

# CROSS LINKED METHODOLOGIES TO ASSESS THE CONTAMINATION EXTENSION OF HYDROCARBON POLLUTED SOIL

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**Keywords:** Hydrocarbon Contamination, Soil diagnosis, Site investigation, Remediation

## 1 INTRODUCTION

During risk assessment of contaminated soil, the evaluation of the pollution extension is a critical step which is often blurred by numerous uncertainties. For these reasons, an effective remediation should always be preceded by an accurate study of the extension and of the spatial location of the pollution. These initial evaluation steps have to be inserted in a closely conducted planning, based on predefined sampling patterns implemented by consulting companies. Their elaboration relies mainly on the historical knowledge of the previous industrial activities which occurred on the site.

The quality of the remediation project is closely linked to the evaluation of the uncertainty on the extension and on the concentrations of the pollutant. On the other hand, the decisions are driven by guidelines levels imposed by the administration. These tasks are always carried out during short time period and rely on the expertise applied to only few samples. One of the main aims of the project concerns the representativity of analyzed samples (number, location and size) and the choice of the most relevant or pertinent tools for real-time field evaluation.

## 2 AIM OF THE PROJECT

This document presents the results obtained during the first part of the LOQUAS project (**L**ocalisation & **q**uantification of organic pollutant in **s**oil) supported since 2006 by ANR in the frame work of the PRECODO 2005. The aim of the project is to define a methodology for the diagnosis of hydrocarbon polluted sites. This methodology includes a soil sampling strategy based on a geostatistical approach associated with different analytical methods, one of which is a geophysical reconnaissance. The first part of the project was focussed on the sampling representativeness and on the comparison of the various diagnosis obtained on a site with different reconnaissance principle (geophysics, gas phase chromatography, measurements of gaseous emission from soil and Pollut-Eval® methodology. The industrial site chosen is polluted by petroleum cuts mainly composed of kerosene.

The main objective is to end up to realistic recommendations for consulting company in charge of the initial phases of reconnaissance and diagnosis. These recommendations will concern the sampling strategies and estimation methods in order to improve site remediation. Our objective is to interface the use of on-site sampling methodologies with appropriate geostatistical estimation methods in order to improve the decision-making process during the management of polluted site by providing more suitable estimation of the pollution delineation (extension and location).

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To achieve this objective, numerous questions should be solved :

- What is the representativeness of the Pollut-Eval® data with the important spatial variability of organic pollutant concentration in soil ?
- How many Pollut-Eval® analyses should be done for each sampling location and how many Pollut-Eval® analyses are equivalent to one CPG determination ?
- Is there any specific influence of the depth on the dispersion of Pollut-Eval® determination due to the volatility of the most volatile fraction of the pollutant ?

The industrial fallow studied in the project is polluted by petroleum cuts mainly composed of kerosene.

### 3 SAMPLING STRATEGY: INSERTED SCALE

For our comparison program, the gas chromatographic methodology, already included in various normalized methodologies, has been chosen as reference. The sampling strategy has been built in order to nest various reconnaissance scales depending on the different investigation techniques used.

- Different geophysical reconnaissance have been evaluated through various detection principles applied to the whole site (17000 m<sup>2</sup>) or to a specific plot of 100 m<sup>2</sup>.
- Conventional gas chromatographic analyses and Pollut-Eval® determination have been evaluated for scale varying from 0.02 m up to 12 m (cf. figure 1). During on-site diagnosis, the average reconnaissance grid often used is about 20 m or more. For this reason, we tried to evaluate the variability of Pollut-Eval® and CPG quantification for smaller scale than the one usually chosen to select soil remediation according to pollution level guidelines. The variogram was compared for the two main directions in order to verify possible anisotropy. Estimation variances were calculated for different sampling pattern (5 or 25 points); The final aim was to examine the accuracy obtained with various sampling pattern on block of different dimensions.

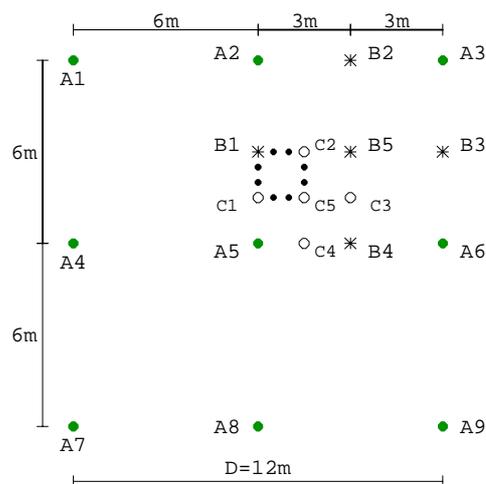


Figure 1: organisation of the different reconnaissance scale for the grid of 12X12 m

For this methodological study, sampling has been mainly studied in the two horizontal dimensions (fig. 1). For the decametric scale, the reference sample was a square of 10X10 cm (named "block"). For the decimetric and centimetric scales, the reference block was a square of 10X10 cm (fig.2). For the CPG and the Pollut-Eval® analyses, this block itself was sampled every 2 cm to obtain a pattern composed of (maximum) 25 points (fig. 2). The initial pattern was composed of only 5 points for most of the reference blocks (blue dots on the graph of figure 2).

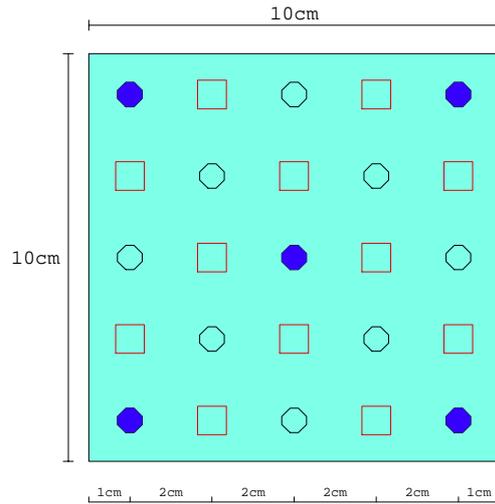


Figure 2 : Sampling pattern for the decimetric and the centimetric scale

Taking into account that GC and Pollut-Eval® were destructive, the "validation" of these two methods could be only based on correlation and supported by a sufficient lot of samples. The spatial variability was characterized with experimental variograms calculated in various directions to verify a possible anisotropy. Our analytical approach concerning spatial variability was successively focussed on small distances, at metric and decametric scale. The historical use of these obsolete industrial zone site leads to various reworking of the soil surface; for this reason, the variograms were built at least on four steps to verify a possible three dimensional structure.

The second part of the study was focused on composite sampling strategy in order to fit with environmental consultancy companies providing interests. To complete the study, additional soil samples were taken at various depths for different location of the site (at 50 cm and 1 m from surface backfill). In order to compare different sampling strategies, variance of estimation was calculated with our variogram for different block sizes (for reference block of 100 cm<sup>2</sup> to 10 m<sup>2</sup>).

## 4 MATERIAL AND METHODS

### 4.1 geophysical methods

#### Self potential

The self potential (PS) is a passive method measuring and mapping the natural electric potential of soil. The origin of this potential is still unknown. For hydrocarbon polluted soils diagnosis, the electrochemical and electro-kinetic potential methods are often used. On polluted sites, electrochemical potentials are linked to oxydo-reduction reactions and to electric dipole measured on soil surface. This "electro-redox" potential is the combination of two phenomena that couldn't be discriminated; one is linked to hydrogeological origin (underground water flow) and the other to electrochemical origin due to pollutant degradation. PS is not directly measuring the pollutant but its degradation by-products.

#### Electrical methods

These methods are based on variation of the electrical potential measured between two electrodes. This variation is due to an electrical current generation applied between outlying electrodes. Two physical basic units are characterized:

- The electrical resistivity is a physical property characterizing the flow of free electric charge in the soil (electron, ion)
- The induced and spectral polarisations are physical properties characterizing the capacitive and inductive effect of soil.

### 4.2 Gas analysis

Gas analysis have been widely used for the evaluation of in-situ remediation process or for the monitoring of natural attenuation of pollutant in soil. Gas phase analysis have been also implemented as an investigation tool for the diagnosis of polluted site. For volatile chlorinated solvent or BTEX monitoring, a direct determination of the gas phase composition has been widely used to characterize the pollutant in soil or aquifer. The volatility of heavier pollutants does not allow their direct analysis in the gas phase but their degradation through aerobic metabolism leads to oxidized by-products and CO<sub>2</sub> production which could be monitored directly in the gas phase. This application has been evaluated in the framework of the LOQUAS project.

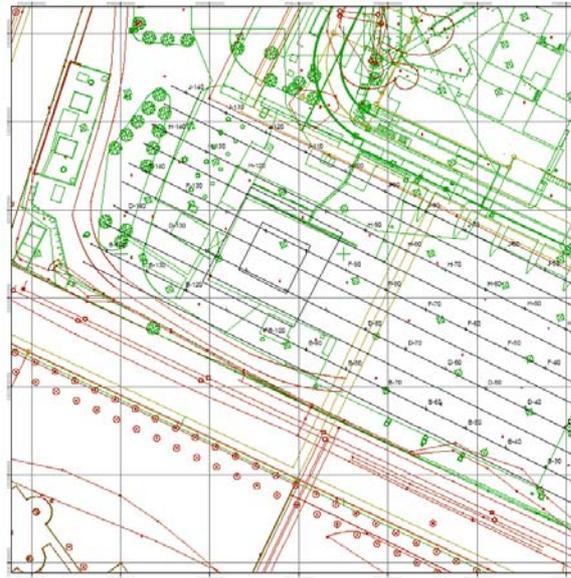


Figure 3: Location of the electrical panels for the 2D tomography. The area studied for the 3D tomography is located on the external square; the internal one is the reference block of 12 x12m

### 4.3 Location of the different grids

Two different scales were studied for geophysical site experiments:

- At the site's scale. The contaminated block studied dimensions were: 142 x 45 m; it was equipped with 10 electrical panels to build a two dimensional tomography following the site development described in fig.3. Induced polarization was measured for grids of 5x10 m
- At decametric scale. The area studied (26 x 24 m) was centred on the reference square block of 12x12 m in order to maintain an accurate resolution. An electrical three dimensional tomography was realized on the 12x12 m reference block.

The monitoring of gas was studied at two different scales :

- At the site scale. A gas phase mapping has been realized for a grid of 10 x 10 m.
- At decametric scale. A mapping of the gas production was realized for a staggered grid of 5X5 m and centred on the reference block.

For the site's scale and the decametric scales, gas composition was also measured by the Ecoprobe 5 analyzer from RS Dynamics. It is equipped with two sensors :

- A PID analyzer (photo ionization detector) measuring the concentration of ionisable volatile organic compounds.
- An IR analyzer (infrared detector) providing four analytical wavelength to measure the specific absorption of methane, volatile hydrocarbon and carbon dioxide.

### 4.4 Pollut-Eval® analysis

Considering the analytical tools usually retained to quantify hydrocarbon pollutant in soil, gas phase chromatography (GPC) is the most widespread and recommended standard AFNOR methods.

These methodologies include lengthy pre-treatments with toxic solvent extraction phase. For practical and safety reasons, these solvents are not used during on-site diagnosis. The Pollut-Eval® method

quantifies hydrocarbon pollutant in soil without any pre-treatment; the petroleum cut is identified on the basis of the boiling point of the organic compounds detected in the contaminated soil.

Its principle is based on the pyrolysis of 100 mg of compounds placed in a temperature programmable oven. Before analysis, the sample is kept in a cooled auto sampler. During the pyrolysis phase, the soil sample is gradually heated from 50°C to 650°C with a gradient of 50°C/min. In 16 minutes, heavy hydrocarbons are first vaporized and then cracked. The heating gradient is adjusted to gradually sweep away the various components of the pollutant entrapped in the soil sample. The vaporization temperature of various referenced petroleum cuts (gasoline, jet fuel, diesel oil, engine oil) have been introduced in a data base in order to define their specific detection zone. The hydrocarbons are quantified with a pre-calibrated flame ionisation detector (FID).

#### 4.5 Gas phase chromatographic analysis

The gas phase chromatographic analysis separates the different volatile components of a mixture according to the conditions of the method used (325°C). After this limit, the heavier hydrocarbons in the sample will not be detected and quantified by the method. This point is important and has to be taken into account before comparing results with those of the Pollut-Eval® method.

The mixture is injected and vaporized in an inert gas phase through a separation capillary column. The components of the pollutant are detected by a flame ionisation detector (FID). Two different gas phase analysers equipped with an automatic sampler have been used: a VARIAN 3800 and a TRACE™ GC 2000. Depending on the analyser, the introduction of the sample is done with a "split" or with a "on column" heated injector.

For heavier compounds, the separation is done on a 6 m length MXT capillary column, and for lighter petroleum cuts a 50 m length PONA column was used (internal diameter of 0,25 mm , phase thickness of 0,1 µm). The inert carrier gas used was helium and the volume of solvent injected was 1 µl. Concerning the pre-treatment and extraction protocols, the soil sampled (~ 20 g) are directly introduced in closed vessels containing the same weight of dichloromethane. The flask is then shaken during 1h30 in order to transfer the pollutants from the soil to the organic solvent which will be then analysed by GPC.

### 5 RESULTS AND DISCUSSIONS

Concerning electrical measures, high resistivity contrasts were observed at the site's scale (fig.4) which could be linked to the lithology. The detailed examination of the electrical profiles revealed 3 successive levels of intensity:

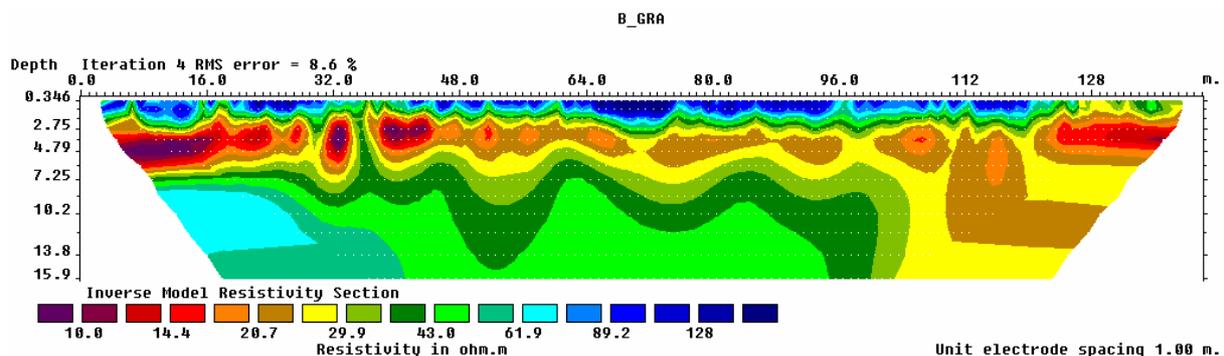


Figure 4 : 2D profile obtained on the site

- The soil surface (between 0 and 1.5 m below ground level) consisting of crushed material of building structure is quite resistant (> 200 ohm.m).
- The underground situated from 1.5 to 6-7 m bgl mainly consisting of loams is less resistant (between 10 to 20 ohm.m).
- The clay till situated below is more resistant (40 to 70 ohm.m).

Concerning induced potential, the more heterogeneous and conductor levels, where the pollution should be located, are situated in the loams. The figure 5 reveal different areas showing high induced potential at 1 m depth, coloured in red at the south west of the site.

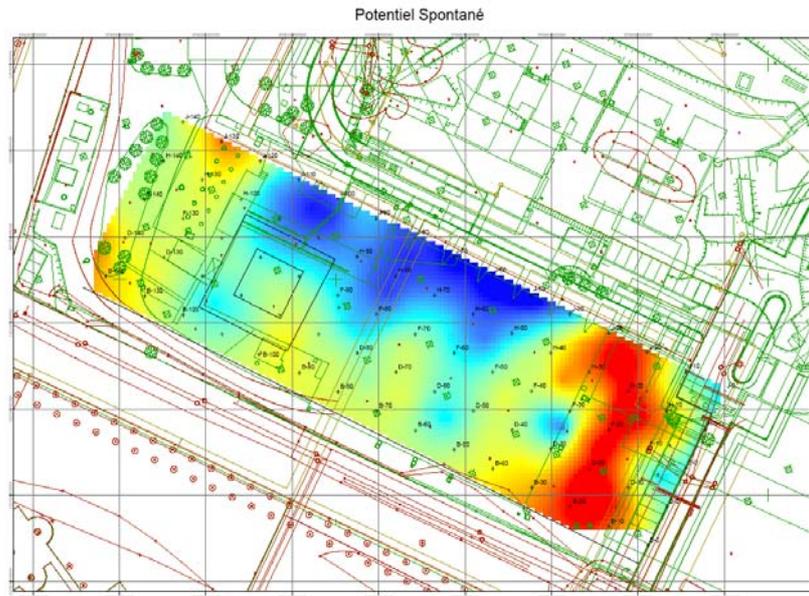


Figure 5 : Map of induced potential. The colour scale is linear from the blue (-8 mV) to the red (+22 mV)

The horizontal and vertical resistivity (see fig.6) revealed that the highest conducting areas are located at the two ends of the site. The results obtained with both geophysical reconnaissance techniques are consistent with the most polluted zone identified during the initial investigations done by GC (initial diagnosis step).

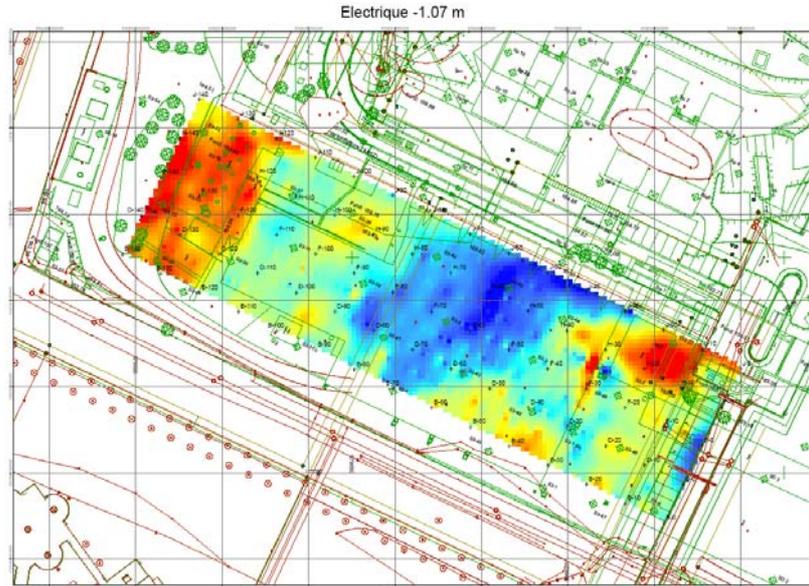
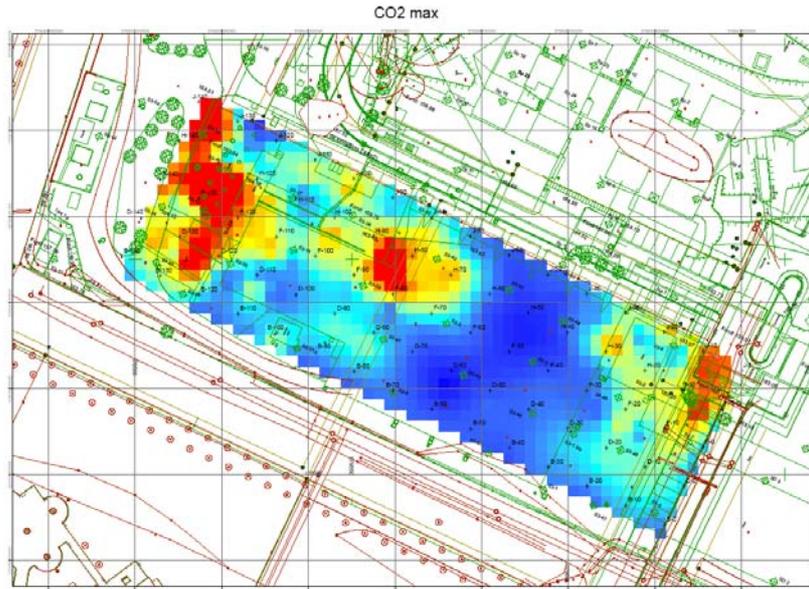


Figure 6 : Horizontal resistivity profile at 1.07 m of depth

Concerning soil gas production, the highest CO<sub>2</sub> production areas were also detected in both ends of the site (fig.7). The correlation between the highest CO<sub>2</sub> concentrations and the smallest resistivity profile (depth from 1.8 to 2.7 m) are globally consistent.



*Figure 7: Mapping of CO<sub>2</sub> production areas on the all site*

A spot revealing high conductivity was identified at approximately 5 m depth. These results confirm that the degradation of hydrocarbon in polluted areas leads to CO<sub>2</sub> production and induces higher conducting levels by acidification of the medium and dissolution of minerals.

Induced polarization measures are noisy and their variogram reveal high pollution heterogeneity. The main tendencies of these potential are representative and the map of PS which has been calculated by kriging, reveals negative potential for the resistant areas situated between the surface down to 3 m depth which are supposed to be non polluted .

At the opposite, positive potentials are monitored for polluted areas situated at the south-east of the site. To resume, the areas with the highest electrical conductivities reveal the highest electrical potential. On other part of the site, resistant areas show low potential. It is important to note that some electrical anomalies were due to metallic pipings.

As a qualitative point of view, the 3 reconnaissance techniques are consistent for the decametric scale and lead to the same conclusions. Their diagnosis concerning the highest polluted and impacted areas are consistent even though these different techniques have not been used to monitor the same underground depth.

For the metric scale, the study was carried out in a pit at 1.5 m depth behind surface backfill.

Results obtained with Pollut-Eval® and CPG analysis were compared to electrical and resistivity measurements to check their usefulness as complementary tools for the diagnostic of hydrocarbon polluted site. The coordinates of the resistivity and CO<sub>2</sub> production areas have been converted in the same Lambert I reference standard. The tendencies observed are equivalent and presented in the map in figure 8. The North area of the square reference block (12X12 m) seems to be more conductor. The highest conductivity detected on the site is located near the highest CO<sub>2</sub> production spot which confirms the qualitative consistence of these reconnaissance techniques.



*Figure 8: Horizontal resistivity profile at 1.5 m depth, obtained with reversed 3D data monitored on the 12x12 m square (3D tomography)*

The pyrogram profile of the Pollut-Eval® analysis also revealed high concentration contrasts. On a qualitative point of view, the pollutants detected are not identical in each part of the site showing the heterogeneous origin of the pollutant. The main pollutant is composed of a volatile fraction which was detected at the same vaporization temperature as kerosene (hydrocarbons less than C<sub>20</sub>). A heavier and minor fraction was also detected (with hydrocarbon between C<sub>20</sub> and C<sub>40</sub>) on the site; their ratio are not identical, depending on samples location.

The concentrations of this fraction in the various samples are highly heterogeneous and shifted from 5 to 8300 mg/kg. They were compared to the results obtained for the volatile fraction detected by GC chromatography. The concentrations of total hydrocarbon vary from 10 to 30000 mg/kg. In most samples, the heterogeneity of the heavy fraction Q<sub>1</sub> is lower than the light one Q<sub>0</sub>.

Concerning gas phase chromatography, the results are showing that the concentrations of volatile compounds (kerosene like fraction) are quite low and near the quantification limit of the methods. Some atypical pyrograms reveal high evolutions of the pollutant composition by evaporation, adsorption or biodegradation processes since their accidental unloading in soil. Globally, the pollution levels detected by GPC are lower than those detected with the Pollut-Eval® method and are ranging between 10 and 200 mg per kg of soil for the petroleum cut containing less than 20 carbon atoms. The pollution levels detected by both reconnaissance techniques differ of one order of magnitude. The respective metrological qualification of both methodologies could not explain these differences which have been attributed to low extraction recoveries. The apolar organic solvent used to transfer the pollutant from the contaminated clay till was not efficient enough. The efficiency of the recommended extraction method is not sufficient for soil matrix having high moisture content, due to poor pollutant accessibility.

Concerning the reproducibility of Pollut-Eval® analysis, the statistical examination of the results obtained with 15 samples (analyzed twice) revealed a non negligible dispersion of the concentration values, demonstrating that a unique Pollut-Eval® determination was not sufficient to characterize hydrocarbon pollution with accuracy (for a reference block of 1 kg as for CPG determination).

The standard deviation of the double measurements is approximately 175 mg of HC per kg of soil. The uncertainty of the measurement is quite high ( $\pm 350$  mg/kg calculated with  $\pm 2\sigma$  interval) compared to the remediation target of 500 mg/kg applied for the selection of contaminated soil during diagnosis phase. This uncertainty integrates the variability of pollutant repartition in soil matrix (spatial distribution) but also the intrinsic metrological properties of the analyzer (signal to noise ratio & quantification limits).

These results demonstrate the poor representativity of a single point sampled in a highly variable environment showing huge "nugget effect" even at centimetric scale. This conclusion is not surprising when compared to the high concentration heterogeneity detected on the site with both reconnaissance techniques. The variability observed shouldn't be attributed to the method itself but to the nature of the sample.

Two successive analysis done on the same sample are giving different results but the variances and average concentrations calculated for the 15 samples (analysed twice in series) are quite close. The results are globally equivalent and no systematic bias or error have been detected in the 2 analysed series.

The detailed variographic study has confirmed the hypothesis initially proposed concerning the independence of the measurement errors. The highest dispersion observed for a single sample between two determination resulted from the same operator during a lag of few hours. The important variability observed at same scale in a single sample must not blank the other components at the origin of the sampling uncertainty.

The concentration value obtained for the central point compared to the average concentration of the 5 spot pattern, revealed clearly the influence of the analysed "volume" on the experimental variance: it is not a bias linked to the sampling strategy but an effect of the respective size of the samples. The dispersion of measurements tend to decrease when the analyzed volume increase.

For the five spot sampling pattern, the statistical values calculated on the basis of the experimental results confirm the evidence of a 3 dimensional correlation, despite the high "nugget effect" previously mentioned.

The results revealed a direct and proportional effect : in a five spot sampling pattern, the higher the average pollution level, the higher the dispersion. The immediate consequence is observed on the estimation accuracy which is enhanced for low pollution levels.

The empirical or theoretical research (by the associated variance) of the optimal number of sampling points confirmed that a single "Pollut-Eval®" sample was not sufficient to characterize the reference square block of 100 cm<sup>2</sup>. This conclusion confirms the multi-point strategy proposed in the frame work of the LOQUAS project.

The five points sampling pattern is sufficient to obtain an average hydrocarbon concentration level with acceptable correlation with the one calculated with 25 points. Nevertheless, our results have demonstrated that the central point of this five spot pattern was not critical. Compared to the average level calculated with the 25 points pattern, the correlation calculated with a four points sampling strategy (built on the angular of the square) was as good as the one calculated with 5 points.

This four points sampling strategy has been retained for the next diagnosis campaign of the project for two main reasons:

- to avoid the risk of implementing sampling campaign based on single point strategy associated to high concentration variability even at small scale.
- for economical reasons, a 25 points pattern was not acceptable

No systematic deviation has been pointed out with the results obtained by both Pollut-Eval® analyzer used during the sampling campaign.

These first important conclusions of the LOQUAS project concerning the sample representativity and the optimal sampling pattern, would nevertheless increase the number of analysis (4 determination for one block) to be done by the operator in charge of the diagnosis. This conclusion was not realistic as an economical point of view. So we implemented a new sampling campaign based on a four point sampling pattern for twelve grids of 5X5 m. The objectives were focussed on the influence of this sampling strategy when applied to Pollut-Eval analysis and compared to conventional GC approach;

The analyses done by the Pollut-Eval® before and after a manual blending, revealed that the mixing of a composite sample tends to increase the average pollution values (Fig. 9) but only for low hydrocarbon levels (concentrations under the critical selection guidelines of 500 mg/kg).

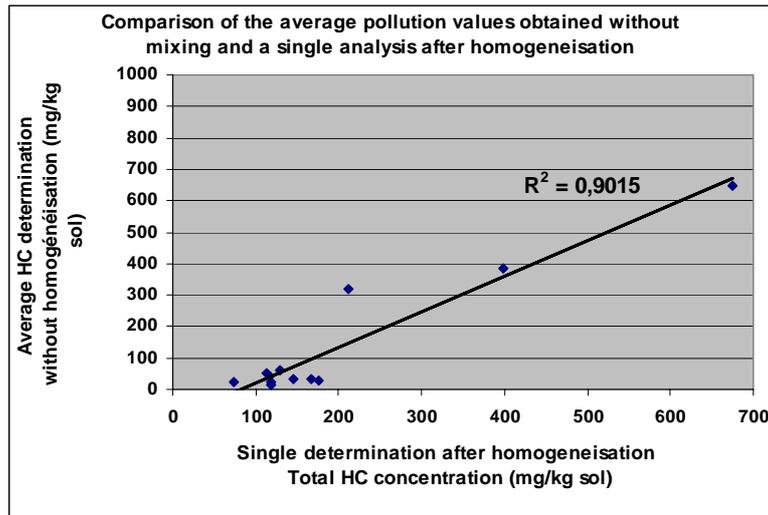


Figure 9 : Influence of a manual homogenisation on the average hydrocarbon pollution level determined with the Pollut-Eval® method (12 grids)

On figure 9 we noticed, for all samples with concentrations below 200 mg/kg, that homogenisation tends to increase the pollution level when compared to the average value determined before treatment. Taking into account the high standard deviation of the series, the average pollution level of the twelve grids is similar before and after homogenisation and the deviation is due to the matrix effect. The comparison of deviation before and after mixing revealed that homogenisation is mixing the high polluted nuggets into the composite sample. Non-accurate diagnosis may lead to soil suspension during the selection phase driven by administrative target ( $\leq 500$  mg/kg for inert waste landfill). For this reason, a technical and economical investigation is already programmed for the next sampling campaign of the project. A balance should be done to compare the advantage of a more accurate diagnosis (leading to less suspension) and the increased cost due to a multi-point sampling strategy.

Concerning the CO<sub>2</sub> production, the examination of the variogram also revealed an important nugget effect. Nevertheless, a spatial component is observed in some samples. Following hydrocarbon biodegradation, the vertical propagation of CO<sub>2</sub> through the soil porosity leads to an impacted area located on soil surface. The experience shows that the size of the impacted area is close to the pollutant source's one. The CO<sub>2</sub> analysis done on the site should be considered as punctual monitoring points which are only representative of the CO<sub>2</sub> production coming from the underground situated straight below its location. In consequence, the size of the reconnaissance grid induces the size of the target. At metric scale, only a slight spatial organization is observed concerning pollutant sources. This result is important and demonstrates that individual CO<sub>2</sub> production data should be carefully interpolated from point to point (with kriging for instance). In practice, the lack of 3 dimensional structure will avoid any precise delineation of potentially polluted areas

## 6. PERSPECTIVES

The first conclusions of the LOQUAS project are focussed on soil sampling pattern, sample representativity and on the uncertainties associated to these strategies. The results have demonstrated that the relevance of Pollut-Eval® determination should be more generally focussed on polluted areas presenting pollution levels near the critical target concentration (here 500 mg/kg). For the next site, the four point sampling strategy will be maintained. Many questions are still addressed concerning GPC and Pollut-Eval® correlations, concerning the repeatability of geophysical reconnaissance techniques and the relevance of composite sampling strategies. The program will be focussed on diagnosis with underground extension. One of the main uncertainty concerning soil selection is commonly due to vertical inaccuracy during diagnosis campaign. All these studies will be implemented in 2008 on another polluted site.

Acknowledgements:

This work is conducted in the context of the PRECODD 2005 project with the French ANR support