# VARIABILITY OF SOIL SOLUTION IONS IN FALLOWLAND FIELDS IN CENTRAL SPAIN

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Abstract. Variability of soil solution properties must be assessed for proper monitoring of many soil processes. Two sampling frames were established in uncultivated agricultural fields. In the first (300 m<sup>2</sup>), 15 single plots were instrumented with porous ceramic cups placed at 0.4 m soil depth. In the second (2500 m<sup>2</sup>), 50 single plots were instrumented. Results showed that the coefficient of variation (CV) of soil solution properties ranged from 30 % for electrical conductivity (EC) to more than 100 % for Cl- and that a minimum of 40 individual samples were required to estimate representative values of spatial variability of soil solution ions for this field (CV<sub>s</sub>). The coefficient of variation linked to sample size (CV<sub>n</sub>) was expressed as a function of CV<sub>s</sub> of each soil solution property, and sample size. The error curve model of soil solution properties shows that, for a stated precision [Standard error (SE) of  $\pm$  5%], the number of samples required was lower than that estimated by standard methods.

Keywords.Soil solution, variability composition, statístical, fallowlands fields

**Resumen.** La variabilidad de las propiedades de la solución del suelo, debe determinarse mediante medials apropiadas de distintas variables del suelo. En suelos agrícolas en barbecho, se establecieron dos diseños de muestreo. El primero (300 m<sup>2</sup>) estuvo constituido por 15 parcelas individuales. El segundo (2500 m<sup>2</sup>)<sup>2</sup>por 50 parcelas. En ámbos, se instalaron cápsulas porosas a 0,4 m de profundidad. Los resultados indicaron que el coeficiente de variación(CV) de las propiedades de la solución del suelo, osciló entre el 30% para la conductividad eléctrica (EC) y más del 100 % para el Cl- Se requirió un mínimo de 40 muestras individuales para estimar valores representativos de la variabilidad espacial de los iones de la solución del suelo en este campo experimental(CV<sub>s</sub>). El coeficiente de variación ligado al tamaño de la muestra (CV<sub>n</sub>)se expresó como una función del CV<sub>s</sub> de cada propiedad de la solución del suelo y del tamaño de la muestra. El modelo de curva de error de la solución del suelo, indicó que para una precisión establecida [error estandar(SE)de  $\pm 5\%$ ]], el número de muestras requerido fue menor que el estimado por los métodos estadísticos convencionale.

Palabras clave. Solución del suelo, composición de la variabilidad, estadística, campos agrícolas sin cultivar.

# INTRODUCTION

Soil solution chemistry plays a central role in the study of some soil processes. When measured in the root-zone it provides a valid measure of the nutrient status of a soil (Adams and Odom., 1985) or monitoring the effect of soil amendments or fertilisers inputs (Simard *et al.*, 1988).

Monitoring the chemistry of soil solution is also required when the objective of the study is to provide insight on soil processes such as salinity hazards or pollution risk by leaching of toxic chemicals or nutrients to the groundwater table (Campbell *et al.*,1989). In these cases, however, concentration of chemicals in the soil solution should be coupled with monitoring of soil water movement.

In farms of the middle basin of the Jarama River (Central Spain), traditional practices of corn cropping (surface-furrow irrigation and higher-than-required rates of N-fertilisation), coupled with low regional rainfall and a relatively shallow groundwater table, posed a risk of salinity and groundwater pollution. The European Union (EU) directive on nitrate pollution (91/676 EC) required member states to identify risk zones by 1996 and implement action plans by 2000 (Coulter et al., 1996). Changing traditional to improved corn irrigation and fertilisation practices required monitoring of soil water movement (Roman et al., 1996; Roman et al,1999), assessing the soil salinity status (Bustos et al., 1996), and providing for estimates of losses of N fertilisers (Diez et al., 2000). Many of these soil processes require periodical on-field monitoring of the soil solution chemistry. For soil solution derived from suction cups, few investigations have been conducted, but most of them were related to forest ecosystems (Grossmann and Kloss., 1994; Manderscheid and Matzner, 1995), or conducted with less than 10 replicates (Alberts et al., 1977). Solution concentration can be dependent on vegetation or crop gradients relative to the distance or crop development (Koch and Matzner., 1993). We assessed significant variations of soil chemistry in an uncultivated agricultural soil with 50 replicates and factors of variations only dependent on natural heterogeneity of the soil. The main objectives of this research were to assess the relationship between sampling intensity and the size of sampling errors

and to determine the relationship between size of sampling frame and spatial variation of solute chemistry.

## **METHODS**

### The experimental site

Soil solution sampling facilities were established in two contiguous experimental fields measuring 15 m by 20 m (field  $1,F_1$ ) and 24 m by 105 m (field  $2,F_2$ ) at La Poveda Field Station (30 km south-east of Madrid, Spain).  $F_1$  was divided into 25 single plots each one measuring 3 m x 4 m, and F<sub>2</sub> was divided into 120 single plots each one measuring 3m x 7 m. In F<sub>1</sub>, 15 randomly selected plots were instrumented with vacuum extractor tubes and in F2, 50 randomly selected plots were instrumented. Minimum distance between samplers was 3 m in the two sampling frames. This experimental set-up was installed during November 1994 (Fig. 1). A simple random sampling procedure was used to select sample units within the grids of rectangular plots. The selection of any given unit was independent of the selection of all other units. Sample units were selected without replacement as it is most common in natural resource sampling (Avery, 1975).

Four samplings were carried out. In the first one (9 January 1995), 15 samples of the soil solution were obtained from  $F_1$ . In the second one (23 February 1995), a similar number of samples were obtained from  $F_1$ . The third sampling was taken on 25 January 1996 and consisted of 15 samples from  $F_1$  and 50 samples from  $F_2$ . The last sampling (23 May 1996), was performed only in  $F_2$  and 50 samples were extracted. Throughout the period of the experiment, adjustment was required on some samplers to perform adequately.

The soil was a Typic Xerofluvent with a sandy-loam texture in the first 0.5 m and an increasingly and less homogeneous sandy texture below. A gravel layer appeared at the variable soil depth of 1.2-2 m (soil profile).



FIGURE 1. The experimental set-up with simple random sampling.

Top: Sampling frame F2 ( single plots 3m x 7m) Down: Sampling frame F1 (single plots 3m x 4m)

r Instrumented plots with vacuum extractors.

Mean water storage capacity for the entire soil profile was estimated at  $309\pm33$  mm and  $125 \pm 17$  mm for the top 0.4 m. Particle-size distribution, organic matter, and bulk density over the entire soil profile have been reported elsewhere (Roman *et al*, 1996). In the first 0.4 m, analyses of the 50 single plots from F<sub>2</sub> gave the following results: sand =  $359 \pm 44$  g kg<sup>-1</sup>; loam =  $443 \pm 29$  g kg<sup>-1</sup>; clay =  $198 \pm 16$ g kg<sup>-1</sup>; organic matter =  $13 \pm 1$ g kg<sup>-1</sup>; pH =  $8.0 \pm 0.01$  and density  $1.43 \pm 0.03$  Mg m<sup>-3</sup>.

Following traditional cropping practices in the area, the experimental fields were cultivated, before the start of the experiment, under irrigated conditions and a winter cereal-corn cropping sequence Barley (*Hordeum vulgare* L), wheat (*Triticum aestivum* L) and oat (*Avena sativa* L) winter cereals were rotated with corn (*Zea mays* L) over the years previous to the experiment. Crop stubbles were incorporated into the soil. Before the experiments were installed, a wheat crop was harvested on July 1994 and its stubble incorporated to the soil on September 1994. During the period of the experiment, F<sub>1</sub> and F<sub>2</sub> remained uncultivated. In the middle of each selected plot a vacuum extractor tube (inside diameter 63 mm) with a porous ceramic cup was placed at the soil depth of 0.4 m to collect the soil solution. This depth was selected as an intermediate layer between the root zone (first 0.3 m) and the soil layer of lower heterogeneity of the soil profile. Below 0.5 m particle-size distribution is more erratic (Roman *et al.*,1996). A minimum distance between samplers of 3 m allowed to assure that a sampler was not extracting solution from a nearly sampler.

Samples of soil solution were extracted by applying a vacuum of 80 kPa to the tubes. The vacuum was maintained for a period of 10 days. After this period, samples were collected using air pressure and measured individually. Occasionally, the amount of soil water extracted from specific samplers did not allow for analysis of the whole set of chemicals

#### Soil solution chemistry

Determination of Ca<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> were performed by flame photometry (Elex 6361, Igoda, Barcelona), and determination of Mg<sup>2+</sup> was done by atomic absorption spectrophotometry (Perking Elmer 403, Perkin Elmer Hispania, Madrid). Analyses for  $NO_{3^-}$ ,  $SO_{4^{2^-}}$  and Cl- were performed by ion chromatography (Dionex 100 equipment, Hucoa-Erlos, Madrid). The HCO<sub>3</sub>- and CO<sub>3</sub><sup>2-</sup> concentrations were measured by alkalymetric titration. Electrical conductivity (EC) of the soil solution was measured with a Crison 525 conductimeter and pH with a Crison 217 pH meter (Crison, Barcelona). The ISRIC (1987) reference was followed for soil analyses and the Standard Methods (APHA, 1995) for the soil solution chemistry.

Some times, an appropriate sample volume could not be collected. Mean rate of sampling in F<sub>1</sub> (9/1/95) for most ions, except  $CO_3^{2-}$  and  $HCO_3^{-}$ , was 100 %. At this date, only in three samplers the amounts of water extracted allowed the analysis of this latter ion. Mean rates of sampling in F<sub>1</sub> on 23/2/95 and 25/1/96- were 100 % and 77%, respectively. Shortage of water extracted in the latter sampling also affected to  $CO_3^{2-}$  and  $HCO_3^{-}$ because these ions required a higher amount of water to perform the analyses. Mean rate of sampling in F<sub>2</sub> was 94 % at both dates (n= 47) for most ions except  $NO_3^{-}$  (n= 50).

#### Data analyses

Taking into account the objetives of this work, classical statistical approaches were used to evaluate the experimental data.

Spatial variability of the soil solution properties was estimated by calculating the mean and CV of each soil solution ion within each experimental field and sampling time. Sample means were calculated on F<sub>1</sub> (15 measurements) and F<sub>2</sub> (50 measurements). Assumption of normality was tested with the Kolomogorov-Smirnov (K-S) test (Rao *et al.*,1979;Ruiz Maya., 1983). The initial value at the 0.1 probability level was obtained from  $1.22 \text{ n}^{-1/2}$  (n= 50 in F<sub>2</sub>).

The natural heterogeneity of the experimental fields for soil solution properties was carried out by taking series of random samples from n =3 to n = 15 in  $F_1$  and from n = 3 to n= 50 in  $F_2$ . Sample mean and CV for each soil solution property were calculated and plotted upon sample size to test whether or not means and coefficients of variation were stabilised in the sampling interval of  $F_1$  (n=3 to n=15) or in the interval of  $F_2$  (n=3 to n=50). In this way, estimates were obtained for the inherent spatial CV (CV<sub>s</sub>) of each soil solution property, the number of samples required for its estimation and whether or not the exploratory sampling intensity performed in  $F_1$  matched the required sampling intensity.

As reasons of economy and labour may preclude intensive sampling, the sampling error curves were obtained to assess the error associated with lower-than-required sampling intensity. Sampling errors of the means, attributable to sample size, were estimated by performing an statistical sampling procedure without replacement with the  $F_2$  samples (n=47) A computer algorithm based on random mixing and selection was designed to generate simulated samples. The pooled samples were generated in an interval from n=3 individual data per lot to n= 40. At each n<sub>i</sub>, about 2000 lots were required per pooled sample for the sample-averages to converge. The coefficient of variation (CV<sub>n</sub>) was plotted upon size of pooled samples. The algorithm used can be considered as an extension of the bootstrap technique (Efrom and Tibshirani., 1993), but in our case, the objective was not to gauge the accuracy of a real sample of a fixed size, but to assess the error associated with lowerthan-required sampling intensity (Daskalakis., 1996). The statistical sampling procedure used to estimate population parameters for pooled samples was carried out without replacement because the variability of natural resource sampling (Avery, 1975), and the great number of pooled samples that can be generated even at n = 40 (more than  $10^{10}$ ), ensure that most of simulated samples will differ from the real one.

Finally, the relationship of the regression parameters of the error models with  $CV_s$  was tested. In this way, a predictive  $CV_n$  was estimated based on CV attributable to inherent natural heterogeneity of the soil ( $CV_s$ ) and additional CV attributable to lower sample size than required ( $f(CV_s)$ ). If the error model can be expressed in terms of  $CV_s$  and n as parameters, an estimate of  $CV_s$  for soil solution quantities would allow for an estimation of CV linked to the sample size (n) of the soil solution properties.

### **RESULTS AND DISCUSSION**

## Spatial variation of soil solution quantities

The spatial variation of ion concentrations in the soil solution was substantial and varied little between sampling times, both in  $F_1$  and  $F_2$ . Within sampled properties of the soil solution, the lowest variation across experimental fields and sampling times were found for EC (mean CV of 35%) and pH (mean CV of 5%).

TABLE 1. Variations of soil solution chemistry ( $`X\pm SD$ ) and CV (in parenthesis) in two experimental fields

	Field 1 <sup>‡</sup>	(n = 15)		Field 2 <sup>‡</sup>	(n = 50)
Ion †§¶	9/1/95	23/2/95	25/1/96	25/1/96	23/5/96
			mgL-1		
Ca <sup>2+</sup>	348±107	247±135	404±205	559±236	472±205
	(30.7)	(54.6)	(50.7)	(42.2)	(43.4)
Mg <sup>2+</sup>	56±54	85±49	191±75	242±93	235±90
	-96,1	(57.6)	(39.3)	(38.4)	(38.3)
Na <sup>+</sup>	223±62	212±50	283±81	534±195	533±198
	(27.8)	(23.6)	(28.6)	(36.5)	(37.1)
K <sup>+</sup>	58±21	35±19	12.±6	10±6	7±5
	(36.2)	(54.3)	(50.0)	(60.0)	(71.4)
Cl-	410±159	236±163	333±230	550±507	373±430
	(38.8)	(69.1)	(69.1)	(92.2)	(115.3)
$SO_4^{2^-}$	673±234	646±111	1318±447	1830±734	2042±768
	(34.8)	(17.2)	(33.9)	(40.1)	(37.6)
CO <sub>3</sub> <sup>2-</sup>	23±17	14±9	1.6±3.1	0.36±1.7	2.6±4
	(73.9)	(64.3)	-193	-472	-154
HC <sub>O</sub> <sup>3-</sup>	114±160	87±144	262±59	229±91	259±110
	(140.4)	(165.5)	(22.5)	(39.7)	(42.5)
No <sup>3-</sup>	362±251	295±288	634±353	1068±545	376±323
	(69.3)	(97.6)	(55.7)	(51.0)	(85.9)
EC(Sm <sup>-1</sup> )	0.28±0.07	0.25±0.08	0.42±0.15	0.56±0.22	0.50±0.20
	(25.6)	(32.0)	(35.7)	(39.3)	(40.0)
рН	8.3±0.6	9.3±0.6	7,9±0.1	7.6±0.2	7.9±0.3
	(7.2)	(6.4)	(1.3)	(2.6)	(3.8)

<sup>†</sup>Most ions showed symmetrical distribution (K-S Test not significant) except  $HCO_{3^{-}}$  (P<0.01) in 2-23-95 and K+ (P<0.05) in 5-23-96 <sup>‡</sup>Field 1 (F<sub>1</sub>) and Field 2 (F<sub>2</sub>), see experimental set-up (Fig 1)

<sup>§</sup>A lag distance of spatially correlated data was not observed when semivariance of data was calculated for each soil solution property within fields and sampling time

"Occasionally, data of CO32-, HCO3- are referred to lower number because of lack of water extracted

When comparing ions, the lowest variation was found for Na<sup>+</sup> (mean CV of 32%) and the highest were found for Cl<sup>-</sup> and NO<sub>3</sub>-(mean CV of 77% and 72%, respectively) across sampling frames and sampling times (Table 1).

The symmetry of distribution of sampling units analyses for each ion and EC was tested within sampling frames and sampling times. It was shown that the distribution of most data did not differ significantly from normality at the 0.1 probability level. In F<sub>1</sub> (n=15), the exception was HCO<sub>3</sub>- (23/2/95) and in F<sub>2</sub> (n=50), the exception was K<sup>+</sup> (23/5/96). Main soil properties of particlesize distribution, organic matter, pH and density in the 50 sampling units of F<sub>2</sub> showed also a symmetrical distribution.

Sampling frames of  $F_1$  and  $F_2$  differ essentially in plot size. Conventional sampling theory assumes that larger plots tend to have less relative variability because they average out the effect of irregular plant or trees distribution (Avery, 1975). In uniform settings, such as our uncultivated plots, changes in plot size had little effect on variance. Our results showed that an area ratio of  $F_2/F_1=8.4$  did not reduce the relative variability of most chemical properties of the soil solution. The relative variability of some ions (Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>) changed little and the pattern of change of most ions was unsteady (Table 1).

#### Sampling optimisation

As sampling measurements were symmetrical and plot size had little influence on variance of main properties of the soil solution, sampling intensity required to match the natural heterogeneity of the experimental fields should be estimated.

Series of random samples from n = 3 to n = 15 in  $F_1$  and from n = 3 to n = 50 in  $F_2$  were selected and corresponding means and CV were calculated for each ion and sampling time .The convergence of CV across of randomly selected series of samples was an indi-

cator of optimum sampling intensity. It was shown that in  $F_1$  (up to n=15) the means and CV of different sampling series were unsteady and linked to sampling intensity. Stated on other way, a sampling intensity up to 15 sampling units did not match the spatial variability linked to the natural heterogeneity of the soil, and did not allow for calculation of the true coefficient of variation of most soil solution properties. In the interest of space, only the convergence of four series of random samples in  $F_1$  (1-9-95) for both the most abundant and least mobile ion (SO<sub>4</sub><sup>2-</sup>) are presented in Fig. 2.

The same sampling process was carried out in  $F_2$  (n = 50). Within this sampling intensity the residual of means and CV over n=40 showed little variation. The main conclusion of this sampling exercise was that a sampling intensity of n = 50 would match the influence of the natural heterogeneity of the soil solution properties, and thus a true CV, or spatial coefficient of variation (CV<sub>s</sub>), can be calculated for each soil solution property. After this exercise, it can be assessed that CV obtained in  $F_2$  with 50 individual samples (Table 1) may represent the true CV of soil solution properties associated to the natural heterogeneity of the experimental field.

This optimum sampling intensity for estimating the true mean of soil solution properties is rather high, and a compromise may be desirable between precision and economic feasibility. In this case, the error associated with below optimum sampling intensity must be estimated.

#### Sampling variation

Once the  $CV_s$  of soil solution properties, associated with the natural heterogeneity of soils, were estimated we can gauge the accuracy of samples at n = 50. But our main objective was to evaluate the sampling error in samples of lower size, and thus to assess the tradeoffs between precision and economy of labour. To do that, the distribution functions of pooled



FIGURE 2. Convergence of CVn in four random series of  $SO_4^{2-}$  samples of in-creasing size in the two sampling frames.

samples were generated. In the range from n=3 to n=40 the number of samples that can be generated without replacement was very high (between 2 x 10<sup>4</sup> and 10<sup>14</sup>) and thus there is no reason to replace individual measurements to ensure differences between generated samples. Above 2000 lots at each  $n_i$ , the distribution functions changed little, the means were stable, the CV changed with the number of random samples included in the lots and the error curves showed normality. This analysis was carried out for all ions and two sampling of plot  $F_2$ , as  $F_1$  sampling intensity was shown to be below optimum.

In Fig. 3, variation of CV upon (n) for Cland  $SO_4^{2-}$  are presented. The least square procedure fitted a model which is linear in the parameters and is defined by the following equation:

$$CV_n = \beta_0 + \beta_1 Ln(n)$$
(3)

where  $CV_n$  represents the coefficient of variation linked to sampling intensity (n). The

parameters of the regression were estimated for each soil solution property and the two sampling times in F<sub>2</sub>. The determination coefficient (R<sup>2</sup>) obtained with 19 data pairs varied from 0.982 for EC (23/5/96) to 0.991 for SO<sub>4</sub><sup>2-</sup> or HCO<sub>3</sub><sup>-</sup> (25/1/96). As the distribution function of the CV<sub>s</sub> was known and the regression model of CV on (n) is linear in the parameters, we regressed the parameters of the model upon CV<sub>s</sub> (Fig. 4). It was shown that CV<sub>s</sub> explained almost entirely the variation of the regression parameters and thus, the CV associated with sampling intensity (CV<sub>n</sub>) can be defined as a proportion of the spatial coefficient of variation (CV<sub>s</sub>):

$$CV_n = CV_s \ (0.7053 - 0.1775 \ Ln \ (n) \ (4)$$

This model states that in our experimental field ( $F_2$ ) the inherent  $CV_s$  for each ion, associated to the natural heterogeneity of the plot, should be increased by a proportion that depends on the sampling intensity. When sampling intensity increased from n = 5 to n



FIGURE 3. Error model of generated pooled samples with stabilized mean and convergence of CVn (Eq.4)



Fig.4

FIGURE 4. Linear regression of parameters of the error model (Eq.4) upon the spatial CV.

= 40, the ratio  $CV_n/CV_s$  decreased from 0.42 to 0.05. For an optimum sampling intensity of n = 54, the coefficient of variation reached zero and the only source of variation for estimating the true mean of each ion would be the natural heterogeneity of the soil (CVs).

Below optimum sampling intensity for each ion increased the corresponding  $CV_s$  to a total coefficient of variation ( $CV_t$ ) given by:

$$CV_t = CV_s + CV_n = CV_s [1 + (0.7053 - 0.1775 Ln(n))]$$
 (5)

As each ion presented an associated  $CV_s$ , the estimated  $CV_t$  linked to the intensity of sampling can be calculated as a proportion of  $Cv_n/Cv_s$  (Table 2).

The intensity of sampling required in the model to assess the mean associated to  $CV_s$  within  $\pm 5$  % was compared with sampling intensity required by standard distribution. Calculations assumed that sampling procedures and field measurements are unbiased and no computational mistakes are included and thus statements of probability account for sampling variation only (Avery, 1975). If the  $CV_n$  is expressed at a fixed 5 % of  $CV_s$  the number of samples required can be calculated to contain the mean at a probability of 68 % ( $CV_n$ ) or 95 % ( $2CV_n$ ).

$$n = \exp \{(0.7053 - 5/CV_s) / 0.1775\}$$
(6)  
or n = exp {(1.41 - 5/CV\_s) / 0.355} (7)

The results for each ion are presented in Table 3. When Eq. 1 was applied, sampling intensity increased by four times when the CV doubled. In the second sampling in  $F_2$ , EC and NO<sub>3</sub><sup>-</sup> showed CV<sub>s</sub> of 40 and 86% res-

TABLE 2. Estimates total coefficient of variation (CVt) of soil solution properties as a function of sample size (n) and spatial coefficient of variation of each chemical determination at two sampling times in field F2.

Sample size									
<u>(n)</u>		2	3	4	5	8	10	20	40
CVn /CVs		0.5823	0.5103	0.4592	0.4196	0.3362	0.2966	0.1736	0.0505
Item									
					CVt%				
EC	1†	62.2	59.4	57.3	55.8	52.5	51.0	46.1	41.3
	2	63.0	60.1	58.1	56.5	53.2	51.6	46.7	41.8
Cl-	1	145.9	139.2	134.5	130.9	123.2	119.5	108.2	96.9
	2	182.4	174.1	168.2	163.7	154.1	149.5	135.3	121.1
SO <sub>4</sub> 2-	1	63.4	60.6	58.5	56.9	53.6	52.0	47.1	42.1
	2	59.5	56.8	54.9	53.4	50.2	48.8	44.1	39.5
HCO <sub>3</sub> -	1	62.8	60.0	57.9	56.4	53.0	51.5	46.6	41.7
	2	67.2	64.2	62.0	60.3	56.8	55.1	49.9	44.6
Ca <sup>2+</sup>	1	66.8	63.7	61.6	59.9	56.4	54.7	49.5	44.3
	2	68.7	65.5	63.3	61.6	58.0	56.3	50.9	45.6
Mg <sup>2+</sup>	1	60.8	58.0	56.0	54.5	51.3	49.8	45.1	40.3
	2	60.6	57.8	55.9	54.4	51.2	49.7	44.9	40.2
Na+	1	57.8	55.1	53.3	51.8	48.8	47.3	42.8	38.3
	2	58.7	56.0	54.1	52.7	49.6	48.1	43.5	39.0
K+	1	103.6	98.9	95.6	93.0	87.5	84.9	76.9	68.8
	2	113.0	107.8	104.2	101.4	95.4	92.6	83.8	75.0
SiO <sub>2</sub>	2	87.8	83.8	81.0	78.8	74.2	72.0	65.1	58.3
NO <sub>3</sub> -	1	80.7	77.0	74.4	72.4	68.1	66.1	59.9	53.6
	2	135.9	129.7	125.3	121.9	114.8	111.4	100.8	90.2

†1: Date 25/1/96; 2: Date 23/5/96

pectively (Table 1). Theoretical sampling intensity required (SE of  $\pm$  5% at a probability level of 0.95) was 246 and 1100 samples for an infinite population (Eq.1). If the correction factor for a finite population on F<sub>2</sub> was applied (Eq.2), 81 and 112 samples of a total of 120 were required.

When the same level of precision was considered in Eq.7, the estimated sampling intensity for EC and  $NO_3$  - were 38 and 46 sampling units, respectively. These results showed that sampling intensity required for estimating population mean of soil solution properties within a required precision level can be lower than predicted by theoretical models. This fact may illustrate that these soil solution properties may not totally behave as whole random variables.

#### CONCLUSIONS

This work shows that the main soil solution properties are normally distributed. The coefficients of variation calculated for soil solution properties were rather high (between 40 and more than 100% ), and researchers should be aware of the higher number of samples required to estimate means with acceptable precision level. A compromise between precision and labour can be desirable, but in this case, sample means will estimate the true means with an additional error linked to lower-than-required sampling intensity. Our sampling analysis allowed for estimating this error that should be added to the error estimate of each soil solution property linked to specific soil conditions.

		Probability 68 %		Probability 95%		
	Item	Actual‡	Theoretical	Actual	Theoretical	
EC	1†	26	61	37	234	
	2	27	65	38	248	
Cl-	1	40	346	46	1326	
	2	42	490	47	1879	
SO42-	1	27	66	38	251	
	2	26	57	37	217	
HCO3-	1	27	64	38	245	
	2	28	73	39	281	
Ca2+	1	28	72	39	274	
	2	28	77	39	294	
Mg <sup>2+</sup>	1	26	59	37	227	
	2	26	59	37	227	
Na+	1	25	53	37	204	
	2	25	55	37	212	
K+	1	35	172	43	660	
	2	36	207	44	795	
NO <sub>3</sub> -	1	31	104	41	400	
	2	39	296	46	1137	
SiO <sub>2</sub>	2	32	124	42	473	

TABLE 3. Sample size required to estimate populations means of soil solution

†1: Date 25/1/96; 2: Date 23/5/96

\* Actual: Eq. (7) and (8); Theoretical: Eq (2) with SE =5% of the mean and corresponding t values.

## ACKNOWLEDGEMENTS

This research was supported by the Regional Government of Madrid (Contract No CRD 0010/94). The authors acknowledge the assistance of A.Caballero and P.J Hernaiz, attached to La Poveda Field Station, in performing most of field work.

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