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Statistical evaluation of recovery of 3,4-dichloroaniline in soil as function of particle size and analyte concentration

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Abstract

A great mean value of recovery for extraction of 3,4-dichloroaniline from a soil is calculated from individual recovery values evaluated for four different fractions of the soil. Then the uncertainty associated to this great mean recovery is calculated and used to know whether to apply or not the correction in routine analysis performed for the same kind of soil and the same analyte. The most representative fractions that, as a function of particle size, can be identified in a soil are: sand (2.000–0.063 mm), coarse silt (0.063–0.020 mm), fine silt (0.020–0.002 mm) and clay (≤0.002 mm). These fractions are here considered as sub matrices of the matrix soil.

To evaluate the mean recovery and its uncertainty, as a function of the sub matrix and the analyte concentration, the four blank soil fractions were spiked with the analyte at three concentration levels (10.0, 50.0 and 100.0 mg/kg) and three replicates were performed for each experiment. The 36 samples were extracted by accelerated solvent system and the amounts of 3,4-dichloroaniline were determined by RP-HPLC analysis. From the 36 individual recovery values, the great mean and its uncertainty are calculated.

Experiments performed on samples of soil of similar composition, spiked with known concentrations of the same analyte showed the goodness of the mean recovery value.

Keywords: 3,4-Dichloroaniline in soil; Recovery uncertainty; Recovery as function of soil particle-size; Recovery as function of concentration

1. Introduction

A fundamental task of environmental analysis is the determination and quantification of trace and ultra-trace levels of analytes in complex matrices, like soils and sediments. The advanced instrumentation nowadays available in analytical laboratories enables the development of analytical methods characterised by high levels of accuracy, reproducibility and sensitivity. However, no meaning has the use of these methods if the recovery in the extraction process that precedes the analysis is not reliably known.

Recovery, as defined by the Harmonised Guidelines for the Use of Recovery Information in Analytical Measurement [1] is "the proportion of the amount of analyte present in or added to the analytical portion of the test material which is extracted and presented for measurement". Recovery R is also expressed as $R = C_{obs}/C_{ref}$, where C_{obs} is the concentration measured and C_{ref} is the expected value. R must be as close as possible to 1. Very hardly recovery percentages in the extraction step are close to 100%. Lower values can anyway be accepted, if systematically evaluated and validated.

The recovery extent is not so easy to be evaluated, since it depends, besides the extraction method used, on the analyte properties, on the kind of the matrix and on the concentration at which the analyte is present [2]. Many environmental analyses require the determination of pollutants in soils [3,4]. Soil is constituted by different components characterised by different properties in retaining pollutants [5,6]. This paper

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deals with the determination in soil of 3,4-dichloroaniline that is a pollutant widespread diffused in the environment, due to the degradation of phytodrugs and to the disposal of wastes produced by dye, painting and pharmaceutical industries [7].

Recovery can be estimated and then used to correct the value of the amount of the analyte obtained after extraction from the same type of matrix, under the same extraction conditions and in the same analyte concentration range. When a reference material is unavailable, a matrix blank is spiked with the analyte at known concentrations. The matrix blank must be as similar as possible to the sample, in order to avoid the so called matrix mismatch, that occurs when a recovery value is estimated for one matrix and applied to another and is as more serious as the two matrices are consistently different in their chemical nature. This can be considered as a bias in the recovery, only if the analytical method is otherwise unbiased. Two kinds of bias can be distinguished: a proportional bias that depends on concentration and matrix (and can be expressed as the recovery percentage) and a constant bias.

Aim of the authors is to evaluate a great mean recovery to be used in routine analysis in which 3,4-dichloroaniline is determined in soils of particle size $\leq$2 mm, to correct the experimental results obtained. This great mean recovery must take into account the presence in soil of different fractions that can be distinguished as a function of particle size.

The soil fractions here considered are: sand (size ranging from 2.000 to 0.063 mm), coarse silt (0.063–0.020 mm), fine silt (0.02–0.002 mm) and clay (<0.002 mm), in agreement with the A.G.I. (Italian Geotecnical Agency) classification with the only difference that we also separated the silt in coarse and fine fractions. The four soil portions are here considered as sub matrices.

Then, following the approach based on a nested experimental design as a function of matrix and analyte concentration, the great mean recovery value, $\bar{\bar{R}}_m$, was estimated, from the recovery values obtained when different amounts of analyte were added to the different fractions of soil [8,9]. The calculation of the total associated uncertainty permitted to evaluate if the recovery value is statistically significant and must be applied to correct the experimental results obtained in routine determination of the same analyte in the same kind of soil.

Accelerated solvent extraction and RP-HPLC methods were employed to evaluate the concentration of the pollutant in soil and in its fractions.

2. Experimental

2.1. Reagents

3,4-Dichloroaniline was purchased from Aldrich. A stock solution was prepared in acetonitrile at a 1000.0 mg/L concentration. All the further dilutions were made in Ultrapure water obtained from a Millipore Milli-Q system (Milford, MA, USA).

The HPLC grade acetonitrile and dichloromethane were purchased from Merck (Darmstadt, Germany) and sodium hexametaphosphate from Carlo Erba Reagenti (Milan, Italy).

2.2. Separation of the fractions for sedimentation

The blank matrix used is a soil collected in an unpolluted region in which the absence of 3,4-dichloroaniline at detectable concentrations was tested by HPLC. The blank soil was firstly sieved at 2 mm to eliminate stones and vegetal parts, then it was carefully homogenised with a suitable mixer and partioned in the four sub matrices (sand, coarse silt, fine silt and clay).

The procedure consisted of two steps: dispersion and sedimentation. In the dispersion step a fixed amount (75.00 g) of sieved soil was mixed into an apposite bottle together with the required volume (180.0 mL) of a 50.00 g/L solution of sodium hexametaphosphate in ultrapure water, which assists in neutralising electrical charges present on the colloidal particles. The suspension was then stirred for 2 h by a horizontal shaker. In the sedimentation process suitable glass columns expressly planned to separate amounts of soil greater than usual were employed [10]. The separation of the size fractions consists, according to the Stokes law, in collecting the fractions at fixed times, namely 1 min and 30 s for sand, 14 min and 53 s for coarse silt. After 24 h and 48 min it was possible to separate from the suspension the clay fraction and from the precipitate the fine silt. The accuracy of the separation method has been checked and described in detail elsewhere [11].

2.3. Spiking of the soil samples

Each single fraction was spiked with the pollutant at three concentration levels (10.0, 50.0 and 100.0 mg/kg). The spiking procedure was carried out according to the following steps [12]. 1.0 kg of the sieved fractions of soil were put into a 35 cm × 24 cm aluminium tray, 10.00 mL of a 10.00 g/L solution of 3,4-dichloroaniline to obtain a spiking of 100.0 mg/kg were spread to completely cover the soil fraction surface. The soil fraction was mixed and an additional volume (around 100.0 mL) of ultrapure water was added. A further homogenisation was obtained by the use of a spoon. The solvent was then evaporated at open air until (2–3 days) it was completely dried. The procedure described resulted to give homogenisation comparable with that obtained with the procedure in which an electrical mixer was used.

2.4. Extraction procedure

The accelerated solvent extraction technique (ASE®, Dionex) was used for the extraction of 3,4-dichloroaniline from soil fractions. Accelerated solvent extractor allows to extract both organic and inorganic compounds from solid and semisolid matrices with the use of solvents at elevated

temperatures and high pressures that maintain the heated solvent in a liquid state.

Preliminary experiments were set up in order to optimise the conditions of extraction. 20.0 g of the soil sieved and spiked with 100.0 mg/kg of 3,4-dichloroaniline were put into the extraction cell together with 2 g of Hydromatrix (high purity inert diatomaceous earth, used as dehydrating and dispersing agent). Dichloromethane was the extraction solvent and the extraction step was followed by three rinse steps. The effect of the static time of extraction of 3,4-dichloroaniline was investigated in a window time ranging between 5 and 40 min. The recovery values increase with time and become practically constant after a static time of 30 min that was chosen as the experimental extraction time.

Each complete experiment of spiking and extraction was performed three times.

The extract (around 50.0–60.0 mL from each extraction) was collected, dried in the rotating evaporator, re-dissolved in two fractions of 10.0 mL dichloromethane, dried in N_2 atmosphere, re-dissolved into 10.0 mL of a 50:50 (v/v) water/acetonitrile mixture and sonicated in ultrasonic bath for 10 min. The extracts were then filtered on a 0.45 μm syringe filter and diluted with known amounts of ultrapure water before injection into the chromatographic system.

2.5. Equipment and chromatographic conditions

The chromatographic determination of 3,4-dichloroaniline was performed by a Merck-Hitachi (Tokyo, Japan) LAChrom chromatograph, equipped with a L-7100 pump, a L-7400 UV detector, a L-7450A diode array detector and a D-7000 interface. A Merck Lichrospher 100 RP-18, 5 μm (250 mm × 4 mm) endcapped column, equipped with a Lichrospher RP-18, 5 μm (50 mm × 4 mm) pre-column was used as the stationary phase. The mobile phase was a mixture of water/acetonitrile 60/40 (v/v) at a flow-rate of 1.0 mL/min. The detection wavelength was set at 240 nm. To evaluate the recovery of 3,4-dichloroaniline for the soil extracts by RP-HPLC analysis a calibration plot was built in the concentration range between 0.5 and 5.0 mg/L. Standard addition method was also employed in the same concentration range: the slope here obtained is statistically comparable to that obtained by the external calibration curve and indicates that no relevant matrix effect is present.

3. Results

3.1. Characterisation of the soil

The different fractions of soil, as a function of their chemical physical properties could adsorb and release pollutant in different amounts. For this reason it is suggestible, prior to any soil analysis, to evaluate the composition of soil by a fractionating technique based on particle size.

The reliability and the reproducibility of the separation technique here employed was checked for each separation by six replicates. The soil in study, typical of Bormida valley (Piedmont, Italy), was separated according to the fractioning method described and gave the following percentage composition: sand 35.5%, coarse silt 17.3%, fine silt 24.9% and clay 22.3% (“sandy loam”, according to the USDA classification). The standard deviation for all the fractions was always lower than 3.0%.

3.2. Evaluation of recovery uncertainty

3.2.1. Experimental design

The final aim of this study is the estimation of an average recovery that can be used to correct the experimental results obtained in the determination of the same analyte in soils of similar composition. The strategy followed is of general interest and can be applied to the determination of any analyte into other real matrix. As a case in study, in this paper is presented the determination of 3,4-dichloroaniline at 10.0, 50.0 and 100.0 mg/kg concentration levels, considering the four fractions of soil separated as the different sub matrices. Each experiment of extraction and chromatographic analysis has been done in triplicate, so that the total number of set up experiments is four (matrices) × three (concentration levels) × three (replicates) = 36.

The structure of the nested experimental design, built according to a model proposed in references [8,9] is shown in Fig. 1. The factors considered are, in hierarchic order, the concentration level i ($i = 1$–I, with $I = 3$), the matrix (i.e. the granulometric fraction) j ($j = 1$–J, with $J = 4$) and the number of replicates k ($k = 1$–K, with $K = 3$). The R_{ijk} obtained for each concentration level, granulometry and replicate are reported in Table 1.

From the data of R_{ijk} the average $\overline{R}_{ij}$ (also reported in Table 1) of the k replicates for each submatrix j and concentration level i are calculated as:

$$\overline{R}_{ij} = \frac{\sum_{k=1}^{3} R_{ijk}}{K} \quad \text{for } i = 1 \text{ to } I \text{ and } j = 1 \text{ to } J \tag{1}$$

In Table 1 are also reported the mean values $\overline{\overline{R}}_i$ of recovery for the concentration level i

$$\overline{\overline{R}}_i = \frac{\sum_{j=1}^{4}\sum_{k=1}^{3} R_{ijk}}{J \times K} \quad \text{for } i = 1 \text{ to } I \tag{2}$$

A mean recovery value $\overline{\overline{R}}_{\mathrm{m}}$ that is a global measure of the recovery of the method can now be calculated as:

$$\overline{\overline{R}}_{\mathrm{m}} = \frac{\sum_{i=1}^{3}\sum_{j=1}^{4}\sum_{k=1}^{3} R_{ijk}}{I \times J \times K} = \frac{\sum_{i=1}^{3}\sum_{j=1}^{4} \overline{R}_{ij}}{I \times J} = \frac{\sum_{i=1}^{3} \overline{\overline{R}}_i}{I} \tag{3}$$

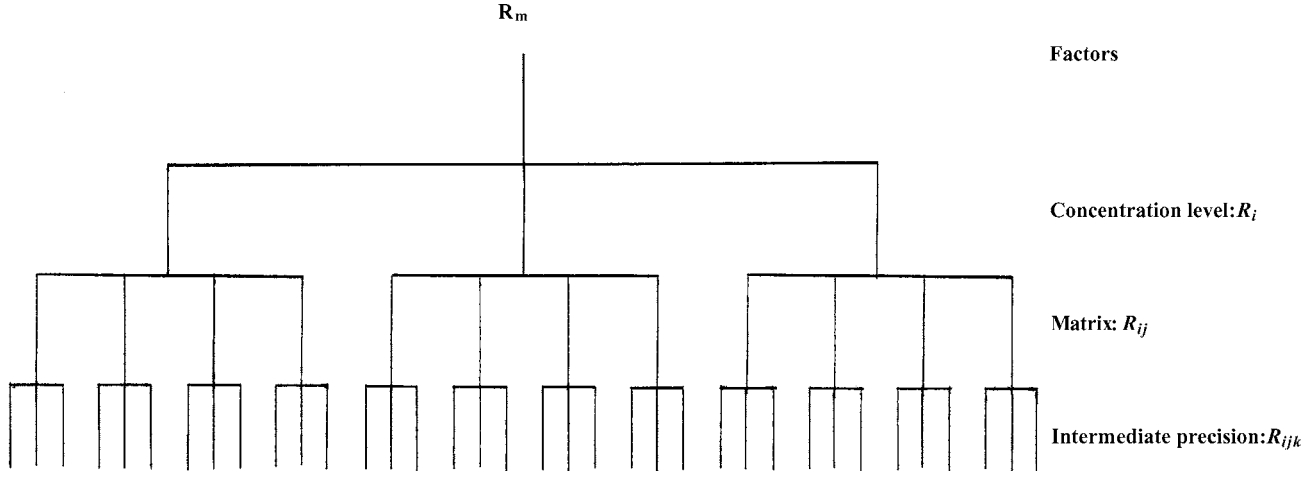

Fig. 1. Nested experimental design for the evaluation of 3,4-dichloroaniline recovery.

3.2.2. Evaluation of proportional bias

Once obtained the value of $\bar{\bar{R}}_m$, which takes into account the different properties of the four sub matrices of soil as well as the analyte concentration levels and the intermediate precision, the question is whether and when the correction for $\bar{\bar{R}}_m$ must be introduced to the analytical result obtained under similar conditions. To take a reliable decision based on a given probability level, the statistical uncertainty associated to $\bar{\bar{R}}_m$ must be estimated according to the following equation:

$$u(\bar{\bar{R}}_m) = \sqrt{\frac{\sum_{i=1,I} u(\bar{\bar{R}}_i)^2}{I^2}} \quad (4)$$

where $u\left(\bar{\bar{R}}_i\right)$, according to [8], corresponds to

$$u(\bar{\bar{R}}_i) = \sqrt{\frac{\sum_{j=1,J} (\overline{R_{ij}} - \bar{\bar{R}}_i)^2}{J(J-1)}} \quad (5)$$

and $\bar{R}_{ij}$and $\bar{\bar{R}}_i$are calculated according the Eqs. (1) and (2).

The estimated values of $\bar{\bar{R}}_m$ and of its uncertainty allows to perform a significance test to decide whether it is necessary to introduce the correction factor:

$$\frac{\left|\bar{\bar{R}}_m - 1\right|}{u(\bar{\bar{R}}_m)} \leq t_{\alpha/2,v_{eff}} \quad (6)$$

where $t_{\alpha/2,v_{eff}}$ is the two-sided t Student's value for a α significance level and v_{eff} is the number of the degrees of freedom. If inequality (6) does not hold and $\bar{\bar{R}}_m$ value is significant at the α significance level the correction for $\bar{\bar{R}}_m$ must be introduced in the experimental result of the analysis.

Since in the case in study the value of t calculated ($t = 6.729$) is greater than the tabulated value for $\alpha = 0.05$ and 33 freedom degrees ($t = 1.698$) the correction factor $\bar{\bar{R}}_m$ must be applied to the results of routine real samples.

Table 1
R_{ijk}, $\bar{R}_{ij}$, $\bar{\bar{R}}_i$, and $\bar{\bar{R}}_m$ recovery values obtained from the 36 experiments of the nested design

Soil fraction	Replicate	R_{ijk} (10 mg/kg)	R_{ijk} (50 mg/kg)	R_{ijk} (100 mg/kg)	$\bar{R}_{ij}$(10 mg/kg)	$\bar{R}_{ij}$(50 mg/kg)	$\bar{R}_{ij}$(100 mg/kg)
Sand	1	0.395	0.579	0.620			
	2	0.331	0.568	0.687	0.373	0.561	0.596
	3	0.392	0.535	0.481			
Coarse silt	1	0.347	0.475	0.351			
	2	0.321	0.471	0.354	0.324	0.460	0.429
	3	0.303	0.434	0.583			
Fine silt	1	0.449	0.518	0.336			
	2	0.463	0.578	0.389	0.434	0.536	0.412
	3	0.389	0.513	0.510			
Clay	1	0.360	0.322	0.422			
	2	0.416	0.221	0.479	0.346	0.332	0.438
	3	0.262	0.453	0.413			
$\bar{\bar{R}}i$	0.369	0.472	0.469				
$\bar{\bar{R}}_m$	0.436						

3.2.3. Evaluation of the true recovery and its uncertainty

The true recovery R of a given routine sample can be defined as:

$$R = \bar{\bar{R}}_{\mathrm{m}} + \Delta R_{\mathrm{matrix}} + \Delta R_{\mathrm{conc}} \quad (7)$$

where $\bar{\bar{R}}_{\mathrm{m}}$ is the average method recovery, $\Delta R_{\mathrm{matrix}}$ the variation of the recovery depending on the matrix analysed and ΔR_{conc} is the variation of recovery depending on the concentration level analysed. The last two components are unknowable, but their uncertainty can be estimated, so that the uncertainty of the true recovery R can be calculated from:

$$u(R) = \sqrt{u(\bar{\bar{R}}_{\mathrm{m}})^2 + u(\Delta R_{\mathrm{matrix}})^2 + u(\Delta R_{\mathrm{conc}})^2} \quad (8)$$

The first term can be estimated by Eq. (4) and the last two uncertainties can be obtained from the analysis of variance (ANOVA) [13] of the recoveries obtained in the experiments of the nested design. The contributions to the total uncertainty are calculated according to the following expressions:

$$u(\Delta R_{\mathrm{I}})^2 = \mathrm{MS_I} \quad (9)$$

$$u(\Delta R_{\mathrm{conc}})^2 = \frac{\mathrm{MS_{conc}} - \mathrm{MS_{matrix}}}{J \times K} \quad (10)$$

and

$$u(\Delta R_{\mathrm{matrix}})^2 = \frac{\mathrm{MS_{matrix}} - \mathrm{MS_I}}{K} \quad (11)$$

where $\mathrm{MS_I}$, is the mean squares associated to the intermediate precision and can be calculated as the square difference between the recovery for each single experiment (R_{ijk}) and the corresponding average recovery, divided by the total freedom degree number, according to the equations:

$$\mathrm{MS_I} = \frac{\sum_{i=1}^{3}\sum_{j=1}^{4}\sum_{k=1}^{3}(R_{ijk} - \bar{R}_{ij})^2}{I \times J \times (K-1)} \quad (12)$$

$$\mathrm{MS_{conc}} = \frac{j \times k\sum_{i=1}^{l}(\bar{\bar{R}}_i - \bar{\bar{R}})^2}{I-1} \quad (13)$$

$$\mathrm{MS_{matrix}} = \frac{k \times \sum_{i=1}^{3}\sum_{j=1}^{4}(\bar{R}_{ij} - \bar{\bar{R}}_i)^2}{I \times (J-1)} \quad (14)$$

The variance and the uncertainty associated to $\bar{\bar{R}}_{\mathrm{m}}$ are reported in Table 2.

From the calculated data of $u(\bar{\bar{R}}_{\mathrm{m}})$, $u(\Delta R_{\mathrm{matrix}})$ and $u(\Delta R_{\mathrm{conc}})$, respectively, equal to 0.0237, 0.0704 and 0.0420, $u(R)$ can be calculated according to the Eq. (8):

$$u(R) = \sqrt{(0.0237)^2 + (0.0704)^2 + (0.0420)^2} = 0.0853$$

3.2.4. Evaluation of constant bias

For the estimation of the constant bias the "Youden blank" method [14] was employed, that consists in analysing two different weights of a sample chosen as representative of the routine samples to be analysed. The constant bias and its uncertainty are calculated and a t-test applied to check if the constant bias is statistically significant.

Samples of soil spiked at 100.0 mg/kg were extracted for 3,4-dichloroaniline in the working conditions; the extracts were analysed and the values of mean recovery were employed to calculate the concentration of 3,4-dichloroaniline in the samples as they were unknown routine samples.

Two samples of polluted soil of different weights (respectively, 10.0 and 15.0 g) were analysed in replicate to evaluate repeatability. The results are given in Table 3, in which 10.0 and 15.0 g were, respectively, W_n and W_{m}.

The constant bias δ_{ct} is given by:

$$\delta_{\mathrm{ct}} = \frac{W_{\mathrm{m}}\bar{x}_n - W_{\mathrm{n}}\bar{x}_{\mathrm{m}}}{W_{\mathrm{m}} - W_n} = \frac{10 \times 1.0025 - 15 \times 0.7553}{10 - 15} = 0.2608 \quad (15)$$

and its uncertainty:

$$u(\delta_{\mathrm{ct}}) = \frac{1}{W_{\mathrm{m}} - W_n}\sqrt{(W_{\mathrm{m}}u(\bar{x}_n))^2 + (W_n u(\bar{x}_{\mathrm{m}}))^2} \quad (16)$$

where

$$u(\bar{x}_{\mathrm{m}}) = \frac{\mathrm{R.S.D._I}\bar{x}_{\mathrm{m}}}{\sqrt{n}} \quad \text{and} \quad u(\bar{x}_n) = \frac{\mathrm{R.S.D._I}\bar{x}_n}{\sqrt{n}}$$

for $n = 2$.

From the values of $u(\bar{x}_{\mathrm{m}}) = 0.0958$ and $u(\bar{x}_n) = 0.1271$ the calculated uncertainty $u(\delta_{\mathrm{ct}})$ is 0.436.

The constant bias value so obtained must be checked with a t-test to verify if it is statistically significant:

$$|\delta_{\mathrm{ct}}| \leq t_{\alpha/2,\mathrm{eff}}u(\delta_{\mathrm{ct}})$$

Since the tabulated value of t for 24 freedom degree number and $\alpha = 0.05$ ($t = 1.711$) is greater than that calculated ($t = 0.591$) the constant bias must be considered not statistically significant but due to the experimental error and therefore to be enclosed into the total uncertainty.

Table 2
Variances and uncertainties associated to $\bar{\bar{R}}_{\mathrm{m}}$

	10.0 mg/kg	50.0 mg/kg	100.0 mg/kg
$\sum_{j=1}^{4}(\bar{R}_{ij} - \bar{\bar{R}}_i)^2$	0.0068	0.0317	0.0220
$\sigma^2(\bar{\bar{R}}_i)$	0.0006	0.0026	0.0018
$u(\bar{\bar{R}}_{\mathrm{m}})^2 = \frac{\sum_{i=1}^{3}u(\bar{\bar{R}}_i)}{3^2}$	0.0006		

Table 3
Data for the evaluation of the constant bias

Sample weight (g)	Amount of 3,4-DCA found (mg/kg)	Mean amount (mg/kg)
10.0 (1)	0.8123	0.7553 ± 0.0807
10.0 (2)	0.6982	
15.0 (1)	0.8825	1.0025 ± 0.1698
15.0 (2)	1.1226	

3.3. Application to spiked samples

The value of $\overline{\overline{R}}_m$ so obtained was furtherly checked in the determination of 3,4-dichloroaniline in samples of soil of granulometry of ≤2 mm, respectively, spiked at 10.0, 50.0 and 100.0 mg/kg of 3,4-dichloroaniline.

The values corrected for the $\overline{\overline{R}}_m$ give the values respectively of 0.867 (±0.088), 0.920 (±0.089) and 1.007 (±0.092).

4. Conclusion

The paper has shown the evaluation for a polluted soil of a great mean recovery and of the uncertainty associated. As concerns the case in study, i.e. the effect on recovery of 3,4-dichloroaniline as a function of particle size and concentration from of a soil collected in Val Bormida (Piedmont, Italy), the following considerations can be made. The more relevant differences observed in the recovery values are not due to the analyte concentration but to the matrix. Control samples of the soil spiked at different concentration levels showed the suitability of the value $\overline{\overline{R}}_m$ to correct the results experimentally obtained by the extraction procedure and the chromatographic analysis.

It can be also noticed as the experimental recovery is generally low, as on the other hand already observed for 3,4-dichloroaniline in soil [15], therefore the correction is made necessary. The great mean evaluated can be applied only for the determination of the same analyte in soils of similar composition. This can be seen as a limitation but in our opinion is the way to have accurate results when studying for example the amount and the diffusion of a toxic target organic species in waste areas of soil characterised by the same composition. The evaluation of the mean great recovery permits the routine analysis of many samples collected in strategic way.

On the other hand, the low recovery indicates that a great amount of pollutant is retained in soil. This information is of great interest since the pollutant seems to be strongly bound in these fractions. Soil and in particular clay and silt could be advantageously used to concentrate pollutants in remediation strategies.

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