electron, ion). The greater the resistivity, the lower the hydrocarbon pollution.

Two Geophysical surveys were performed on Area B as follows (Figure 9):

- Profiles, at the site scale: 10 electrical panels located in the 142 m x 45 m rectangle to build a two dimensional tomography (grid 5 x 1 m);
- Square, at the decametric scale: the studied area is 26 m long and 24 m width (grid 1 x 1 m) and is centred on the 12 x 12 m reference square to ensure an accurate resolution.

COMPARISON BETWEEN POLLUT-EVAL® AND GPC

Pollution and Quantification Thresholds

For this industrial site, the hydrocarbon concentration of 500 mg/kg is the accepted pollution threshold. In addition Pollut-Eval® and GPC methods have quantification thresholds (values lower than this limit are not reliable) which are important to know. This limit is about 10 mg/kg for the GPC. For the Pollut-Eval® it is about 460 mg/kg which is very close to the pollution threshold. However this quantification threshold is not incompatible with its use on industrial zones as an on-site complementary tool. Moreover it has been proved that this quantification threshold can be reduced if the preventive on-site maintenance is improved (Benoit et al., 2008).

Comparisons between two Pollut-Eval® and GPC Data, on Area A

Area A sampling scheme was designed to compare the two different Pollut-Eval® gauges and each Pollut-Eval® gauge with the GPC method. The results are shown on Figure 2 (each Pollut-Eval® point is the mean of several measurements which ensures a good representativeness). The correlation between the two gauges (2-c) appears to be strong even if there are only seven points. However the linear correlation between the Pollut-Eval® and GPC is quite poor for the second gauge (2-b) and good but strongly influenced by few points for the first one (2-a). We also notice that a low value of one method may be related to a high concentration for the other one, which results in some false sortings (according to the pollution threshold). However below the quantification threshold, these false sortings can come from an imprecise measurement. Then these results do not question the new gauge as an on-site complementary method.

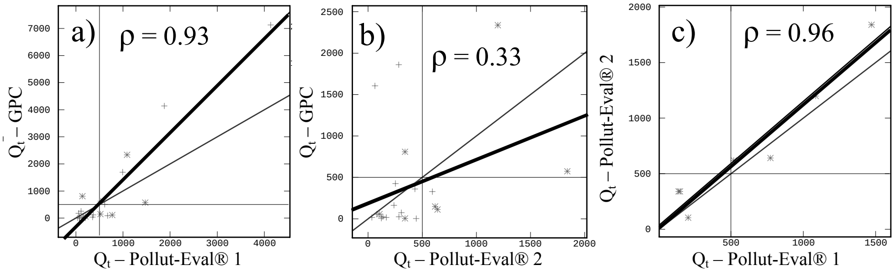

Figure 2: a) and b) Scatter plots between each Pollut-Eval® data set and GPC data set c) Scatter plot between the two Pollut-Eval® data sets (stars: points analysed by both Pollut-Eval® , horizontal and vertical lines: 500 mg/kg threshold, black line: bisector and bold line: linear regression).

ANALYSIS OF THE POLLUT-EVAL® DATA ON AREA B

As one measurement is relatively cheap and the analysed sample's weight is very small, the Pollut-Eval® enables to make a lot of measurements, some of them being very close. But what is the representativeness of such a small sample? On Area B, the representativeness and reproducibility of these on-site measurements are first examined; then a multi-scale variographic analysis is performed.

Representativeness of a Pollut-Eval® Sample

The sampling scheme is nested from distances of 0.02 m up to 12 m (Figure 3). These distances are smaller than those generally used during on-site diagnosis and this enables the study of the representativeness of a sample. Since Pollut-Eval® and GPC analyses are destructive we cannot use exactly the same sample for both of them.

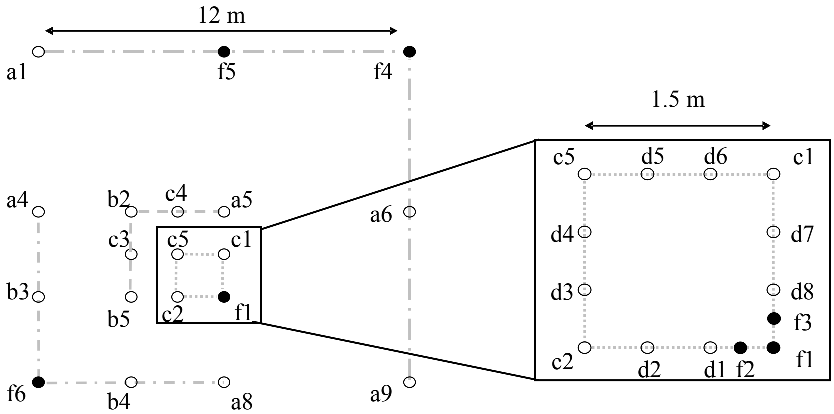

Figure 3: Sampling scheme used for the Pollut-Eval® investigation (left) and zoom on the centre (right). A circle represents a Pollut-Eval® site (● f1 to f6). Dotted lines are used in the geostatistical analysis part.

Each Pollut-Eval® site (about 10 x 10 x 2 cm) is sampled with five or twenty-five (for sites f1 to f6) points (left part of Figure 4) and the residue is kept for the GPC analysis (in grey on Figure 4). The 25-point pattern is assumed to be sufficient to estimate the average hydrocarbon concentration of the complete Pollut-Eval® site. The mean of a 5-point pattern (in black on Figure 4) shows a good correlation with the average of a 25-point pattern (right part of Figure 4). However, if less than 4 samples are taken from the site the correlation with the 25-pattern is poor; this reveals the influence of the analysed support. In the following, the support is designated as 5-pattern and 25-pattern.

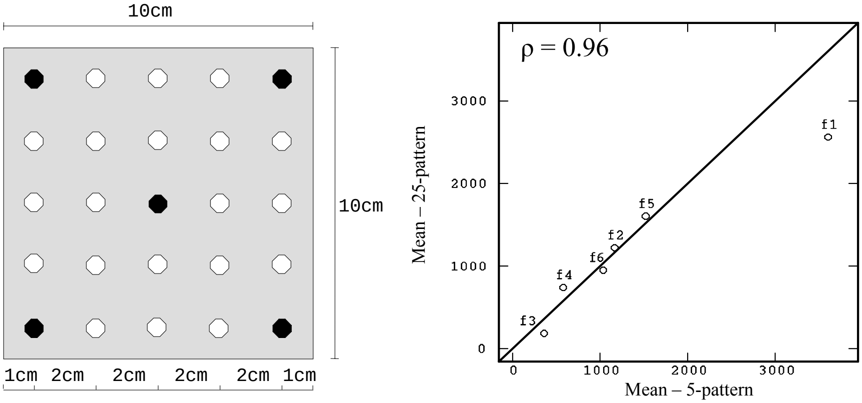

Figure 4: a) 5-pattern (●) and 25-pattern (○) of a Pollut-Eval® site, ■ residue kept for GPC analyses and b) Correlation between 5- and 25-pattern based on six Pollut-Eval® sites.

Multi-Scale Sampling and Reproducibility of a Pollut-Eval® Analysis

To evaluate the measurement's uncertainty, fifteen samples belonging to the same site have been analysed twice (by two different operators). Analyses are destructive but thanks to the small volume needed for one measurement some samples have been divided into two parts.

Z_1 and Z_2 corresponding to the two data sets of 15 samples each, let us consider:

$$Z_1 = Y + e_1 \text{ and } Z_2 = Y + e_2 \tag{1}$$

where Y denotes the "real" concentration supposed identical for the two parts and e_1 and e_2 the measurement's errors. Under error independence hypothesis and assuming that the two errors have the same expectation (supposed null) and variance, the variogram of the average is written:

$$\gamma_{\frac{Z_1+Z_2}{2}} = \gamma_Y + \frac{1}{4}\left(\sigma^2_{e_1} + \sigma^2_{e_2}\right) = \gamma_Y + \frac{\sigma^2_e}{2} \tag{2}$$

and the cross variogram: $\gamma_{Z_1,Z_2} = \gamma_Y$. (3)

The variograms of each data set (left part of Figure 5) have about the same sill ($\sigma_{Z1}^2 \approx \sigma_{Z2}^2$), even if 15 points are not enough to make robust variograms. To estimate the variance of the measurement's error (σ_e^2), the variogram of the mean of the two data sets ($\gamma_{(Z1+Z2)/2}$) and the cross-variogram $\gamma_{Z1,Z2}$ are calculated (right part of Figure 5). The difference between these two variograms gives the variance of measurement's error as explained in equations (2) and (3) It is about 30000 (mg/kg)².

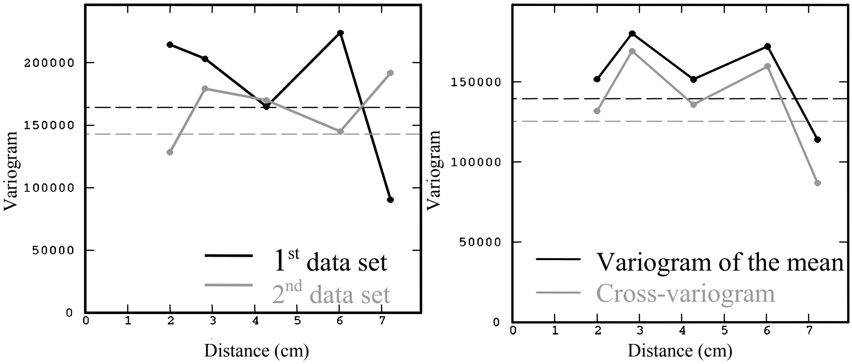

Figure 5: Omnidirectional variograms of the two data sets.

This variance of measurement's error is much smaller than the dispersion variance of each 15 points set (σ_{Z1}^2 and σ_{Z2}^2 are about 160000 – left part of Figure 5). Therefore the spatial variability at very small distances is much higher than the measurement error. Then the reproducibility of the measurements is high.

Finally, we check the error independence hypothesis by calculating the correlation coefficient (under the same hypotheses as for equations (2) and (3)):

$$\rho_{Z_1,Z_2} = \frac{\mathrm{cov}(Z_1,Z_2)}{\sigma_{Z_1} \cdot \sigma_{Z_2}} = \frac{\sigma_Y^2}{\sigma_Y^2 + \sigma_e^2} = \frac{\sigma_Y^2}{\sigma_Z^2} = 0.84 \qquad (4)$$

σ_Y^2 is found using the sill of the variogram of the difference (Z_1-Z_2) (not displayed) which gives 2 σ_e^2 and the sill of the variogram of (Z_1+Z_2)/2 (cf. equation 2). The result is very convincing since the experimental linear correlation coefficient between the two data sets is equal to 0.82. The initial hypotheses are accepted.

Multi-Scale Geostatistical Analysis

The spatial variability of hydrocarbon concentrations is studied on three scales:

- centimetric, between points belonging to the same 25-pattern. This work is based on six Pollut-Eval® sites (f1 to f6);
- decimetric, between the closest three sites (f1, f2 and f3 on Figure 3);
- from 0.5 to some meters between 5-pattern sites.

Figure 6 displays the omnidirectional variogram of the six Pollut-Eval® 25-pattern sites, and a fitted model. The main result is a very high spatial variability at very short distances.

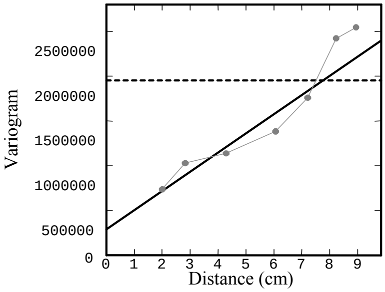

Figure 6: Omnidirectional variogram of the six Pollut-Eval® slices with 25 samples each.

The next variability scale is between the three sites f1, f2 and f3, from 10 to about 30 cm. A range of about 20 cm appears (Figure 7); the sill equals twice the nugget effect.

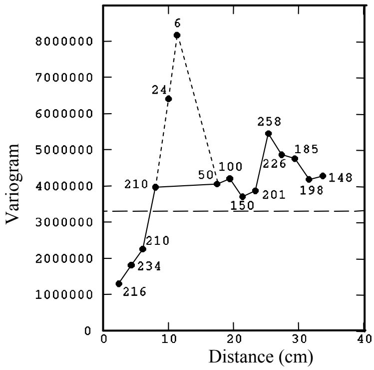

Figure 7: Omnidirectional variogram between f1, f2 and f3 Pollut-Eval® slices. Numbers of pairs are written for each distance.

Finally the plurimetric scale is studied. Because of the nested sampling scheme, four variograms are calculated on four sets defined by the distance between Pollut-Eval® sites, *i.e.* from 0.25 m up to 6 m (cf. dotted lines on Figure 3 which define the four sets). The left part of Figure 8 shows these variograms for the logarithm of concentrations: the contrast between variograms is clear and these differences are even bigger for variograms of raw concentrations.

Using a proportional effect is not efficient to adjust these four variograms together. Since there is always a common distance d_i for two successive variograms γ_i and γ_{i+1} , a global variogram (right part of Figure 8) is obtained by multiplying each variogram by the ratio $\gamma_{i+1}(d_i)/\gamma_i(d_i)$. The reference variogram is the last one in order to represent the spatial variability on a plurimetric scale. This variogram reveals another spatial structure, that can be fitted with a range of about 5 m. To conclude, even if the spatial variability at centimetric scale is very high, there is other defined spatial structures at larger distances.

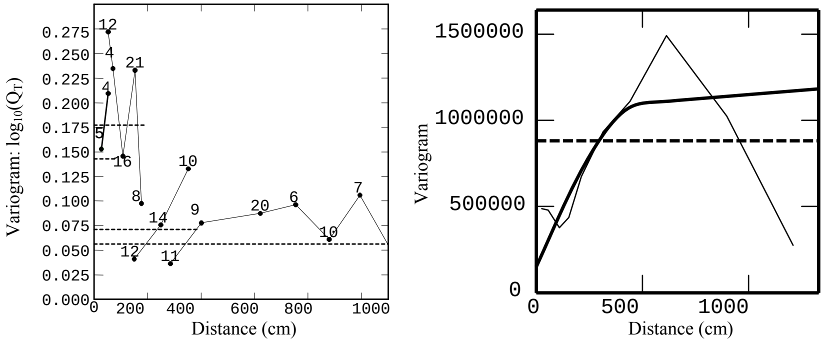

Figure 8: Variograms of the four sets (log of concentrations) and global resulting variogram with fitted model (raw concentrations).

ELECTRICAL RESISTIVITY

Electrical resistivity has been measured on Area B inside the 25m-square and along the profiles. For each data set, several levels were investigated at different depths, going up to 16 m for the profiles and up to 6 m for the square (Figure 9).

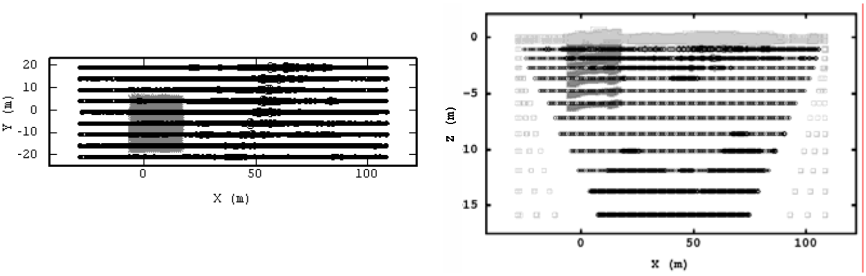

Figure 9: Base maps of electrical resistivity (horizontal and vertical projections). Profiles data (black), square's data (dark grey) and non used data (light grey).

Variographic Analysis

Profiles and square are studied separately and at different levels. The correlation coefficients between adjacent levels being very high (between 0.65 and 0.98), only four levels are studied for each set. All of them show an anisotropic and clear structure of the variable. The next figure presents a variogram of one level for the profiles and for the square, and the associated fitting.

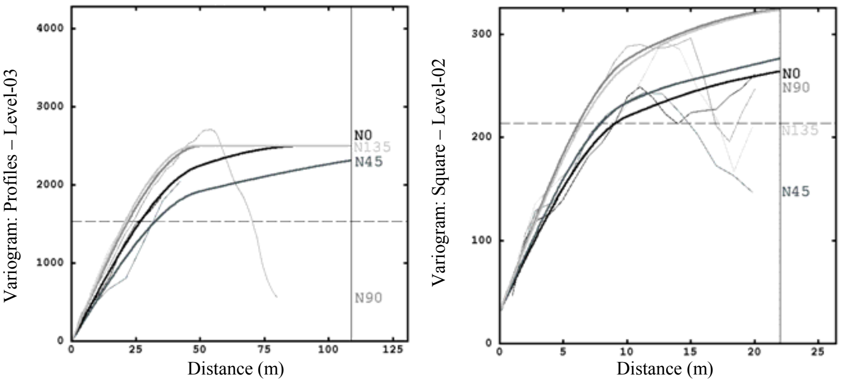

Figure 10: Anisotropic variograms and variogram fitting for level-03 for the profiles (left) and for level-02 for the square (right).

The electrical method induces a regularisation which is perceptible on variograms: they present a very continuous behaviour at the origin and generally a lower sill for the deepest levels.

It is important to know if the results obtained on the profiles and on the square are similar over their intersection. The analysis of the cross-variograms (up to a small tolerance on the location, Figure 11) or the examination of the scatter plots lead to relatively poor results even if the sills are quite similar over the two simple variograms. Indeed the cross variogram is far from the maximal authorised envelope of the linear coregionalisation model. This suggests that electrical measurements give only relative results because two surveys made on the same site are somewhat different.

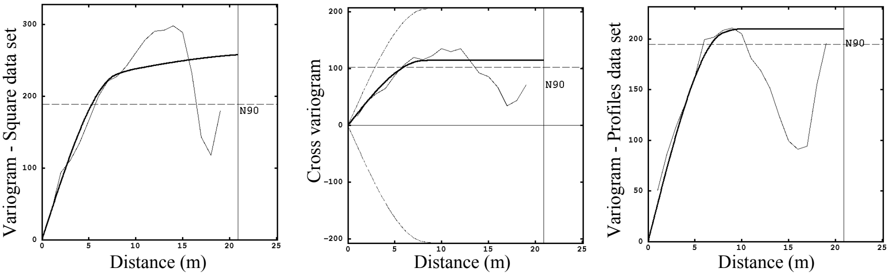

Figure 11: Simple variograms of the profiles and square's data sets (left and right) and cross variogram with maximal authorised envelope (middle). Example of North 90°.

Comparison between Electrical Resistivity and Pollut-Eval® Data

The sample locations being different from one method to another, the comparison is made on the basis of the kriging maps (blocks of 5 x 5 x 0.5 m) on the 12m-square, taking into account the precision of the estimation. For the Pollut-Eval®, the standard deviation is large next to the sides of the kriging map. Thus these blocks are not considered for the scatter plot. The correlation cloud is relatively scattered (Figure 12), despite the linear coefficient correlation of -0.6. Large

Pollut-Eval® concentrations coincide with low resistivity values. Therefore the resistivity survey can detect the presence of pollution but it remains necessary to perform additional analyses in particular for small resistivity values.

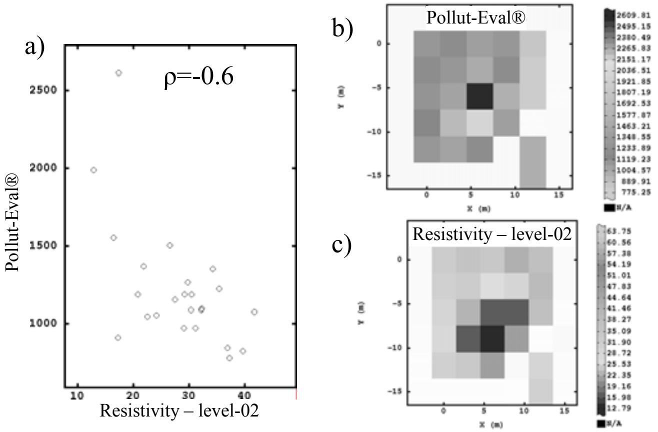

Figure 12: a) Scatter plot between Resistivity (abscissa) and Pollut-Eval® (ordinates) b) Kriging map of Pollut-Eval® data c) Kriging map of resistivity (level-02). White blocks (on maps) are not considered.

CONCLUSIONS

Correlations between different methods seem mediocre but the Pollut-Eval® gauge can clearly give useful on-site indications on polluted areas. This study also points out the very large variability of hydrocarbon concentrations at small distances which leads in practice to imprecise estimations on metric dimensional meshes. The uncertainty related to the estimation must be taken into account when comparisons to pollution thresholds are made. In addition, the quantification threshold must also be determined and taken into account.

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