

**Certification of soil-pH (suspensions of water
and CaCl_2) and adsorption coefficients for
atrazine, 2,4-D and lindane in six different
reference soils (EUROSOILS)
IRMM-443**

joint research centre
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Mission

The mission of IRMM is to promote a common European measurement system in support of EU policies, especially internal market, environment, health and consumer protection standards.

**IRMM information
REFERENCE MATERIALS**

**Certification of soil-pH (suspensions of
water and CaCl_2) and adsorption coefficients
for atrazine, 2,4-D and lindane in six different
reference soils (EUROSOILS)
IRMM-443**

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ABSTRACT

The Institute for Reference Materials and Measurements has characterised and certified a set of six European reference soils, the so-called EUROSOLS - under the number IRMM-443. This unique set reference soils has been originally designed by the former JRC Environment Institute (now Institute for Environment and Sustainability – IES). After a successful validation and trial period it was decided to transfer the project to IRMM in order to produce a new type of certified reference materials.

This report describes the certification of pH in suspensions of pure water and 0.01 M CaCl₂ as well as of the adsorption coefficients for atrazine, 2,4-D and lindane in these soils. Additionally, indicative values for the pedological parameters C_{tot}, C_{org} and N_{tot} are given. The adsorption coefficients were obtained according to the prescriptions made in the OECD Testguideline 106 whereas for the pedological parameters the respective ISO Standards were followed.

The certified values ($\pm$ expanded uncertainty U_{CRM} with a coverage factor k=2) are:

<i>Parameter</i>	<i>EUROSOIL 1</i>	<i>EUROSOIL 2</i>	<i>EUROSOIL 3</i>	<i>EUROSOIL 4</i>	<i>EUROSOIL 5</i>	<i>EUROSOIL 7</i>
K _f of atrazine	7.0 $\pm$ 1.5	2.7 $\pm$ 0.7	2.4 $\pm$ 0.7	0.7 $\pm$ 0.4	13 $\pm$ 6	4.8 $\pm$ 1.1
1/n of atrazine	0.91 $\pm$ 0.10	0.93 $\pm$ 0.12	0.91 $\pm$ 0.13	0.87 $\pm$ 0.22	0.9 $\pm$ 0.4	0.92 $\pm$ 0.15
K _f of 2,4-D	2.5 $\pm$ 1.0	0.99 $\pm$ 0.30	1.31 $\pm$ 0.28	0.39 $\pm$ 0.21	18 $\pm$ 7	8.2 $\pm$ 1.8
1/n of 2,4-D	0.9 $\pm$ 0.4	0.96 $\pm$ 0.15	0.93 $\pm$ 0.15	0.86 $\pm$ 0.31	0.9 $\pm$ 0.4	0.88 $\pm$ 0.15
K _f of lindane	*	48 $\pm$ 11	*	8.3 $\pm$ 2.2	*	*
1/n of lindane	*	0.98 $\pm$ 0.15	*	0.96 $\pm$ 0.12	*	*
pH in water	6.21 $\pm$ 0.30	8.1 $\pm$ 0.9	6.2 $\pm$ 0.4	7.5 $\pm$ 0.7	4.1 $\pm$ 1.5	5.1 $\pm$ 0.8
pH in 0.01 M CaCl ₂	5.65 $\pm$ 0.24	7.5 $\pm$ 0.8	5.5 $\pm$ 0.4	6.8 $\pm$ 0.6	3.1 $\pm$ 1.1	4.3 $\pm$ 0.7

The reference materials are intended to control and optimise the performance of adsorption testing, as well as to improve the measurement quality and comparability of pedological parameter measurements, especially in relations to the respective European legislation.

GLOSSARY

ANOVA	Analysis of Variance
BCR	Community Bureau of Reference
CEC	Cation-exchange Capacity
CRM	Certified Reference Material
EI	Environment Institute
ES	EUROSOIL
GUM	Guide to the Expression of the Uncertainty in Measurement
HPLC-DAD	High pressure liquid-chromatography with diode-array detector
IES	Institute for Environment and Sustainability (formerly EI)
IRMM	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardisation
K'	concentration dependent adsorption coefficient
K _f	Freundlich isotherm-derived adsorption coefficient
MSB	Mean square between groups (ANOVA)
MSW	Mean square within groups (ANOVA)
1/n	Slope of linearised Freundlich isotherm
N	Number of replicates
OECD	Organisation for Economic Co-operation and Development
Pow	Octanol/water partition coefficient
RSD	relative standard deviation
SI	international system of units
SOP	standard operating procedure
U _{CRM}	expanded uncertainty of the CRM (k=2)
u _{char}	standard uncertainty of the characterisation
S _{betw}	standard deviation between certification laboratories (ANOVA)
u _{bb}	between-bottle uncertainty used for the calculation of U _{CRM}
S _{wb}	within-bottle variation (ANOVA)
S _{bb}	standard deviation between bottles (ANOVA)
TG	Test Guideline
u _{Its}	standard uncertainty of stability during storage
u _{Sts}	standard uncertainty of stability during transport
WDXRF	Wavelength-dispersive X-ray fluorescence spectrometry
XRF	X-ray fluorescence spectrometry

DEFINITIONS

Soil Adsorption is the process of adhesion or bonding of ions or molecules onto the surface of soil particles.

Reference Soil is a soil, which has been identified according to a number of pre-established representativity criteria upon statistical analysis.

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1. INTRODUCTION

Human activities are closely related to the dispersion of chemical substances in the environment. These environmental chemicals are either deliberately distributed to the different compartments or arrive due to an uncontrolled or accidental process in our natural environment. Every year approximately 1000 new substances are added to the list of commercial chemical substances [1] and the study of the possible interactions between a compound and the environmental compartments has become mandatory for the producer. In the respective evaluation schemes for environmental risk assessment interactions with soil play a special role, because the soil compartment includes the other compartments water and atmosphere [2]. Owing to the complex and heterogeneous structure of soil it is particularly difficult to obtain representative and comparable data for soil-related measurements, tests and analyses. In recent years the threat to drinking water resources by contaminated soil and the public understanding of the relationship between safe food and uncontaminated soil have increased the interest in soil-related studies. This development resulted also in the modification of the legal framework dealing with the issue of soil protection and quality. Thus, the European Commission will introduce limit values for heavy metals in function of soil-pH within the framework of the revised European Sludge Directive [3]. Measurements of other parameters like nitrogen content (N_{tot}), cation-exchange capacity (CEC) or organic carbon contents (C_{org}) are gaining importance not only regarding their effects on the soil mobility of chemical substances, but also for the control of agricultural practise regarding fertilisation and pest control. As any analytical data soil-related measurements must be reliable in order to be of any use for regulatory purposes. Therefore, the European Commission's Institute for Environment and Sustainability (formerly EI) developed in close collaboration with other EC Directorate Generals and several national institutions a set of reference soils to be used as standard matrices and reference materials for soil testing of chemicals and the determination of pedological parameters [4]. Originally, these soils had been designed only for sorption testing in the framework of OECD Test Guideline 106, but soon after their successful implementation in 1990 the soils found a by far broader application range [5]. In 1994, the decision was taken to prepare a second generation of the EUROSOLS as candidate reference materials and in 1999, the comparison between the new and the old set showed that the main properties of the original five soils could be reproduced in the remakes [6, 7]. In order to consider the particular geo-morphological conditions of the Alpine region after the EU-Accession of Austria in 1995, a new soil was included in the set [8]. Considering the positive feedback from the interested laboratories it was decided that the JRC's Institute for Reference Materials and Measurements, being the European Commission's Transnational Metrological Institute, organises a certification campaign for the second generation of EUROSOLS. The results of this campaign, which aimed at the certification of the adsorption behaviour of three reference substances (atrazine, lindane and 2,4-D) according to the OECD Test Guideline 106, and some pedological parameters according to the respective ISO Guidelines, i.e. pH of soil suspension, total nitrogen content, total and organic carbon content, are presented in this report.

2. PARTICIPATING LABORATORIES

Soil identification and field work

European Commission, DG Joint Research Centre, Institute for Environment and Sustainability (formerly EI), Ispra (IT);

Universität Kiel, Institut für Geographie, Kiel (DE).

Candidate material production

European Commission, DG Joint Research Centre, Institute for Environment and Sustainability (formerly EI), Ispra (IT).

Homogeneity and stability studies

European Commission, DG Joint Research Centre, Institute for Environment and Sustainability (formerly EI), Ispra (IT);

European Commission, DG Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel (BE).

Certification exercise

Aventis Crop Science GmbH, Umweltchemie, Frankfurt a. M. (DE);

Biologische Bundesanstalt für Land- und Forstwirtschaft, Institut für Ökotoxikologie, Berlin (DE);

Consejo Superior de Investigaciones Científicas, Estacion Experimental del Zaidín, Granada (ES);

Ecole Nationale Supérieure d'Agronomie et des Industries Alimentaires, Laboratoire Associé Sols et Environnement, Vandœuvre (FR);

Fraunhofer-Institut für Umweltchemie und Ökotoxikologie, Schmallenberg (DE);

National Center of Public Health, National Research Institute for Radiobiology and Radiohygiene, Budapest, (HUN);

Planteforsk, Norsk Institutt for Planteforsking, Plantevernet, Ås (NOR);

Umweltbundesamt, Labor für Bodenanalytik, Berlin (DE);

Unilever Research, Port Sunlight Laboratory, Ecotoxicology Section, Bebington (UK);

Universität für Bodenkultur, Institut für Bodenforschung, Wien (AU).

Evaluation

European Commission, DG Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel (BE).

Project management

The EUROSOLS-Project was launched by the former JRC Environment Institute (now IES) in 1989, but during the second phase of the project, it was decided to transfer the responsibility for the certification of the resulting reference materials to IRMM. This transfer was done after the candidate material production of the second generation of the EUROSOLS. The materials were re-grouped under the label IRMM-443 – EUROSOLS.

3. PREPARATION OF THE MATERIAL

A more detailed description of the individual preparation steps as well as on the underlying statistical principals of representative soil samples is given elsewhere [9]. However, in the following sections details on the production of the candidate material *per se* are given. In addition to that, the criteria for the selection of the soils are briefly summarised.

3.1 Choice of the soils

The soils selected were chosen in such a manner, that the entire set reflects in a representative way the most frequent and typical soil types of the EU-area [4, 10]. To this end three representativity criteria were established:

Representativity of soil characteristics: the selected soils cover a broad range of properties affecting the mobility and fate of a chemical substance in soil like pH, cation-exchange capacity, clay content or organic carbon content;

Representativity with respect to frequency distribution: if the reference soils are typical representatives of the most frequent soil associations, the measurements derived from them are to a certain extend valid for a large area of the EU;

Regional representativity: the sites – also identified as reference sites for the particular soils [10] – were chosen in a manner that typical regional association pattern with other soils and the main climatic conditions in the EU were included. Furthermore, care was taken to consider the main types of plant communities and land use patterns.

Table 1 briefly summarises the soil locations selected according to these criteria.

Table 1 - The EUROSOILS-Locations and some field characteristics measured during the sampling using fresh untreated samples.

Soil	Origin	FAO soil unit	Clay [%]	C _{org} [%]	pH (0.01 M CaCl ₂)
EUROSOIL 1	Sicily (Italy)	Vertic Cambisol	75.0	3.3	5.7
EUROSOIL 2	Peloponnesos (Greece)	Rendzina	22.6	2.4	7.2
EUROSOIL 3	Wales (U. K.)	Dystric Cambisol	17.0	3.3	5.9
EUROSOIL 4	Normandy (France)	Orthic Luvizol	20.3	1.4	6.8
EUROSOIL 5	Schleswig-Holstein (Germany)	Orthic Podzol	6.0	4.4	3.2
EUROSOIL 6 ^(a)	Normandy (France)	(BC Horizon of EUROSOIL 4)	16.0	0.25	7.2
EUROSOIL 7 ^(b)	Lungau (Austria)	Dystric Cambisol	18.8	6.7	4.4

(a) EUROSOIL 6 is not a reference soil in the defined sense. Sampling for a re-make was omitted, as there was no need to reproduce the material. However, to avoid any confusion the designation as EUROSOIL 6 was maintained

(b) EUROSOIL 7 was included as a new member of the set

3.2 Sampling and pre-treatment

In 1991, at each of the specified locations the vegetational cover was removed and a sufficient amount of top soil material (ca. 150-200 kg) to a maximum depth of 30 cm was collected, passed over a coarse sieve (10 mm) and transported to the JRC-IES for further processing.

3.3 Homogenisation and bottling

After air-drying and a gentle, manual crushing, the resulting materials were passed over a 2-mm aperture sieve. The fraction >2mm was discarded while the fraction <2mm was

homogenised in a single batch using a roll-bed mixer and a specially designed PE-Mixing drum. The soils were homogenised for 2 weeks. Finally, the soils were bottled into brown borosilicate bottles (250 mL) in units of approximately 200g. The bottles were closed with a PE-insert and a screw cap. After performance of a bulk and final homogeneity study a preliminary stability study using atrazine adsorption behaviour as indicator was performed [11]. With begin of the certification project a more thorough short and long-term stability study has been initiated. A total of approximately 400 units per soil have been produced. The certification exercise took place in 2000 (March to November) and results were discussed and scrutinised in a certification meeting in Geel, Belgium on the 24-25 January 2001.

4. CERTIFICATION MEASUREMENTS

4.1 Adsorption of atrazine, 2,4-D and lindane

These three well-known pesticides cover a certain polarity range and are easy to be analysed in soil. Thus, they are most indicated as reference substances to assess and describe the adsorption properties of soil/solution systems.

The test method in this campaign is based on the generally accepted OECD Testguideline 106 [12] and as such in agreement with the scheme employed for adsorption measurements in the framework of environmental risk assessment and packaging and labelling of new chemical substances. The test guideline has been revised recently [12] and the European Commission has implemented this updated version into Annex V of Directive 67/548/EEC, which is regularly revised and amended. The testing scheme used for certification is based on this update, but several parameters have been fixed to achieve a higher degree of standardisation and thus to make the exercise more feasible with a better comparability among the individual results. Known volumes of solutions of the test substance, non-labelled or radio-labelled, at known concentrations in 0.01 M CaCl_2 were brought into contact with a defined amount of soil. The mixture was agitated for an appropriate time. The soil suspensions were then separated by centrifugation, and, if so wished, filtration and the aqueous phase was analysed. The amount of test substance adsorbed on the soil sample was calculated as the difference between the amount of test substance initially present in solution and the amount remaining at the end of the experiment (indirect method).

As an option, the amount of the test substance adsorbed could also be directly determined by analysis of soil (direct method). Although this makes the analytical procedure more tedious, involving stepwise soil extraction with an appropriate solvent, it may be recommended in cases where the difference in the solution concentration of the substance cannot be accurately determined.

In a first step a screening was required to establish analytical conditions. Freundlich isotherms [13] were then determined at room temperature (20-25°C). No desorption testing was performed. Details on the instructions given to the participants can be found in Annex I to this report.

4.2 pH using a suspension of water and 0.01M CaCl_2 (ISO 10390)

The method used was based on the ISO standard 10390. According to this standard, pH of a soil suspension may be measured in pure water, in a solution of calcium chloride or in a solution with KCl. The latter option however, is less indicated for agricultural soils as the ionic strength introduced by the strong access of KCl modifies considerably the original

properties of the soil. The participants in campaign measured pH in a suspension of soil in five times its volume of the water or a 0.01 mol/L solution of calcium chloride (CaCl_2) in water under reproducibility conditions. Details on the procedure applied can be found in Annex I.

4.3 Measurement of contents of total C, N and organic C

In the original design of the certification exercise it was planned to certify also the contents of total carbon and nitrogen and organic carbon. Unfortunately, the number of laboratories, which volunteered to participate in these exercises, was too low to allow certification of the derived data. Nevertheless, these data are included in this report as indicative values as they may be interesting to understand better the certified values of the adsorption coefficients and the pH. The applied procedures were as in the case of pH derived from the respective ISO standards currently in force. The detailed procedure can be found in Annex I, whereas the data are re-group under the heading “Indicative Values” in Chapter 7 of this report.

5. RESULTS

5.1 Certification collaborative study

The certification took place between April and November 2000. Analyses were done under reproducibility conditions on two different bottles. The results submitted were subjected to technical scrutinisation during a certification meeting held at IRMM in January 2001. Technical details on the analytical procedures are given in the annexes to this report.

In case of adsorption measurements for atrazine and 2,4-D one laboratory had measured only at the two higher initial concentrations due to technical problems in detecting lower concentrations. As this may cause an artifact it was decided not to use these results. Another laboratory reported problems when working with a soil intake of 2 g, although this is the minimum soil intake allowed by OECD TG 106. In cases where adsorption was particularly vigorous the laboratory decided to withdraw its results, because the analytical technique applied was not precise enough to allow correct quantification of the substance amount adsorbed onto soil. During the certification meeting Lab 10 presented evidence for adsorptional losses in case of lindane due to adsorption on the test containers used and withdrew its result.

Owing to a large scattering of data and the related high uncertainty statement it was decided not to certify all adsorption data. For further details refer to the section below.

For the soil pedological parameters all data sets were accepted. However, owing to the low number of data, it was decided not to certify parameters N_{tot} , C_{org} and C_{tot} . These values are given as indicative values, i.e. without uncertainty statement.

An analysis of variance (ANOVA) was performed, the results of which are shown in the respective tables. The results show that the variation of laboratory averages can be mainly attributed to differences between the averages while variation within the laboratories is only a minor contribution.

The uncertainty from the interlaboratory study is referred to as u_{char} and comprises uncertainties from between-laboratory reproducibility and within-laboratory repeatability. The standard error of the mean (s_e)

$$s_e = \frac{s}{\sqrt{N}}$$

with s being the standard deviation of the mean and N the number of laboratories was used as the best estimation of the combined effect of these influences.

Laboratory means for the adsorption testings were calculated from the individual results obtained per bottle and per laboratory. The mean values were calculated by performing linear regression analysis (least-squares method) on the pooled data sets per laboratory. From these data Freundlich isotherm coefficients were calculated. Uncertainty of these laboratory means was expressed as standard error (and not as standard deviation), because the outcome of the regression analysis is based already on a mean value per initial concentration (two replicates per concentration level). In this situation the application of the Gaussian error on the mean, i.e. s_e , is a more realistic and appropriate estimate of the uncertainty related to the adsorption coefficients, rather than the Gaussian error on the single value, i.e. s . The usually applied scheme for laboratory means plus standard deviation was used only in the case of the pH in suspensions.

It should also be stressed that the individual adsorption data as well as the uncertainty statement were obtained from a linear regression of logarithmic data. The derived standard errors were then translated into their exponential form, which may have caused an over-estimation of the related uncertainty in case of the K_f . In cases where adsorption is almost negligible, this may also lead to the fact that the range covered by the uncertainty includes 0.

5.1.1 Atrazine

The individual results are given in Annex II. Laboratory averages of 16 measurements on two bottles (2 times four initial concentrations on each bottle), standard error of the Freundlich isotherms coefficients K_f (from intercept) and $1/n$ (from slope) from the accepted data-sets are given in Table 2 to Table 7. All results were rounded to the same decimal position).

Table 2 – Summarised results for atrazine adsorption on EUROSIL 1

EUROSIL 1		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 1	7.4721 ± 1.0322	0.9449 ± 0.0133
	Lab 5	6.1474 ± 1.0220	1.0637 ± 0.0099
	Lab 6	7.2555 ± 1.0530	0.9031 ± 0.0204
	Lab 7	6.0602 ± 1.0426	0.7049 ± 0.0282
	Lab 8	7.7719 ± 1.0398	0.9216 ± 0.0167
	Lab 9	7.1928 ± 1.0104	0.8931 ± 0.0043
	Lab 10	6.9586 ± 1.0832	0.9106 ± 0.0327
Mean of means		6.9769	0.9060
Standard deviation between means s		0.6516	0.1059
Number of laboratories N		7	
Standard error of the mean of means		0.2463	0.0401
ANOVA	s within labs	0.6932	0.0258
	s between labs	0.3734	0.0886

With the exception of EUROSIL 1 the observed between-laboratory variability is larger than the respective within-laboratory value. In case of EUROSIL 1 $s_{\text{within labs}}$ is slightly higher than $s_{\text{between labs}}$. This may be attributed to the rather strong and almost complete adsorption of atrazine on the clayish soil material. This particularity emphasises and amplifies to a certain

extend heterogeneity effects, which are difficult to be excluded for such a coarse substrate (< 2mm instead of the usual <90 μm for soil reference materials). However, the observed results are in an acceptable range.

Table 3 – Summarised results for atrazine adsorption on EUROSOIL 2

EUROSOIL 2		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 1	2.6638 ± 1.0142	0.9398 ± 0.0067
	Lab 5	2.0100 ± 1.0288	0.9581 ± 0.0141
	Lab 6	2.6077 ± 1.0486	0.9508 ± 0.0224
	Lab 7	3.3434 ± 1.0184	0.8097 ± 0.0146
	Lab 8	3.2026 ± 1.0389	0.9549 ± 0.0189
	Lab 9	2.6265 ± 1.0109	0.9088 ± 0.0052
	Lab 10	2.6673 ± 1.0388	0.9746 ± 0.0185
Mean of means		2.7316	0.9281
Standard deviation between means s		0.4382	0.0560
Number of laboratories N		7	
Standard error of the mean of means		0.1657	0.0212
ANOVA	s within labs	0.2553	0.0318
	s between labs	0.3753	0.0389

Table 4 – Summarised results for atrazine adsorption on EUROSOIL 3

EUROSOIL 3		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 1	2.2696 ± 1.0241	0.9326 ± 0.0115
	Lab 5	1.9614 ± 1.0421	0.9708 ± 0.0206
	Lab 6	2.0632 ± 1.0736	0.9497 ± 0.0342
	Lab 7	3.2435 ± 1.0469	0.6497 ± 0.0338
	Lab 8	2.7609 ± 1.0429	0.9945 ± 0.0214
	Lab 9	2.3096 ± 2.3116	0.9213 ± 0.0061
	Lab 10	2.54601 ± 1.0259	0.9584 ± 0.0124
Mean of means		2.4498	0.9110
Standard deviation between means s		0.4425	0.1177
Number of laboratories N		7	
Standard error of the mean of means		0.1675	0.0445
ANOVA	s within labs	0.2688	0.0383
	s between labs	0.3336	0.0874

Table 5 – Summarised results for atrazine adsorption on EUROSOIL 4

EUROSOIL 4		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 1	0.7142 ± 1.0279	0.8991 ± 0.0142
	Lab 5	0.2836 ± 1.0759	0.8861 ± 0.0391
	Lab 6	0.5557 ± 1.1864	1.0207 ± 0.0878
	Lab 7	1.2841 ± 1.0118	0.6675 ± 0.0097
	Lab 8	0.7863 ± 1.0743	0.8188 ± 0.0381
	Lab 9	0.7005 ± 1.0270	0.8654 ± 0.0141
	Lab 10	0.8764 ± 1.0192	0.9644 ± 0.0100
Mean of means		0.7430	0.8746
Standard deviation between means s		0.3058	0.1127
Number of laboratories N		7	
Standard error of the mean of means		0.1156	0.0426
ANOVA	s within labs	0.1106	0.0907
	s between labs	0.2557	0.0723

Table 6 – Summarised results for atrazine adsorption on EUROSIL 5

EUROSIL 5		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 1	15.8965 $\pm$ 1.0245	0.9428 $\pm$ 0.0085
	Lab 2	10.6495 $\pm$ 1.0518	0.8840 $\pm$ 0.0186
	Lab 5	10.4202 $\pm$ 1.0877	0.9403 $\pm$ 0.0324
	Lab 6	15.5360 $\pm$ 1.0364	0.9318 $\pm$ 0.0123
	Lab 8	15.2383 $\pm$ 1.0195	0.9107 $\pm$ 0.0070
	Lab 9	12.9640 $\pm$ 1.0316	0.9069 $\pm$ 0.0113
	Lab 10	13.2393 $\pm$ 1.0187	0.9250 $\pm$ 0.0067
Mean of means		13.4204	0.9202
Standard deviation between means s		2.2669	0.0210
Number of laboratories N		7	
Standard error of the mean of means		0.8569	0.0080
ANOVA	s within labs	0.9756	0.0259
	s between labs	2.094	0.0294

Table 7 – Summarised results for atrazine adsorption on EUROSIL 7

EUROSIL 7		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 1	5.5513 $\pm$ 1.0089	0.9370 $\pm$ 0.0036
	Lab 5	3.0717 $\pm$ 1.0340	0.9894 $\pm$ 0.0162
	Lab 6	5.1795 $\pm$ 1.0344	0.9391 $\pm$ 0.0145
	Lab 7	4.4082 $\pm$ 1.0923	0.7592 $\pm$ 0.0658
	Lab 8	5.5177 $\pm$ 1.0195	0.9274 $\pm$ 0.0087
	Lab 9	5.1755 $\pm$ 1.0124	0.9184 $\pm$ 0.0054
	Lab 10	4.8218 $\pm$ 1.0168	0.9589 $\pm$ 0.0075
Mean of means		4.8180	0.9185
Standard deviation between means s		0.8664	0.0740
Number of laboratories N		7	
Standard error of the mean of means		0.3275	0.0280
ANOVA	s within labs	0.1814	0.0094
	s between labs	0.8792	0.0585

5.1.2 2,4-D

The values of 7 laboratories have been accepted for certification of the adsorption coefficients of 2,4-D on the EUROSILS. Laboratory averages of 16 measurements on two bottles as well as the error estimates (standard error) of K_f and $1/n$ are summarised in Table 8-13.

The respective individual data per laboratory are summarised, visualised and compared to the mean of laboratory means in Annex II. As expected 2,4-D, which the most polar of the three reference compounds used for the adsorption testing features the lowest tendency for adsorption onto soil.

The observed scattering of results is still acceptable, i.e. fit-for-purpose and reflects well the expected variability owing to different analytical methods used for detection and quantification of the phenoxyacetic derivate. In particular in case of the poor adsorptive soils (EUROSIL 2 and 4) larger variations can be observed with the adsorption coefficient approaching zero. This is also expressed by a larger uncertainty, which in some cases are as large as the adsorption coefficient itself. Yet, the results are suitable for certification.

Table 8 – Summarised results for 2,4-D adsorption on EUROSOIL 1

EUROSOIL 1		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 2	2.5099 ± 1.0784	1.0026 ± 0.0415
	Lab 5	2.6067 ± 1.0195	0.9470 ± 0.0108
	Lab 6	2.6507 ± 1.0339	0.8158 ± 0.0173
	Lab 7	2.4087 ± 1.0763	1.0533 ± 0.0500
	Lab 8	2.5610 ± 1.0256	0.8526 ± 0.0138
	Lab 9	2.5024 ± 1.0203	0.8712 ± 0.0108
	Lab 10	2.1200 ± 1.0231	0.8930 ± 0.0127
Mean of means		2.4799	0.9194
Standard deviation between means s		0.1769	0.0855
Number of laboratories N		7	
Standard error of the mean of means		0.0669	0.0324
ANOVA	s within labs	0.4840	0.1659
	s between labs	*	0.1394

* cannot be calculated as MSW > MSB.

Table 9 – Summarised results for 2,4-D adsorption on EUROSOIL 2

EUROSOIL 2		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 2	0.6331 ± 1.1855	1.0880 ± 0.0016
	Lab 5	1.5124 ± 1.0328	0.9767 ± 0.0186
	Lab 6	0.6372 ± 1.0174	1.0785 ± 0.0125
	Lab 7	1.0883 ± 1.1116	0.9326 ± 0.0674
	Lab 8	1.0990 ± 1.0489	0.8270 ± 0.0270
	Lab 9	1.0675 ± 1.0319	0.8823 ± 0.0178
	Lab 10	0.9074 ± 1.0526	0.9638 ± 0.0298
Mean of means		0.9921	0.9641
Standard deviation between means s		0.3053	0.0958
Number of laboratories N		7	
Standard error of the mean of means		0.1154	0.0362
ANOVA	s within labs	0.0779	0.0416
	s between labs	0.2997	0.0908

Table 10 – Summarised results for 2,4-D adsorption on EUROSOIL 3

EUROSOIL 3		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 2	1.2120 ± 1.1110	1.2175 ± 0.0637
	Lab 5	1.8299 ± 1.0334	0.9189 ± 0.0186
	Lab 6	1.1749 ± 1.0171	0.8578 ± 0.0094
	Lab 7	1.0930 ± 1.0602	0.8984 ± 0.0371
	Lab 8	1.3911 ± 1.0424	0.8545 ± 0.0234
	Lab 9	1.3092 ± 1.0257	0.8886 ± 0.0142
	Lab 10	1.1793 ± 1.0488	0.9023 ± 0.0273
Mean of means		1.3128	0.9340
Standard deviation between means s		0.2479	0.1272
Number of laboratories N		7	
Standard error of the mean of means		0.0937	0.0481
ANOVA	s within labs	0.1008	0.0517
	s between labs	0.2358	0.1219

Table 11 – Summarised results for 2,4-D adsorption on EUROSOIL 4

EUROSOIL 4		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 5	0.6559 ± 1.0460	0.8496 ± 0.0258
	Lab 6	0.1831 ± 1.1468	1.0274 ± 0.0789
	Lab 7	0.3391 ± 1.2024	0.7543 ± 0.1248
	Lab 8	0.3778 ± 1.2739	0.7666 ± 0.1388
	Lab 9	0.4038 ± 1.0803	0.7921 ± 0.0442
	Lab 10	0.3748 ± 1.0662	0.9554 ± 0.0375
Mean of means		0.3891	0.8576
Standard deviation between means s		0.1528	0.1111
Number of laboratories N		6	
Standard error of the mean of means		0.0624	0.0454
ANOVA	s within labs	0.0780	0.1390
	s between labs	0.1421	0.0478

Table 12 – Summarised results for 2,4-D adsorption on EUROSOIL 5

EUROSOIL 5		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 2	15.6506 ± 1.0765	1.0235 ± 0.0340
	Lab 5	18.3415 ± 1.0404	0.9082 ± 0.0160
	Lab 6	18.3480 ± 1.0480	0.8855 ± 0.0181
	Lab 7	16.6824 ± 1.1883	0.8187 ± 0.0580
	Lab 8	18.9371 ± 1.0263	0.8754 ± 0.0102
	Lab 9	16.6603 ± 1.0480	0.8753 ± 0.0185
	Lab 10	16.6603 ± 1.0480	0.8763 ± 0.0065
Mean of means		17.8579	0.8947
Standard deviation between means s		1.6184	0.0629
Number of laboratories N		7	
Standard error of the mean of means		0.6117	0.0238
ANOVA	s within labs	0.8283	0.0358
	s between labs	1.6202	0.0627

Table 13 – Summarised results for 2,4-D adsorption on EUROSOIL 7

EUROSOIL 7		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 2	7.2139 ± 1.0400	0.9967 ± 0.0204
	Lab 5	7.4819 ± 1.0485	0.8798 ± 0.0227
	Lab 6	9.3707 ± 1.0253	0.8703 ± 0.0118
	Lab 7	6.9392 ± 1.2250	0.7785 ± 0.0801
	Lab 8	8.9366 ± 1.0139	0.8650 ± 0.0064
	Lab 9	9.5554 ± 1.0187	0.8691 ± 0.0081
	Lab 10	8.1540 ± 1.1660	0.8953 ± 0.0771
Mean of means		8.2360	0.8792
Standard deviation between means s		1.0662	0.0640
Number of laboratories N		7	
Standard error of the mean of means		0.4030	0.0242
ANOVA	s within labs	0.4816	0.0277
	s between labs	0.9671	0.0578

5.1.3 Lindane

The following tables summarise the certification data for the determination of Freundlich isotherms of lindane on the EUROSOLS and give an overview on the statistical evaluation via analysis of variances. In case of lindane five data sets have been used to establish the certified values for the adsorption parameters. As expected due to its physico-chemical properties γ -HCH shows the strongest adsorption of the three reference substances on all soil substrates.

As the analytical concentrations to be determined in the supernatant aqueous phase decreases exponentially with an increasing adsorption, the variability of the same analytical results increases as well. Indeed, the strongly adsorptive EUROSOIL 1 and 5 show a considerable larger distribution of the individual adsorption coefficients than in the case of the other soils, in particular EUROSOIL 2 and 4. Nevertheless the results are in full agreement with the degree of precision being achievable with the experimental set-up according to the Testguideline 106. Individual data and a better graphical overview concerning the scattering of results can be gained from the data in Annex II.

Table 14 – Summarised results for lindane on EUROSOIL 1

EUROSOIL 1		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 1	91.9628 $\pm$ 1.3575	1.0083 $\pm$ 0.0634
	Lab 2	92.7014 $\pm$ 1.3700	1.0546 $\pm$ 0.0739
	Lab 5	59.4669 $\pm$ 1.0763	0.9296 $\pm$ 0.0153
	Lab 6	44.9455 $\pm$ 1.2706	0.8370 $\pm$ 0.0400
	Lab 8	51.3571 $\pm$ 1.1450	0.8317 $\pm$ 0.0269
Mean of means		68.0867	0.9323
Standard deviation between means s		22.7247	0.0999
Number of laboratories N		5	
Standard error of the mean of means		10.1628	0.0447
ANOVA	s within labs	23.6466	0.0947
	s between labs	12.6320	0.0789

Table 15 – Summarised results for lindane on EUROSOIL 2

EUROSOIL 2		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 1	52.9114 $\pm$ 1.0476	1.0041 $\pm$ 0.0106
	Lab 2	52.7826 $\pm$ 1.4621	1.0302 $\pm$ 0.0900
	Lab 5	43.5622 $\pm$ 1.0390	0.9519 $\pm$ 0.0086
	Lab 6	43.9268 $\pm$ 1.1748	0.9266 $\pm$ 0.0299
	Lab 8	44.7457 $\pm$ 1.0829	0.9835 $\pm$ 0.0189
Mean of means		47.5857	0.9792
Standard deviation between means s		4.8221	0.0411
Number of laboratories N		5	
Standard error of the mean of means		2.1565	0.0184
ANOVA	s within labs	4.0434	0.0514
	s between labs	6.4751	0.0300

Table 16 – Summarised results for lindane on EUROSOIL 3

EUROSOIL 3		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 1	42.6387 ± 1.0797	0.9801 ± 0.0178
	Lab 2	39.2431 ± 1.2073	0.9958 ± 0.0473
	Lab 5	32.7971 ± 1.0640	0.9749 ± 0.0151
	Lab 6	37.2604 ± 1.2896	0.9254 ± 0.0483
	Lab 8	30.3390 ± 1.0756	0.9144 ± 0.0170
Mean of means		36.4557	0.9581
Standard deviation between means s		4.9358	0.0359
Number of laboratories N		5	
Standard error of the mean of means		2.2074	0.0161
ANOVA	s within labs	17.0894	0.0367
	s between labs	4.8321	0.0152

Table 17 – Summarised results for lindane on EUROSOIL 4

EUROSOIL 4		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 1	10.2314 ± 1.0523	0.9662 ± 0.0155
	Lab 2	10.2918 ± 1.0821	0.9451 ± 0.0237
	Lab 5	6.9705 ± 1.0487	0.8823 ± 0.0146
	Lab 6	5.6055 ± 1.2836	0.7506 ± 0.0573
	Lab 8	8.3423 ± 1.0392	0.9197 ± 0.0121
Mean of means		8.2883	0.8928
Standard deviation between means s		2.0449	0.0854
Number of laboratories N		5	
Standard error of the mean of means		0.9145	0.0382
ANOVA	s within labs	0.4405	0.0189
	s between labs	2.2104	0.0887

Table 18 – Summarised results for lindane on EUROSOIL 5

EUROSOIL 5		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 1	100.1344 ± 1.1781	0.9782 ± 0.0323
	Lab 2	135.4985 ± 1.4814	0.9764 ± 0.0833
	Lab 5	109.7216 ± 1.1506	0.9685 ± 0.0270
	Lab 6	50.9106 ± 1.5476	0.8327 ± 0.0700
	Lab 8	98.0009 ± 1.1126	0.9448 ± 0.0209
Mean of means		98.8532	0.9401
Standard deviation between means s		30.6670	0.0615
Number of laboratories N		5	
Standard error of the mean of means		13.7147	0.0275
ANOVA	s within labs	46.3644	0.0826
	s between labs	19.1676	0.0214

Table 19 – Summarised results for lindane on EUROSOIL 7

EUROSOIL 7		$K_f \pm s_e$	$1/n \pm s_e$
Laboratory Means	Lab 1	60.0550 ± 1.4956	0.8783 ± 0.0825
	Lab 2	41.9951 ± 1.3970	0.7757 ± 0.0690
	Lab 5	74.6821 ± 1.1679	0.9917 ± 0.0328
	Lab 6	42.3855 ± 1.1780	0.7915 ± 0.0275
	Lab 8	68.4774 ± 1.1099	0.9667 ± 0.0224
Mean of means		57.5190	0.8808
Standard deviation between means s		14.9257	0.0984
Number of laboratories N		5	
Standard error of the mean of means		6.6750	0.0441
ANOVA	s within labs	19.5116	0.1166
	s between labs	*	*

* cannot be calculated as MSW > MSB.

5.1.4 pH in suspensions of pure water and 0.01 M CaCl₂

Seven laboratories determined the soil-pH in suspension of pure water whereas eight participants measured the same parameter 0.01M CaCl₂. A summary of the individual results, statistical evaluation data and mean values can be seen in Table 20 to

Table 25 Additional information about the scattering of the mean values and the mean of means can be seen from the data in Annex II.

As one can see the pH-measurements in pure water were approximately 0.5 to 0.8 pH-units above the respective measurements in 0.01 M CaCl₂. This is typical finding for most European soils and lies in alignment with the expectations [14]. Highest pH values were observed for the calcareous EUROSOIL 2, lowest for the acidic podzol EUROSOIL5.

Owing to the strict operation procedures given all mean values observed fall within a range of $\pm 10\%$ of the mean of means.

Table 20 - Statistical evaluation data for laboratory means for pH in suspensions of water and 0.01M CaCl₂ for EUROSOIL 1

EUROSOIL 1		pH in water ($\pm s$)	pH in CaCl ₂
Laboratory Means	Lab 1	6.32 ± 0.19	5.71 ± 0.15
	Lab 3	6.07 ± 0.04	5.53 ± 0.05
	Lab 5	6.11 ± 0.05	5.55 ± 0.13
	Lab 6	6.14 ± 0.11	5.53 ± 0.10
	Lab 7		5.76 ± 0.04
	Lab 8	6.21 ± 0.02	5.67 ± 0.02
	Lab 9	6.15 ± 0.03	5.65 ± 0.01
	Lab 10	6.45 ± 0.03	5.83 ± 0.01
Mean of means		6.21	5.65
Standard deviation between means s		0.13	0.11
Number of laboratories N		7	8
Standard error of the mean of means		0.05	0.04
ANOVA	s within labs	0.10	0.07
	s between labs	0.11	0.11

Table 21 - Statistical evaluation data for laboratory means for pH in suspensions of water and 0.01M CaCl₂ for EUROSOIL 2

EUROSOIL 2		pH in water	pH in Ca Cl₂
Laboratory Means	Lab 1	8.15 ± 0.12	7.60 ± 0.11
	Lab 3	8.03 ± 0.05	7.40 ± 0.08
	Lab 5	8.05 ± 0.08	7.15 ± 0.21
	Lab 6	8.01 ± 0.11	7.20 ± 0.10
	Lab 7		7.62 ± 0.04
	Lab 8	8.33 ± 0.02	7.54 ± 0.01
	Lab 9	7.82 ± 0.12	7.22 ± 0.05
	Lab 10	8.37 ± 0.06	7.84 ± 0.03
Mean of means		8.11	7.45
Standard deviation between means s		0.19	0.25
Number of laboratories N		7	8
Standard error of the mean of means		0.07	0.09
ANOVA	s within labs	0.09	0.08
	s between labs	0.18	0.23

Table 22 - Statistical evaluation data for laboratory means for pH in suspensions of water and 0.01M CaCl₂ for EUROSOIL 3

EUROSOIL 3		pH in water	pH in Ca Cl₂
Laboratory Means	Lab 1	6.11 ± 0.17	5.50 ± 0.11
	Lab 3	5.97 ± 0.06	5.31 ± 0.03
	Lab 5	6.42 ± 0.13	5.65 ± 0.16
	Lab 6	6.23 ± 0.25	5.83 ± 0.36
	Lab 7		5.51 ± 0.10
	Lab 8	6.19 ± 0.10	5.43 ± 0.09
	Lab 9	6.19 ± 0.10	5.58 ± 0.08
	Lab 10	6.25 ± 0.03	5.53 ± 0.02
Mean of means		6.19	5.54
Standard deviation between means s		0.14	0.15
Number of laboratories N		7	8
Standard error of the mean of means		0.05	0.06
ANOVA	s within labs	0.14	0.15
	s between labs	0.13	0.14

Table 23 - Statistical evaluation data for laboratory means for pH in suspensions of water and 0.01M CaCl₂ for EUROSOIL 4

EUROSOIL 4		pH in water	pH in Ca Cl₂
Laboratory Means	Lab 1	7.51 ± 0.17	7.09 ± 0.11
	Lab 3	7.46 ± 0.08	6.73 ± 0.05
	Lab 5	7.30 ± 0.10	6.73 ± 0.21
	Lab 6	7.29 ± 0.08	6.56 ± 0.10
	Lab 7		6.91 ± 0.06
	Lab 8	7.57 ± 0.02	6.85 ± 0.01
	Lab 9	7.31 ± 0.08	6.59 ± 0.08
	Lab 10	7.71 ± 0.10	7.12 ± 0.03
Mean of means		7.45	6.82
Standard deviation between means s		0.16	0.21
Number of laboratories N		7	8
Standard error of the mean of means		0.06	0.08
ANOVA	s within labs	0.11	0.08
	S between labs	0.14	0.20

Table 24 - Statistical evaluation data for laboratory means for pH in suspensions of water and 0.01M CaCl₂ for EUROSOIL 5

EUROSOIL 5		pH in water	pH in Ca Cl₂
Laboratory Means	Lab 1	4.04 ± 0.25	3.23 ± 0.25
	Lab 3	3.91 ± 0.03	2.94 ± 0.07
	Lab 5	4.11 ± 0.09	3.09 ± 0.18
	Lab 6	4.27 ± 0.08	3.16 ± 0.03
	Lab 7		3.04 ± 0.04
	Lab 8	4.21 ± 0.12	3.13 ± 0.06
	Lab 9	4.08 ± 0.03	3.15 ± 0.02
	Lab 10	4.28 ± 0.06	3.17 ± 0.02
Mean of means		4.13	3.11
Standard deviation between means s		0.13	0.09
Number of laboratories N		7	8
Standard error of the mean of means		0.05	0.03
ANOVA	s within labs	0.12	0.10
	s between labs	0.12	0.06

Table 25 - Statistical evaluation data for laboratory means for pH in suspensions of water and 0.01M CaCl₂ for EUROSOIL 7

EUROSOIL 7		pH in water	pH in Ca Cl₂
Laboratory Means	Lab 1	5.07 ± 0.21	4.57 ± 0.13
	Lab 3	5.00 ± 0.02	4.29 ± 0.04
	Lab 5	4.67 ± 0.34	4.01 ± 0.17
	Lab 6	5.20 ± 0.05	4.30 ± 0.06
	Lab 7		4.35 ± 0.03
	Lab 8	5.14 ± 0.01	4.35 ± 0.02
	Lab 9	5.10 ± 0.01	4.36 ± 0.01
	Lab 10	5.25 ± 0.05	4.47 ± 0.02
Mean of means		5.06	4.34
Standard deviation between means s		0.19	0.16
Number of laboratories N		7	8
Standard error of the mean of means		0.07	0.06
ANOVA	s within labs	0.13	0.07
	s between labs	0.15	0.14

5.1.5 Total carbon and organic carbon content

Results for the determination of total carbon content (C_{tot}) and organic carbon content (C_{org}) according to the respective ISO standards are given in Annex II, whereas the methods themselves are described in Annex I. Only three data sets determined with two independent methods for C_{tot} and four data sets with two independent methods for C_{org} were submitted (Flash-combustion with chromatographic detection and dry combustion). As already mentioned it was decided not to certify these parameters as the submitted data was deemed to be insufficient to guarantee a randomisation of error.

Values scattered for both parameters around ± 10% of the mean values with the exception of EUROSOIL 7 where a larger variation was observed (Figure 31 to Figure 36). No technical reasons for this behaviour were found.

5.1.6 Total nitrogen content

Annex II gives an overview on the obtained results in the individual laboratories. Two independent methods (Kjeldahl and microcombustion) have been used for the determination of the total nitrogen content (N_{tot}) in the EUROSOLS. The distribution of the results observed follows the same behaviour than in case of C_{tot} and C_{org} and lies within a range of $\pm 10\%$ around the respective mean of means. Despite this reasonable agreement the submitted data was deemed to be insufficient to allow certification.

EUROSOIL 5 forms an exception owing to its granulometry and the related differences of specific weight of distinct fractions. This heterogeneity effect is known and has already been discussed [14]. It does not prevent a general applicability of the material. Thus, the data for N_{tot} might still be useful for the interested end-user.

5.2 Stability

5.2.1 Short-term stability study

A short-term stability was organised after consultation by Prof. Dr. W. Blum, Universität für Bodenkultur (Vienna, Austria). Owing to his expertise it was decided to monitor water content and water activity of each EUROSOIL, because these parameters would be the most sensitive ones for any alteration of the soil-substrates, especially in view of the parameters to be certified, i.e. adsorption behaviour, pH, nitrogen and carbon content.

The Dutch group of Houba and Novazamsky [15] has examined the influence of storage time and temperature of air-dried soils on pH and extractable nutrients using a calcareous and a rather acid, sandy soil. They reported instability problems especially for the extractable nutrients after longer storage at elevated temperatures, i.e. at 40°C and 70°C for 24 months. However, the samples, which were monitored over 24 months remained stable at room temperature for the monitored parameters, even if the authors recommended in their conclusions to store the samples at temperature $<4^{\circ}\text{C}$.

The short-term stability study was performed following an isochronous set-up, i.e. the simultaneous analysis of reference and test samples. Samples (one bottle of each soil) were stored for 0, 2, 4, 6 and 8 weeks at $+40^{\circ}\text{C}$ and reset to a reference temperature of 4°C . Commonly, soil samples are stored at room temperature, however, a lower temperature was chosen a reference in order to keep the risk of degradation as low as possible. Storage below 0°C could result in an alteration of the soil matrix and was consequently not considered. All samples were taken from the stock of bottles set at reference temperature of 4°C . In the end of the study the samples were analysed simultaneously for water activity and water content.

Based on the available results [16] and their evaluation it was concluded that the EUROSOLS are not altered if stored for brief period at elevated temperatures (40°C). The respective uncertainty contribution could be neglected in the overall-uncertainty as it is at approximately one order of magnitude smaller than the remaining uncertainties. Dispatch of samples can be done under normal conditions. With reference to previous results it is expected that the samples should be stable when stored at 20°C . This is also confirmed by the experience gained with the first generation of EUROSOLS [9].

5.2.2 Estimate for the uncertainty of stability

Usually, the uncertainty of stability may be estimated by extrapolation of the standard error of the slope as described at several occasions [17, 18, 19]. While the uncertainty of degradation during transport (u_{sts}) can be assumed negligible, as no degradation was found after storage at 40 °C for 8 weeks, no evidence is given to make a similar assumption regarding the long-term study. At present a long-term isochronous study is on-going and results are expected for 2004.

Table 26 - During the short-term stability study observed s_{bb} (ANOVA) for the water content determination. The relative expression of this term is used as an estimate of u_{lis} .

Soil	s_{bb} in wgt. %	relative in %
EUROSOIL 1	0.12	1.68
EUROSOIL 2	0.22	4.98
EUROSOIL 3	0.06	1.74
EUROSOIL 4	0.15	4.07
EUROSOIL 5	0.51	17.11
EUROSOIL 7	0.23	7.10

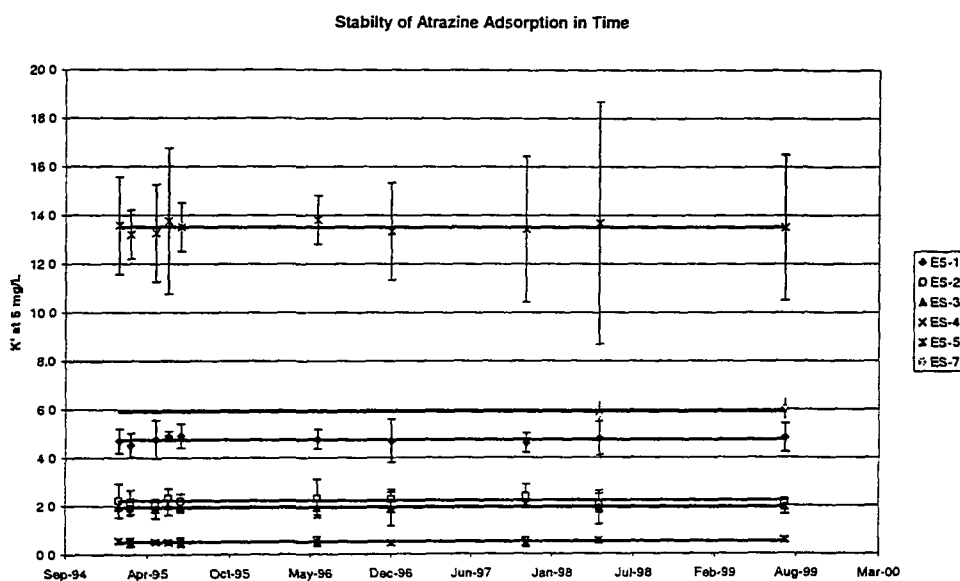


Figure 1 – Stability of atrazine adsorption on EUROSOILS (add uncertainties and linear fits)

Similarly, repeated measurements of atrazine adsorption coefficients (Figure 1) proved that the EUROSOILS featured the same adsorption behaviour over 4 years. As the sensible reaction of atrazine's sorption behaviour towards any variation of soil parameters like pH or organic matter content may be used also an indicator for these pedological parameters one can assume the materials to be stable.

Considering the lack of data it is preferable to over-estimate an uncertainty. It is therefore suggested to use the relative standard deviation for the water content determination, which is derived from the aforementioned short-term study, as an estimate for u_{lis} applied to the respective K_F -values (Table 26).

5.3 Homogeneity

Some data for the assessment of homogeneity have been published previously [9, 20]. At these occasions, the distribution of various matrix elements as well as the atrazine adsorption behaviour have been studied. The results are summarised in the following.

5.3.1 EUROSIL-homogeneity by means of WDXRF

For each soil ten bottles were selected randomly. Approximately 3 g were sub-sampled from each bottle to form a pellet (2.5 cm) for wavelength-dispersive XRF-analysis. Instrument and analytical conditions are described elsewhere [21]. Then, 10 sub-samples were taken out of one of the randomly chosen bottles and analysed in the same way. The contribution of the measurement variability was assessed by repeating ten-times the same measurement on the same pellet. In all cases the variability of the measurement was < 2 %. The observed coefficients of variations (interbottle and intrabottle) are displayed in Figure 2 to Figure 7.

The obtained data proved that the distribution of the inorganic soil key-components, i.e. Si, Al, Ca, K, F, Mg and Ti (all expressed as their oxides), was homogenous, i.e. generally < 5%, which is an acceptable threshold for those compounds. Some of the coefficients of variation may be explained by relative large size distribution (< 2000 μm). Classical reference materials for analytical purposes feature a maximum particle size of 125 μm to 60 μm , thus permitting a better homogenisation of the material.

The observed coefficients of variations were more or less expected and were judged to be insufficient for postulating a real inhomogeneity. Furthermore, some of the measured contents of these elements were close to the instrument's detection limits, which caused a further increase of the variability.

The second version of EUROSIL 5 manifested an anomaly for Al_2O_3 and TiO_2 . However, EUROSIL 5 features only poor contents of Al- and Ti-containing compounds which is due to its genesis. Similar observations were made for the most of the other typical soil constituents like CaO or Fe_2O_3 , which were undetectable by means of WDXRF. Indeed, analysis of the matrix elements carbon and nitrogen revealed that EUROSIL 5 is basically made up from α -quartz (SiO_2) and highly podzolised organic matter. Taking into account the XRF-data for SiO_2 and the results of the atrazine adsorption test the material was considered to sufficiently homogenous for the purpose.

5.3.2 Homogeneity study for sorption properties

In order to evaluate the homogeneity of the soil sorption behaviour of the new EUROSILS a homogeneity testing for the atrazine adsorption behaviour was performed. Atrazine was chosen as model substance as its sorption behaviour is known to be very sensitive towards any sorption controlling parameter like organic carbon content, clay content or cation-exchange capacity [22, 23].

Before performing sorption studies the soil material to be used must be sterilised in order to exclude any microbial activity of the test substrate, because occurring microbiological degradation may eliminate the studied substance from the system, thus giving higher adsorption values than expected, if the equilibrium concentration in the aqueous phase is measured as in our case. The question which method is the most appropriate one was intensively studied by Oepen *et al.* [24]. The following methods of sterilisation may be distinguished:

- Exposure to γ -irradiation,
- Autoclavation of the material,
- Addition of compounds with bacteriacidal or fungicidal effects (e.g. HgCl_2 , NaN_3),
- Decrease of temperature during the experiment.

Certainly, autoclavation is the method of choice within the framework of OECD TG 106, as it maintains the structural integrity of the soil constituents, but allows a complete sterilisation. However this method is not suitable to produce a set of sterilised reference materials, owing to the large number of units and the respective volume to be handled. An elegant alternative, especially for soil and similar materials is the exposure of the bottled material to γ -irradiation. Besides, some authors generally demand this method to be used in all types of sorption studies [25, 26]. Thus, a sub-set of each EUROSIL was treated in that way by exposure to a Co-source.

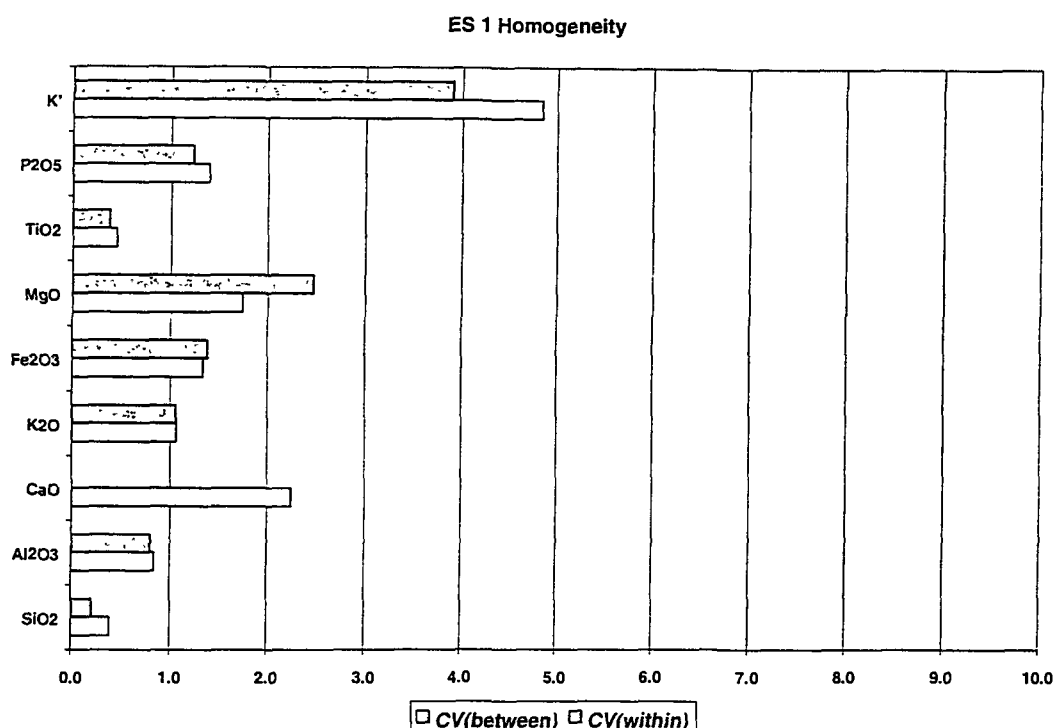


Figure 2 – Results of the homogeneity testing of EUROSIL 1. K' refers to the CV observed in the homogeneity study, the other CVs to those determined during XRF-Analysis.

The study was performed in agreement with usual homogeneity testing principles for environmental reference material production – a test with one sample from ten randomly chosen bottles, and a test with the ten-fold repetition on one bottle [20]. The testing scheme was described at other occasions – sample intake ranged from 4.0 to 4.5 g. Water content of the air-dried soils ranged from 3.2 % (EUROSIL 5) to 6.7 % (EUROSIL 1). An initial atrazine concentration of 5 mg/L was chosen for all tests and the concentration-dependent adsorption coefficient (K') was calculated after equilibration. A contribution of the analytical

measurement (HPLC-DAD) was obtained by performing five-fold replicated injection and analysis of the content of one vial. The obtained coefficients of variation for the XRF analysis and the adsorption study are summarised in the figures displayed below (Figure 2 to Figure 7). It has to be outlined that the experimental set-up of an adsorption test is very sophisticated and contains numerous single operation steps being all possible sources of error. Thus the variability of the data is significantly larger than in the case of analytical measurements. However, the observed coefficients of variations were all in the range of 3.8 to 5.5 %, which is acceptable under the mentioned conditions. The within-bottle values observed for ES-5 are outside this range (6.5 %). This may be explained by a problem of segregation in the moment of sub-sampling (SiO_2 -crystals and organic matter). Nevertheless, considering the contribution of analytical method and the experimental set-up itself, these results are also acceptable. An estimate for the contribution of the analytical method itself (not the entire experimental set-up) was obtained by performing a five-fold replicated analysis of the test-solution for an initial concentration of 2 mg/L. The observed CVs for the analytical method itself ranged from 1.7 % (EUROSOIL 1) to 2.5 % (EUROSOIL 4).

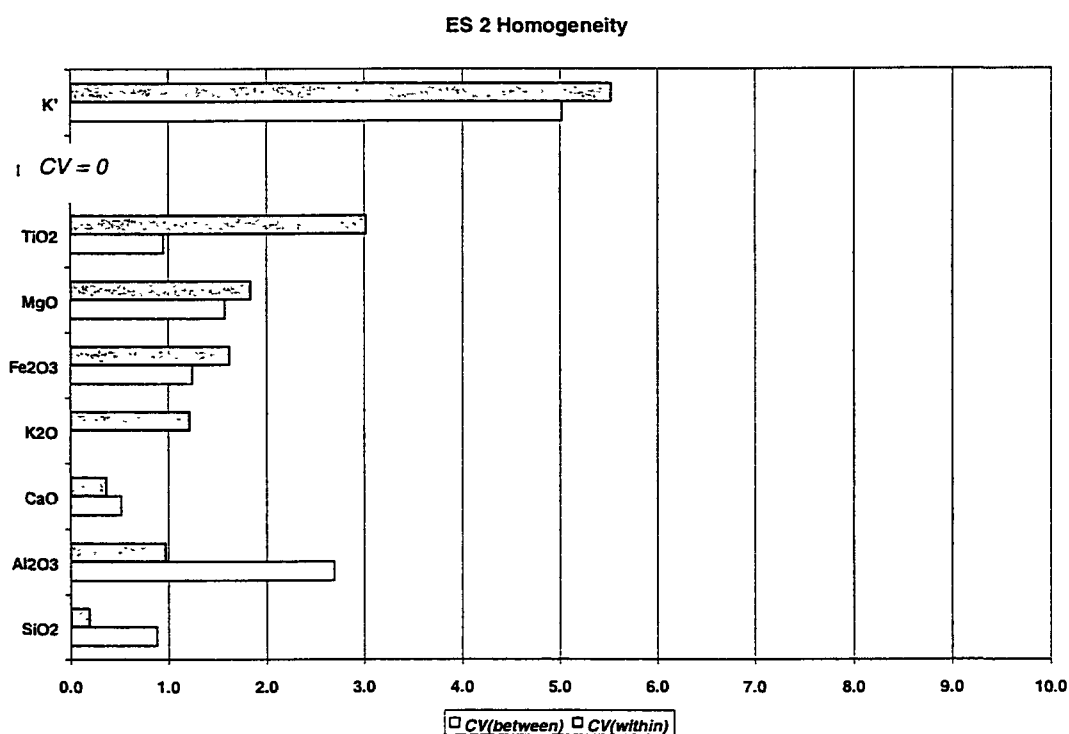


Figure 3 – Results of the homogeneity testing of EUROSOIL 2. K' refers to the CV observed in the homogeneity study, the other CVs to those determined during XRF-Analysis.

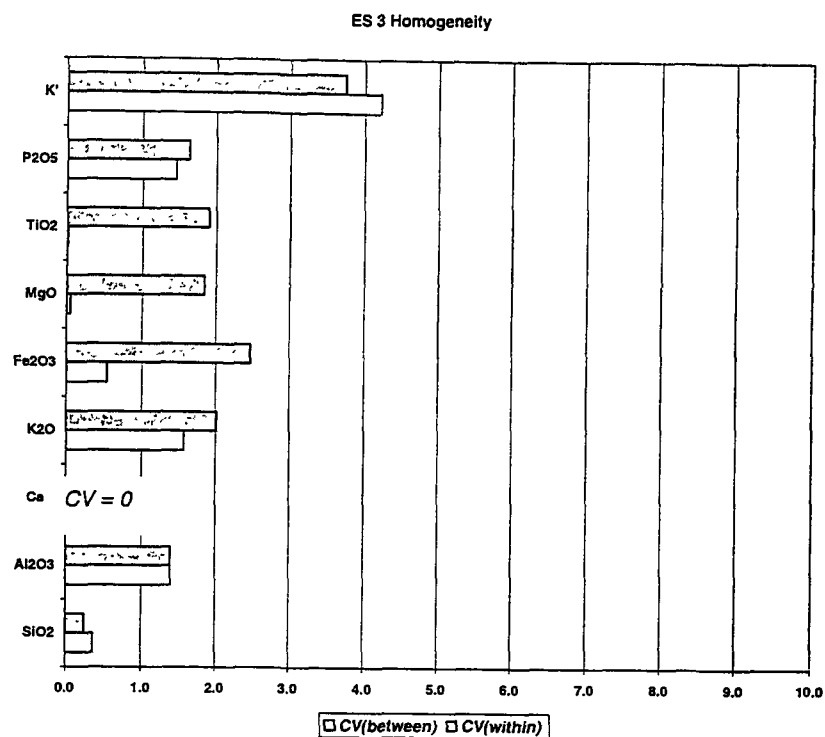


Figure 4 – Results of the homogeneity testing of EUROSOIL .3 K' refers to the CV observed in the homogeneity study, the other CVs to those determined during XRF-Analysis.

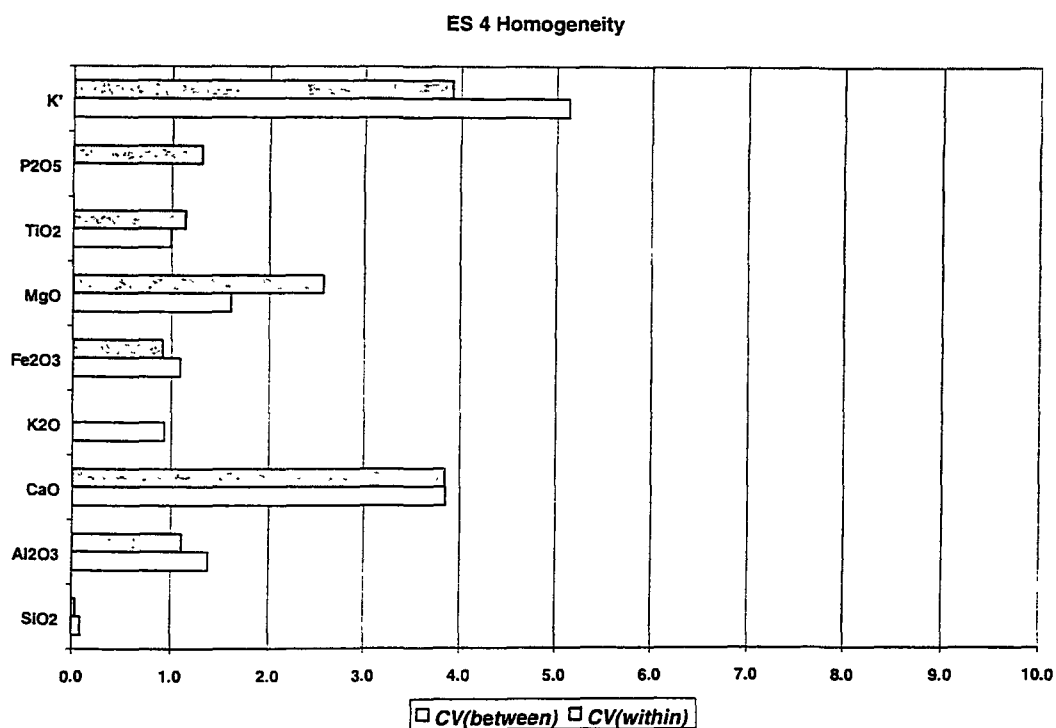


Figure 5 – Results of the homogeneity testing of EUROSOIL 4. K' refers to the CV observed in the homogeneity study, the other CVs to those determined during XRF-Analysis

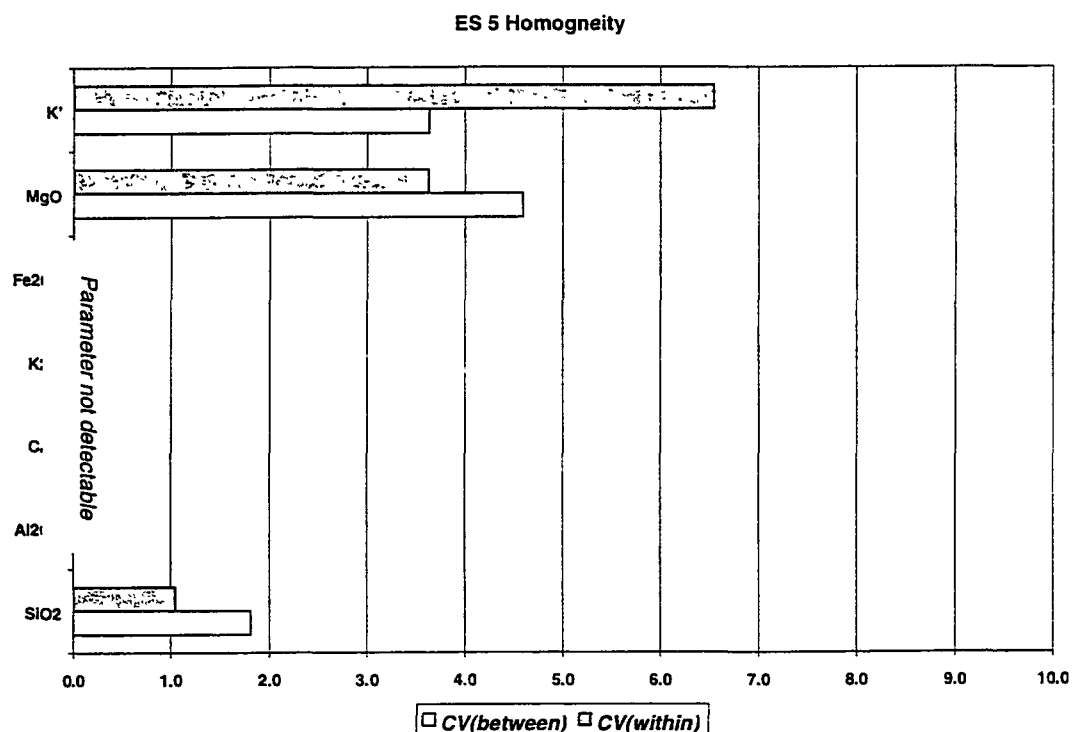


Figure 6 – Results of the homogeneity testing of EUROSOIL 5. K' refers to the CV observed in the homogeneity study, the other CVs to those determined during XRF-Analysis.

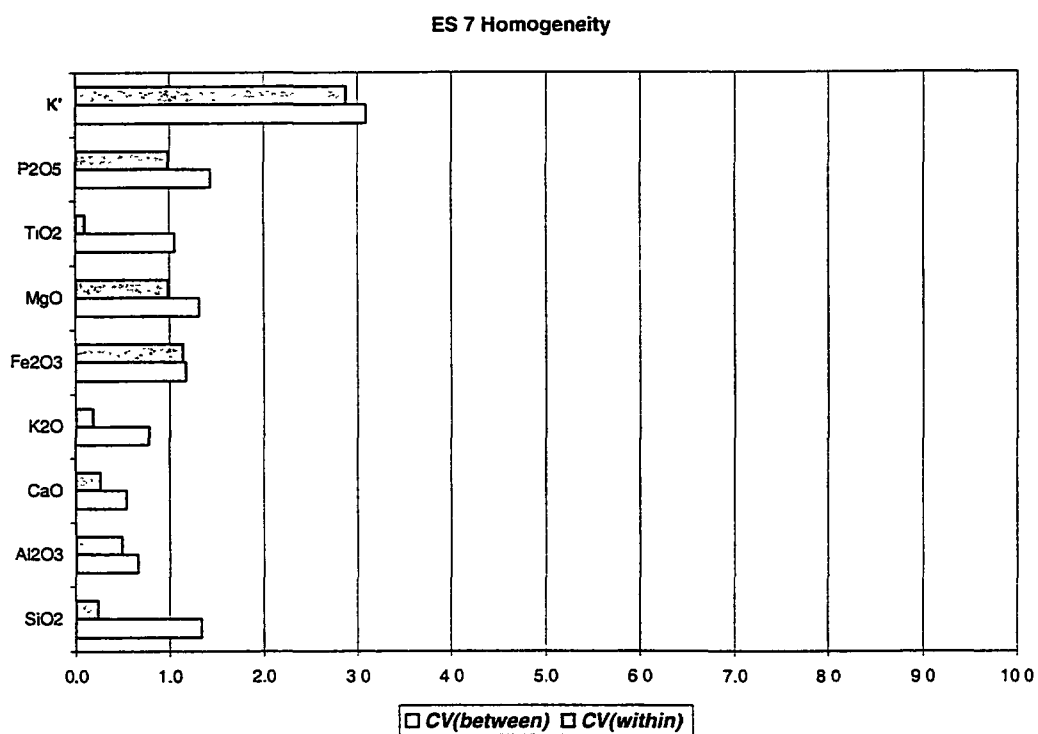


Figure 7 – Results of the homogeneity testing of EUROSOIL 7. K' refers to the CV observed in the homogeneity study, the other CVs to those determined XRF-Analysis

5.3.3 Evaluation of uncertainty contribution, u_{hom}

The variety of data displayed above proof the materials to be sufficiently homogenous for the intended purposes. Yet, the available information is not suitable to quantify the uncertainty contribution to the overall budget.

A better estimate may be derived from the spread of data observed during the certification campaign, i.e. s_{within} . Despite the fact that this term contains still a hidden uncertainty caused by the variability of the test method - and the applied analytical detection method in case of the adsorption study - it includes the uncertainty caused by the heterogeneity of the soils. It goes without saying that s_{within} is an over-estimation of the u_{hom} . On the other hand, the term was derived for each parameter in each soil and it is therefore a better estimate. Consequently, the respective uncertainties were added to the respective budgets (Table 27 to 32).

Table 27 - Uncertainty budgets for parameters to be certified in EUROSIL 1

Parameter	u_{char}	u_{hom}	u_{lis}	u_{sts}	U_{CRM}	Unit	Expressed in %
K_f of atrazine	0.2463	0.6932	0.1177	*	1.4900		21.4
1/n of atrazine	0.041	0.0258	0.0152	*	0.1001		11.0
K_f of 2,4-D	0.0669	0.4840	0.0417	*	0.9808		39.5
1/n of 2,4-D	0.0324	0.1659	0.0155	*	0.3395		36.9
K_f of lindane	10.1628	23.6466	1.2412	*	51.5358**		75.7**
1/n of lindane	0.0447	0.0947	0.0159	*	0.2118		22.7
pH in water	0.05	0.1	0.1	*	0.30	pH	4.8
pH in 0.01 M CaCl ₂	0.04	0.07	0.09	*	0.24	pH	4.3

* uncertainty contribution negligible, ** not certified

Table 28 - Uncertainty budgets for parameters to be certified in EUROSIL 2

Parameter	u_{char}	u_{hom}	u_{lis}	u_{sts}	U_{CRM}	Unit	Expressed in %
K_f of atrazine	0.1657	0.2553	0.1364	*	0.6671		24.4
1/n of atrazine	0.0212	0.0318	0.0462	*	0.1199		12.9
K_f of 2,4-D	0.1154	0.0779	0.0495	*	0.2955		29.8
1/n of 2,4-D	0.0362	0.0416	0.048	*	0.1462		15.2
K_f of lindane	2.1565	4.0434	2.3926	*	10.3391		21.7
1/n of lindane	0.0184	0.0514	0.0488	*	0.1465		15.0
pH in water	0.07	0.09	0.4	*	0.83	pH	10.3
pH in 0.01 M CaCl ₂	0.09	0.08	0.37	*	0.78	pH	10.4

* uncertainty contribution negligible, ** not certified

Table 29 - Uncertainty budgets for parameters to be certified in EUROSIL 3

Parameter	u_{char}	u_{hom}	u_{lis}	u_{sts}	U_{CRM}	Unit	Expressed in %
K_f of atrazine	0.1675	0.2688	0.0428	*	0.6392		26.1
1/n of atrazine	0.0445	0.0383	0.0159	*	0.1217		13.4
K_f of 2,4-D	0.0937	0.1008	0.0229	*	0.2790		21.3
1/n of 2,4-D	0.0481	0.0517	0.0163	*	0.1449		15.5
K_f of lindane	2.2074	17.0894	0.7357	*	34.4941**		94.6**
1/n of lindane	0.0161	0.0367	0.0169	*	0.0870**		9.1**
pH in water	0.05	0.14	0.11	*	0.37	pH	6.0
pH in 0.01 M CaCl ₂	0.06	0.15	0.1	*	0.38	pH	6.9

* uncertainty contribution negligible, ** not certified

Table 30 - Uncertainty budgets for parameters to be certified in EUROSIL 4

Parameter	u_{char}	u_{hom}	u_{lis}	u_{sts}	U_{CRM}	Unit	Expressed in %
K_f of atrazine	0.1156	0.1106	0.0304	*	0.3257		43.8
1/n of atrazine	0.0426	0.0907	0.0356	*	0.2127		24.3
K_f of 2,4-D	0.0624	0.078	0.016	*	0.2023		52.0
1/n of 2,4-D	0.0454	0.139	0.035	*	0.3007		35.1
K_f of lindane	0.9145	0.4405	0.3273	*	2.1331		25.7
1/n of lindane	0.0382	0.0189	0.0359	*	0.1114		12.5
pH in water	0.06	0.11	0.3	*	0.65	pH	8.7
pH in 0.01 M CaCl ₂	0.08	0.08	0.28	*	0.60	pH	8.9

• uncertainty contribution negligible

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Table 31 - Uncertainty budgets for parameters to be certified in EUROSIL 5

Parameter	u_{char}	u_{hom}	u_{lis}	u_{sts}	U_{CRM}	Unit	Expressed in %
K_f of atrazine	0.8569	0.9756	2.2962	*	5.2759		39.3
1/n of atrazine	0.0080	0.0259	0.1574	*	0.3195		34.7
K_f of 2,4-D	0.6117	0.8283	3.0555	*	6.4486		36.1
1/n of 2,4-D	0.0238	0.0358	0.1531	*	0.3180		35.5
K_f of lindane	13.7147	46.3644	16.9138	*	102.4466**		103.6**
1/n of lindane	0.0275	0.0826	0.1609	*	0.3658**		38.9**
pH in water	0.05	0.12	0.706643	*	1.44	pH	34.8
pH in 0.01 M CaCl ₂	0.03	0.1	0.532121	*	1.08	pH	34.9

* uncertainty contribution negligible, ** not certified

Table 32 - Uncertainty budgets for parameters to be certified in EUROSIL 7

Parameter	u_{char}	u_{hom}	u_{lts}	u_{sts}	U_{CRM}	Unit	Expressed in %
K_f of atrazine	0.3275	0.1814	0.3421	*	1.0143		21.1
1/n of atrazine	0.0280	0.0094	0.0652	*	0.1432		15.6
K_f of 2,4-D	0.4030	0.4816	0.5848	*	1.7161		20.8
1/n of 2,4-D	0.0242	0.0277	0.0624	*	0.1449		16.5
K_f of lindane	6.6750	19.5116	4.0838	*	42.0445**		73.1**
1/n of lindane	0.0441	0.1166	0.0625	*	0.2789**		31.7**
pH in water	0.07	0.13	0.35926	*	0.78	pH	15.4
pH in 0.01 M $CaCl_2$	0.06	0.07	0.30814	*	0.64	pH	14.8

* uncertainty contribution negligible, ** not certified

5.4 Estimation of the combined uncertainty

The uncertainty of the CRM can be estimated by summation of the contributions of characterisation, homogeneity and stability [17-19]. The individual uncertainty components for characterisation, inhomogeneity and instability described in the equation below are added, and multiplied by a coverage factor of 2 to give a combined expanded uncertainty. As uncertainties have the format of standard deviations, addition is done quadratically.

$$U_{CRM} = k \sqrt{u_{char}^2 + u_{bb}^2 + u_{lts}^2 + u_{sts}^2}$$

U_{CRM} expanded uncertainty of the CRM

k coverage factor

u_{char} uncertainty of the certified property of the batch

u_{bb} between-bottle inhomogeneity

u_{lts} uncertainty of long-term stability (storage)

u_{sts} uncertainty of stability during transport

Transport conditions are chosen in such a way that the uncertainty of stability during transport is negligible. The uncertainty budgets with the respective values for u_{char} of the batch, u_{bb} and u_{lts} are displayed in Table 27 to Table 32. The expanded uncertainty U_{CRM} was calculated using a coverage factor of two according to the following formula

$$U_{CRM} = 2 \cdot \sqrt{u_{char}^2 + u_{bb}^2 + u_{lts}^2} = x \text{ [units]} \hat{=} y \text{ [%]}$$

6. CERTIFIED VALUES

The certified value and the corresponding expanded uncertainty are given in the Table below. Certified values and uncertainties are rounded to the same digit. According to the standards in force this rounding place is chosen in such a manner that the unit of the last quoted digit corresponds to at least 1/30 and at most 1/3 of the uncertainty. The uncertainty is always rounded up, unless after rounding of the second non-retained digit the first non-retained digit would be 0.

Table 33 – Certified values for IRMM-443

<i>Parameter</i>	<i>EUROSOIL 1</i>	<i>EUROSOIL 2</i>	<i>EUROSOIL 3</i>	<i>EUROSOIL 4</i>	<i>EUROSOIL 5</i>	<i>EUROSOIL 7</i>
K_f of atrazine	7.0 ± 1.5	2.7 ± 0.7	2.4 ± 0.7	0.7 ± 0.4	13 ± 6	4.8 ± 1.1
1/n of atrazine	0.91 ± 0.10	0.93 ± 0.12	0.91 ± 0.13	0.87 ± 0.22	0.9 ± 0.4	0.92 ± 0.15
K_f of 2,4-D	2.5 ± 1.0	0.99 ± 0.30	1.31 ± 0.28	0.39 ± 0.21	18 ± 7	8.2 ± 1.8
1/n of 2,4-D	0.9 ± 0.4	0.96 ± 0.15	0.93 ± 0.15	0.86 ± 0.31	0.9 ± 0.4	0.88 ± 0.15
K_f of lindane	*	48 ± 11	*	8.3 ± 2.2	*	*
1/n of lindane	*	0.98 ± 0.15	*	0.96 ± 0.12	*	*
pH in water	6.21 ± 0.30	8.1 ± 0.9	6.2 ± 0.4	7.5 ± 0.7	4.1 ± 1.5	5.1 ± 0.8
pH in 0.01 M CaCl_2	5.65 ± 0.24	7.5 ± 0.8	5.5 ± 0.4	6.8 ± 0.6	3.1 ± 1.1	4.3 ± 0.7

7. INDICATIVE VALUES

Based on the uncertainty budget some mean values for K_f of lindane were not certified owing to the spreading of the data. Uncertainties of >50% may be acceptable in cases of extreme weak adsorption, for instance in the case of a poor adsorptive soil and a polar substance. However in case of strong adsorption this becomes problematic as the resulting adsorption coefficients and the related uncertainty would not allow a meaningful statement whether the compound is adsorbed or not, e.g. a K_f of 100 ± 100 . Consequently, it was decided to reject 4 of the 6 Freundlich isotherms observed for lindane. Nevertheless, the observed data may be useful to the end user. They are therefore displayed as indicative value, i.e. as sheer arithmetic mean without an uncertainty statement.

In case of N_{tot} , C_{tot} and C_{org} , the underlying values were based on three data sets only. Despite a general good agreement among these dataset, it was felt that the statistical weight of the data was too weak to guarantee a randomisation of errors and thus to allow certification.

Table 34 – Indicative values for IRMM-443

<i>Parameter</i>	<i>EUROSOIL 1</i>	<i>EUROSOIL 2</i>	<i>EUROSOIL 3</i>	<i>EUROSOIL 4</i>	<i>EUROSOIL 5</i>	<i>EUROSOIL 7</i>
K_f of lindane	68	*	36	*	99	58
1/n of lindane	0.9	*	1.0	*	0.9	0.9
C_{tot} [g/kg]	33.9	108.1	32.5	14.5	64.3	58.7
C_{org} [g/kg]	32.7	37.2	30.1	13.1	59.6	56.2
N_{tot} [g/kg]	3.4	2.5	3.1	1.6	2.3	4.8

In contrast to previously certified materials for which the 95 % confidence interval of the mean of laboratory means was used as uncertainty, an expanded combined uncertainty according to the GUM was calculated for IRMM-443. This included also influences of homogeneity and stability. The certified uncertainty of the present certification is therefore larger than it would be according to the classical scheme.

8. ADDITIONAL INFORMATION

The EUROSOLS belong probably to the most intensively analysed and characterised matrix reference materials. This intense work was necessary to ensure a certain comparability of values derived from the different generations of the set. Moreover, the number of possible applications are still growing as the scientific community welcomes the idea of a standardised soil matrix for testing purposes.

It was also proofed that the main properties of the soils could be conserved among the different generations of a soil [6, 7]. This opens the possibility to re-produce easily new versions of the soil in case that a material has been consumed. To provide users with a broadest possible range concerning the matrix of the soils, the EUROSOLS were analysed and compared with respect to their sorption behaviour, pedological properties, chemical composition, trace element contents, pesticides residues, polycyclic aromatic hydrocarbons and polychlorinated biphenyls, dibenzo-p-dioxins and -furans and other chlorinated hydrocarbons [6, 7,27]. Based on this knowledge it was possible to gain an insight and understanding of possible interactions between different soil parameters and the behaviour of chemicals [14-16].

The National Center of Public Health, National Research Institute for Radiobiology and Radiohygiene, Budapest, in Hungary provided some additional measurements regarding the effective cation exchange capacity of the materials. These data are added to the Annex IV.

9. USE OF THE CRM

9.1 Dispatch and instructions for use

Dispatch to the customer will be done under normal conditions. Upon receipt by the customer, it is advisable to keep the material at room temperature (20 °C) for long-term storage. The opened material can be stored refrigerated (2-8 C) for not longer than 12 months.

Note that spoilage by mould may occur at moisture contents exceeding 10 % by mass. This ruins the whole sample.

9.2 Using the CRMs

The following notes are a guide to the user of these reference materials following the procedures and restrictions made in the report. The materials consist of a soil sample in a glass bottle, containing about 200 g of powder. Before a bottle is opened, it should be shaken manually so that the material within is re-homogenised.

The test portion necessary for the determinations and adsorption tests should be taken as is. The correction to dry mass for the adsorption experiments should follow the requirements laid down in OECD TG 106. During the certification exercise it was found that the minimum sample intake specified in the guideline (2g) may cause in case of extremely strong or

extremely weak adsorption. It is therefore strongly recommended to use a sample intake of at least 4g per test.

All glassware used should be thoroughly cleaned in a single batch before use and blank determinations should be performed to check this. Reagent blanks should be determined with each new batch of reagent and regular checks should be taken to maintain reproducible conditions for all blanks, external standards, reference materials and samples.

If the materials are used for checking a chemical procedure or the performance of a method, the user can refer to the results of this certification campaign after having ascertained that the reproducibility of his method is satisfactory.

The user may assess the laboratory bias from the difference between the mean value of replicate measurements (x_{mean}) and the certified value (m): $x_{\text{mean}} - m$.

The criterion for acceptance is given in ISO Guide 33 [28] as follows:

$$-a_2 - 2s_L < x_{\text{mean}} - m < a_1 + 2s_L$$

in which a_1 and a_2 are adjustment values, chosen by the user according to economic or technical limitations or stipulations, and s_L is the long-term within laboratory standard deviation of the user's method.

However, if the reference material is used for confirming a calibration, the value to be used for each parameter is the certified mean value with the stated standard uncertainty.

9.3 Other uses

The materials are also intended to be used reference matrix for the sorption testing of new chemical compounds. Results can then be made traceable to the respective CRM by controlling the experimental set-up with one of the reference samples that is most similar (in terms of polarity) to the new test compound.

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11. ANNEX I – INSTRUCTIONS FOR THE TESTING

This annex gives the precise instructions and recommendations sent to the participating laboratories. In order to standardise also the reporting format the participants were also asked to use pre-designed forms for the submission of data. In addition to that, the laboratories were provided with a questionnaire aiming on particular information on the analytical methods used, such as calibration, standards used and devices used for measurements. This information was evaluated and a compilation can be found in Annex III of this report.

11.1.1.1 Apparatus and chemical reagents

Standard laboratory equipment was required, especially the following:

- Tubes or vessels to conduct the experiments. It was important that these tubes or vessels fitted directly in the centrifuge apparatus in order to minimise handling and transfer errors. They were made of an inert material, preferably glass, which minimised adsorption of the test substance on its surface.
- An overhead shaker or an equivalent equipment, which kept the soil in suspension during shaking, had to be used.
- A centrifuge (preferably high-speed and temperature controlled) capable of removing particles with a diameter greater than 0.2 μm from aqueous solution was recommended. The containers had to be capped during agitation and centrifugation to avoid any losses. To minimise adsorption on them, deactivated caps such as PTFE lined screw caps were recommended.
- Optionally, a filtration device could be used. In this case sterile single use filters of 0.2 μm porosity had to be employed. Care was taken in the choice of the filter material, to avoid any losses of the test substance on it.
- The analytical instrumentation suitable for measuring the concentration of the test chemicals was selected by each participant (Annex III).
- A laboratory oven, capable of maintaining a temperature of 103° to 110°C was required to determine the dry mass of the soils.

11.1.1.2 Preparation of the test substance for application to soil

The test substance was dissolved in a 0.01 M solution of calcium chloride (CaCl_2); this was done to improve centrifugation and to minimise cation exchange. It was recommended that the concentration of the stock solution should preferably be several orders of magnitude higher than the detection limit of the analytical method used. This threshold safeguards accurate measurements. Stock solutions were prepared just before their application. They were kept closed in the dark at 4°C.

11.1.1.3 The analytical method

Key parameters that can influence the accuracy of sorption measurements include the accuracy of the analytical method of the analysis of both, the solution and adsorbed phases as well as the stability and purity of the test substance, the attainment of sorption equilibrium,

the magnitude of the solution concentration change and changes in soil structure during the equilibrium process.

The reliability of the analytical method used had to be checked at the concentration range, which was likely to occur during the test. Appropriate means that ensure accuracy, precision, reproducibility, detection limits and recovery had to be taken. The technical details on the analytical methods used are displayed in Annex III to this report.

An appropriate volume of 0.01 M CaCl_2 , e.g. 100 cm³, was agitated during 4 h with a certain amount of soil, e.g. 20 g (soil/solution ratio of 1:5). The mixture was centrifuged and the aqueous phase was be filtrated. A certain volume of the test substance stock solution was added to the latter to reach a nominal concentration within the concentration, which was likely to occur during the test. This solution was analysed.

One blank run consisting of the system soil and CaCl_2 solution without test substance was included in order to check for artifacts in the analytical method and for matrix effects caused by the soil.

11.1.1.4 Equilibrium time and general conditions

Each participant received two randomly chosen bottles per soil for the adsorption testing. Each experiment (one soil and one solution) was done at least in duplicate. In every experiment, one blank and a control sample were run.

Instead of measuring adsorption kinetics the participants agreed based on the sufficient knowledge on the substances' behaviour in soil that fixed equilibration time had to be set. Therefore the equilibration time was set to 24 h. The sampling for analysis was done after the 24 h contact time. However, times of analysis were considered with flexibility.

Care was taken to avoid any microbial activity that may occur during the testing. Sterilisation of the test solution and the soil substrates was recommended.

11.1.2 Freundlich isotherms

Freundlich isotherms were measured with 4 initial concentrations covering two orders of magnitude (Table 35). All soils were tested.

A duplicate sample was prepared for each bottle and concentration. After 24 h the mixture was centrifuged to separate the phases. A small aliquot of the aqueous phase was taken and analysed for the test substance (indirect method). The equilibrium concentrations in the solution were determined and the amount absorbed was calculated from the depletion of the test substance in the solution. The adsorbed mass per unit mass of soil was plotted as a function of the equilibrium concentration of the test substance.

Alternatively, the adsorbed amount of the test substance could be determined on the soil directly (direct method).

11.1.3 Test substances

The following three substances have been selected:

- γ -Hexachlorocyclohexane (Lindane),
- 2-Chloro-4-ethylamino-6-methylethylamin-s-triazine (Atrazine),

- 2,4-Dichlorophenoxy acetic acid (2,4-D).

The chemical and physico-chemical behaviour of these substances is well documented in the literature. Besides, they are considered to be sufficiently stable to biotic and hydrolytical degradation during the test period. Furthermore, the properties of test compounds cover a range of parameters, which are looked upon as the most relevant for sorption testing (Table 36). Lindane exhibits a high affinity to the organic matter of the soil matrix ($\text{Log}(P_{ow}) = 3.7$). Atrazine with its two secondary amine moieties represents a moderate pH-dependancy, while 2,4-D stands for anionic structures ($\text{pK}_a = 3.6$) with a considerable water solubility.

Suitable and sensitive analytical procedures for the detection of even small amounts are documented. In addition to that they can be commercially purchased in their ^{14}C -radiolabelled form. The selected test compounds – already used for the validation of the first EUROSIL generation – are not very volatile and soluble in water to at least 8 mg/L. Biotic and abiotic degradation processes are likely to be negligible for duration of the testing period.

Table 35 – Initial test concentrations recommended for the adsorption testing

	<i>Atrazine</i>	<i>2,4-D</i>	<i>Lindane</i>
Stock solution	10.00 $\mu\text{g}/\text{cm}^3$ (*)	20.00 $\mu\text{g}/\text{cm}^3$ (*)	4.00 $\mu\text{g}/\text{cm}^3$ (*)
Level 1	0.05 $\mu\text{g}/\text{cm}^3$	0.10 $\mu\text{g}/\text{cm}^3$	0.02 $\mu\text{g}/\text{cm}^3$
Level 2	0.25 $\mu\text{g}/\text{cm}^3$	0.50 $\mu\text{g}/\text{cm}^3$	0.10 $\mu\text{g}/\text{cm}^3$
Level 3	1.00 $\mu\text{g}/\text{cm}^3$	2.00 $\mu\text{g}/\text{cm}^3$	0.40 $\mu\text{g}/\text{cm}^3$
Level 4	5.00 $\mu\text{g}/\text{cm}^3$	10.00 $\mu\text{g}/\text{cm}^3$	2.00 $\mu\text{g}/\text{cm}^3$

* in 0.01 M CaCl_2

Table 36 – Physical and chemical data of the test substances used for the adsorption tests

<i>Property</i>		<i>Lindane</i>	<i>Atrazine</i>	<i>2,4-D</i>
Molecular weight	[g/mol]	290.8	215.7	221.0
Water soluble	[mg/L]	8	24	600
Log(P_{ow})		3.7	2.3	0.1
Vapour pressure	[Pa]	1.2×10^{-3}	4.0×10^{-5}	$< 1.0 \times 10^{-5}$

11.1.4 Freundlich isotherm

The Freundlich adsorption isotherm equation relates the amount of the test substance adsorbed to the concentration of the test substance in solution at equilibrium [13].

$$c_s^{ads}(eq) = K_F \cdot c_{aq}^{ads}(eq)^{1/n} \quad (\mu\text{g g}^{-1})$$

or in the linear form:

$$\log(c_s^{ads}(eq)) = \log(K_F) + \frac{1}{n} \cdot \log(c_{aq}^{ads}(eq))$$

where: $1/n$ = regression constant, $1/n$ generally ranges between 0.7 – 1.2, indicating that sorption is frequently nonlinear.

K_F = Freundlich adsorption coefficient.

The concentration-independent adsorption coefficient K_F is derived from a Log-Log-plot of x/m versus C_e .

11.2 pH using a suspension of water and 0.01M CaCl_2 (ISO 10390)

11.2.1 Principle of the procedure

The method used was based on the ISO standard 10390. A suspension of soil was made up in five times its volume of the water or a 0.01 mol/L solution of calcium chloride (CaCl_2) in water. The pH of the suspension was measured using a pH-meter. Each participant was asked to analysis two bottles (on two different days).

11.2.2 Recommendations for the testing

11.2.2.1 Chemical reagents

Only reagents of recognised analytical grade were used. More precisely, the following instructions were given:

- Water, with a specific conductivity not higher than 0.2 mS/m at 25°C and a pH greater than 5.6 (grade 2 water according ISO 3696).
- Calcium chloride solution, $c(\text{CaCl}_2) = 0.01$ mol/L. Obtained from the dissolution of 1.47 g of calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) in water (quality see above) and dilution to 1000 mL at 20°C.
- Solutions for the calibration of the pH-meter; commercially available buffer solutions were admitted. Otherwise the following solutions had to be prepared. At least two of these calibration solutions had to be used.
- Buffer solution pH 4.0 at 20°C; dissolution 10.21 g of potassium hydrogen phthalate in water and dilution to 1000 mL at 20°C. Potassium hydrogen phthalate had to be dried before use for 2 h at 110° to 120°C.
- Buffer solution pH 7.0 at 20°C; dissolution of 3.800 g of potassium dihydrogen phosphate and 3.415 g of disodium hydrogen phosphate in water and dilution to 1000 mL at 20°C. Potassium dihydrogen phosphate had to be dried before use for 2 h at 110°C to 120°C.
- Buffer solution pH 9.22 at 20°C; dissolution of 3.80g of disodium tetraborate decahydrate in water and dilution to 1000 m L at 20°C.

11.2.2.2 Apparatus

The use of the following devices was requested:

- Shaking or mixing machine;

- pH-Meter with slope adjustment and temperature control;
- Glass electrode and a reference electrode, or a combined electrode of equivalent performance;
- Thermometer capable of measuring to the nearest 1°C, complying with type C according to ISO 1770;
- Sample bottle of capacity at least 50 mL, made of borosilicate glass or polyethylene with a tightly fitting cap or stopper.

11.2.2.3 Laboratory sample

A sub-sample of the bottles distributed for certification was to be taken. Results referred also to the bottle number. The bottles (two per participant) were shaken for at least 5 min before opening. Dust particles in the headspace of the bottles were allowed to settle (approx. 2 min).

A minimum of five replicates were done for each soil in both solutions. 3 replicates were made on one bottle on the first day, two on the second day using the second bottle (or vice versa).

11.2.3 Procedure

11.2.3.1 Calibration of the pH-Meter

The pH-Meter was calibrated as prescribed in the manufacturer's manual using the buffer solutions described above. At least, a two point calibration was necessary.

11.2.3.2 Preparation of the suspension and pH measurement

The intake of the test portion in the guideline is based on a volumetric unit, e.g. 5 mL from the laboratory sample using a spoon. This is a rather arbitrary approach and reproducibility is questionable. Therefore, the test portion was weighed and 4.50 g (according to some pre-tests this corresponds to 5 mL) of soil substrate were used as sample intake. 25 mL of analytical grade of water or 0.01 M CaCl₂, respectively, were added. Samples were shaken vigorously for 5 min, in a way that the soil was kept in suspension, followed by a waiting period of 4 hours, and re-shaking of the suspension just before measurement of pH. pH-meters were adjusted as indicated in the respective manufacturer's manual. The pH was measured in the settling suspension and values were recorded to two decimal places. Measurements were done under temperature controlled conditions at 20°C ± 1°C. Temperature was recorded with the pH.

11.3 Organic and total carbon after dry combustion (ISO 10694)

11.3.1 Principle of the procedure

The procedure is based on the oxidation of the carbon present in the soil to carbon dioxide by heating the soil to at least 900°C in a flow of oxygen-containing gas that is free from carbon dioxide. The amount of carbon dioxide released is then measured by titrimetry, gravimetry, conductometry, gas chromatography or using an infrared detection method, depending on the apparatus used. When the soil is heated to a temperature of at least 900°C, any carbonates

present are completely decomposed. For the determination of the organic carbon content, any carbonates present are previously removed by treating the soil with hydrochloric acid. Alternatively, if the carbonate content of the examined samples is known, corrections are made for the carbonates present when the organic carbon content is calculated.

11.3.2 Recommendations for the testing

11.3.2.1 Chemical reagents

It was recommended to use only reagents of recognised analytical grade. More precisely the following instructions had to be followed:

- Water, with a specific conductivity not higher than 0.2 mS/m at 25°C and a pH greater than 5,6 (grade 2 water according ISO 3696);
- Calibration substances, e.g. acetanilide, atropine, calcium carbonate, spectrographic graphite powder and potassium hydrogen phthalate;
- Hydrochloric acid, $c(\text{HCl}) = 4 \text{ mol/L}$; Dilute 340 mL of concentrated hydrochloric acid ($\rho = 1.19 \text{ g/mL}$) to 1000 mL with water.
- Depending on the method of detection applied reagents and/or catalysts were required for reduction, oxidation, removal and/or fixing combustion gases, which interfere with the analysis. The manufacturer's manual had to be consulted for the apparatus to be used.

11.3.2.2 Apparatus and glassware

The use of the following equipment was requested:

- Standard laboratory glassware;
- Analytical balance (0.1 mg accuracy) or microbalance (0.01 mg accuracy);
- Apparatus for determination of the total carbon content, by combustion of the sample at a temperature of at least 900°C, including a detector for measuring the carbon dioxide formed. Some modern instruments are capable of determining organic and inorganic carbon separately in one run, by increasing the temperature gradually and continuously measuring carbon dioxide. Other instruments are capable of simultaneously determining total nitrogen and total carbon in soils.
- Crucibles made of porcelain, quartz, silver, tin or nickel, of various sizes.

11.3.2.3 Laboratory sample

A sub-sample of the distributed soils was taken and reference was made to the bottle number. The bottles were shaken for at least 5 min before opening. Dust particles in the headspace of the bottles were allowed to settle (approx. 2 min).

11.3.3 Procedure

The procedure consisted of the determination of either:

- the total carbon content including that carbon present as carbonate; or
- the organic carbon content after removal of carbonate.

All analysis were repeated all analysis in four replicates.

11.3.3.1 Calibration of the apparatus

The apparatus were calibrated as described in the relevant manual. For calibration or establishing a calibration graph, one of the aforementioned substances was used.

11.3.3.2 Determination of the total carbon content

The amount of test portion taken for analysis depended on the expected total carbon content and on the apparatus used. 1 g of the air-dried sample was weighed in a crucible. Analyses were carried out in accordance with the manufacturer's manual for the respective apparatus.

When the organic carbon content was to be determined, the carbonates present were removed first. In this case, the procedure described in the next paragraph was followed.

11.3.3.3 Determination of the organic carbon content

An excess of hydrochloric acid was added to the crucible containing a weighed quantity of air-dried soil, and mixed. After 4 h the crucible was dried for 16 h at a temperature of 60°C to 70°C. Then, the analysis were carried out in accordance with the manufacturer's manual for the respective apparatus.

The quantity of hydrochloric acid to be added depended on the weighed amount of test portion and on the carbonate content. In all cases, an excess of hydrochloric acid was added. Care was taken that the crucibles used were large enough to avoid problems when transporting crucibles containing samples to which hydrochloric acid had been added.

11.3.4 Calculations

11.3.4.1 Total carbon content

The total carbon content of the sample, on the basis of oven-dried soil, was calculated using the following equation:

$$w_{C,t} = 1000 \cdot \frac{m_2}{m_1} \cdot 0.2727 \cdot \frac{100 + w_{water}}{100}$$

where

$w_{C,t}$ is the total carbon content, in grams per kilogram, on the oven-dried soil;

m_1 is the mass, in grams, of the test portion;

m_2 is the mass, in grams, of carbon dioxide released by the soil sample

0.227 is the conversion factor for CO₂ to C

w_{water} is the water content, expressed as a percentage by mass, on a dry mass basis, determined according to ISO 11465.

11.3.4.2 Organic carbon content

11.3.4.2.1 Indirect method

Total carbon content of the sample, on the basis of oven-dried soil, was calculated using the following equation:

$$w_{C,o} = w_{C,t} - (0.12 \cdot w_{CaCO_3})$$

where

$w_{C,o}$ is the organic carbon content, in grams per kilogram, on the oven-dried soil;

$w_{C,t}$ is the total carbon content, in grams per kilogram, on the oven-dried soil;
0.12 is the conversion factor;

w_{CaCO_3} is the carbonate content of the soil, in grams per kilogram, expressed as calcium carbonate equivalent on the basis of oven-dried soil, determined according to ISO 10693.

11.3.4.2.2 Direct method

If the carbonates were removed beforehand (following the aforementioned procedure), the organic carbon content was determined according to the instructions given for the determination of the total carbon content.

11.4 Total nitrogen according to ISO 11261

11.4.1 Principle of the procedure

This method is based on the Kjeldahl-digestion, but titanium dioxide is used as the catalyst instead of selenium. Alternatively to this method the content of total nitrogen was determined by elementary analysis (flash combustion).

11.4.2 Recommendations for the testing

11.4.2.1 Chemical reagents

It was requested to use only reagents of recognised analytical grade. More precisely the following instructions were given:

- Water, with a specific conductivity not higher than 0.2 mS/m at 25°C and a pH greater than 5,6 (grade 2 water according ISO 3696).

- Salicyclic acid/sulphuric acid; dissolve 25 g of salicyclic acid in 1 litre of con-centrated sulfuric acid ($\rho=1.84 \text{ g/cm}^3$).
- Potassium sulfate catalyst mixture; Grind and thoroughly mix 200 g of potassium sulfate, 6 g of copper (II) sulfate pentahydrate and 6 g of titanium dioxide.
- Sodium thiosulfate pentahydrate; Crush the crystals to form a powder that passes through a sieve with an aperture of 0.25 mm.
- Sodium hydroxide, $c(\text{NaOH}) = 10 \text{ mol/L}$.
- Boric acid solution, $\rho(\text{H}_3\text{BO}_3) = 20 \text{ g/L}$.
- Mixed indicator; Dissolve 0.1 g of bromocresol green and 0.02 g of methyl red in 100 mL of ethanol.
- Sulphuric acid, $c(\text{H}^+) = 0.01 \text{ mol/L}$.
- Grind and thoroughly mix 200 g of potassium sulfate, 6 g of copper (II) sulfate pentahydrate and 6 g of titanium dioxide. Grind and thoroughly mix 200 g of potassium sulfate, 6 g of copper (II) sulfate pentahydrate and 6 g of titanium dioxide.

11.4.2.2 Apparatus

The use of the following equipment was requested:

- Standard laboratory glassware.
- Digestion flasks or tubes, of nominal volume 50 mL, suitable for the digestion stand.
- Digestion stand.
- Distillation apparatus, preferably of the Parnas-Wagner type.
- Burette, graduated in intervals of 0.01 mL or smaller.

11.4.2.3 Laboratory sample

Test portions were taken from the samples distributed for certification. Reference was made to the bottle number. The bottles were shaken for at least 5 min before opening and the dust particles in the headspace of the bottles were allowed to settle (approx. 2 min).

If elementary analysis was applied (flash combustion), a sufficiently large test portion was ground and crushed, homogenised thoroughly and a sub-samples of this test portion was used for the analysis.

11.4.3 Procedure

A test portion of the air-dried soil sample, of about 0.2 g (expected content approx. 0.5 %) to 1 g (expected nitrogen content approx. 0.1 %), was placed in the digestion flask. 5 mL of salicyclic/sulfuric acid was added and the flask was swirled until the acid was thoroughly mixed with the soil. The mixture was allowed to stand for at least several hours (or overnight). 0.5 g of sodiumthiosulfate were added through a dry funnel with a long stem that reached down into the bulb of the digestion flask. The mixture was heated cautiously on the digestion stand until frothing had ceased.

Then, the flask was cooled and 1.1 g of the catalyst mixture were added. The mixture was heated until it became clear. The mixture was boiled gently for up to 5 h so that the sulfuric acid condensed about 1/3 of the way up to the neck of the flask. Care was taken that the temperature of the solution did not exceed 400°C.

After completion of the digestion step, the flask was allowed to cool and about 20 mL of water were added slowly while shaking. The flask was swirled to bring any insoluble material into suspension and the contents were transferred to the distillation apparatus. 5 mL of boric acid were added to a 100 mL conical flask and the flask was placed under the condenser of the distillation apparatus in such a way that the end of the condenser dipped into the solution. 20 mL of sodium hydroxide were added to the funnel of the apparatus and the alkali was run slowly into the distillation chamber. About 40 mL of condensate (the amount for quantitative results depends on the dimensions of the apparatus) were distilled and the end of the condenser was rinsed. After addition of a few drops of indicator to the distillate, the solution was titrated with sulfuric acid to a violet endpoint. Potentiometric titration is an alternative. In this case endpoint of titration had to be pH=6.0.

Four replicates per soil were performed.

11.4.4 Calculations

The total content of nitrogen, (w_N), in milligrams per gram, is calculated using the equation:

$$w_N = \frac{(V_1 - V_0) \cdot c(H^+) \cdot M_N}{m} + \frac{100 + w_{water}}{100}$$

where

V_1 is the volume, in millilitres, of the sulfuric acid used in the titration of the sample;

V_0 is the volume, in millilitres, of the sulfuric acid used in the blank test;

$c(H^+)$ is the concentration of H^+ on the sulfuric acid, in moles per litre;

M_N is the molar mass of nitrogen, in grams per mole;

m is the mass, in grams, of the air-dried sample of soil;

w_{water} is the water content, expressed as a percentage by mass, on the basis of oven dried soil, determined according to ISO 11465

Results were round to two significant figures.

12. ANNEX II – INDIVIDUAL RESULTS AND GRAPHICAL REPRESENTATIONS

Table 37 – Individual results of Freundlich isotherm determinations of atrazine on EUROSIL 1

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
1	400	7.6349	1.0554	0.9473	0.0225	0.9966
	206	7.3150	1.0409	0.9428	0.0168	0.9981
5	269	5.9496	1.0342	1.0661	0.0154	0.9987
	393	6.3349	1.0193	1.0617	0.0086	0.9996
6	235	7.7845	1.0760	0.9238	0.0291	0.9941
	329	6.7874	1.0770	0.8841	0.0292	0.9935
7	289	nd				
	345	6.0602	1.0426	0.7049	0.0282	0.9905
8	12	8.6856	1.0556	0.9606	0.0233	0.9965
	215	7.0190	1.0181	0.8870	0.0077	0.9996
9	2	7.2163	1.0141	0.8946	0.0058	0.9997
	183	7.1694	1.0174	0.8916	0.0071	0.9996
10	24	6.3354	1.1735	0.8961	0.0660	0.9685
	311	7.6552	1.0095	0.9270	0.0038	0.9999

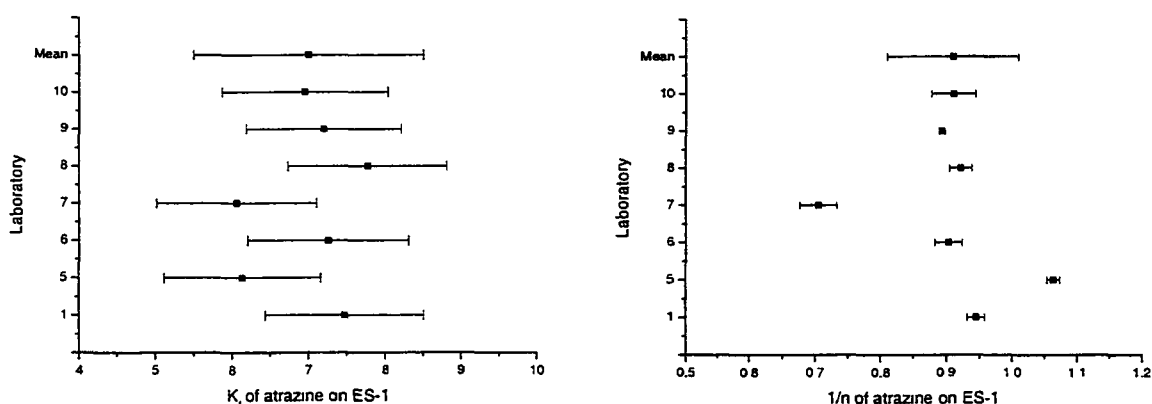


Figure 8 – Graphical comparison between individual adsorption coefficients K_f and $1/n$ for atrazine on EUROSIL 1 and the certified value ($\pm U_{CRM}$).

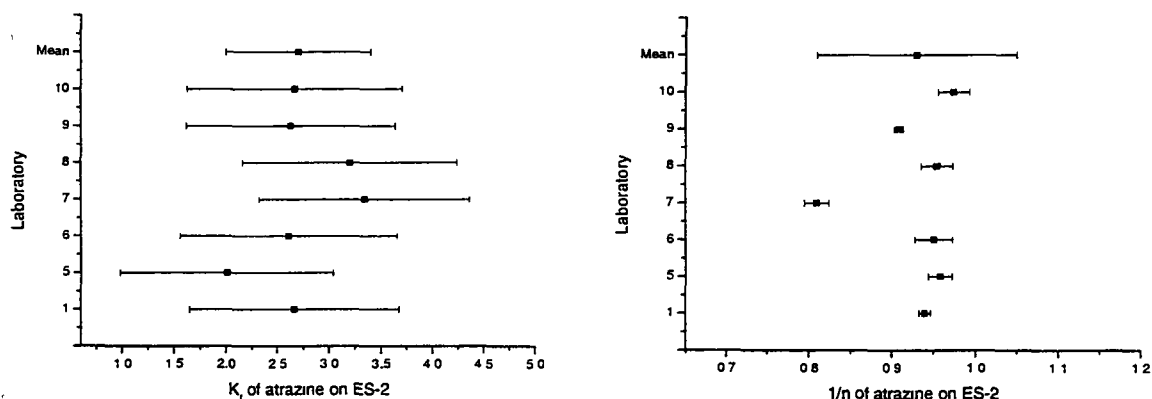


Figure 9 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for atrazine on EUROSIL 2 and the certified value ($\pm U_{CRM}$).

Table 38 - Individual results of Freundlich isotherm determinations of atrazine on EUROSIL 2 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
1	111	2.6939	1.0155	0.9407	0.0074	0.9996
	289	2.6341	1.0257	0.9389	0.0121	0.9990
5	3	2.0557	1.0249	0.9507	0.0122	0.9990
	294	1.9657	1.0529	0.9658	0.0257	0.9958
6	195	2.3674	1.0622	0.9240	0.0283	0.9944
	301	2.8839	1.0619	0.9800	0.0284	0.9950
7	62					
	274	3.3434	1.0184	0.8097	0.0146	0.9980
8	73	3.5663	1.0498	1.0000	0.0243	0.9965
	223	2.8937	1.0191	0.9138	0.0093	0.9994
9	42	2.6227	1.0158	0.9046	0.0076	0.9996
	89	2.6303	1.0165	0.9130	0.0080	0.9995
10	162	2.5575	1.0659	0.9932	0.0314	0.9941
	266	2.7841	1.0186	0.9575	0.0089	0.9995

Table 39 - Individual results of Freundlich isotherm determinations of atrazine on EUROSIL 3 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
1	88	2.1166	1.0195	0.9226	0.0094	0.9994
	269	2.4367	1.0226	0.9434	0.0107	0.9992
5	61	2.0340	1.0767	0.9734	0.0368	0.9915
	275	1.8920	1.0452	0.9685	0.0222	0.9969
6	7	1.8080	1.1084	0.9018	0.0492	0.9824
	352	2.3711	1.0819	1.0022	0.0382	0.9914
7	13	3.2435	1.0469	0.6497	0.0338	0.9840
	291					
8	103	3.0548	1.0634	1.0373	0.0316	0.9945
	378	2.5081	1.0294	0.9551	0.0147	0.9986
9	27	2.2260	1.0104	0.9130	0.0051	0.9998
	142	2.3972	1.0123	0.9299	0.0060	0.9998
10	202	2.7035	1.0268	0.9559	0.0128	0.9989
	337	2.3891	1.0181	0.9620	0.0088	0.9995

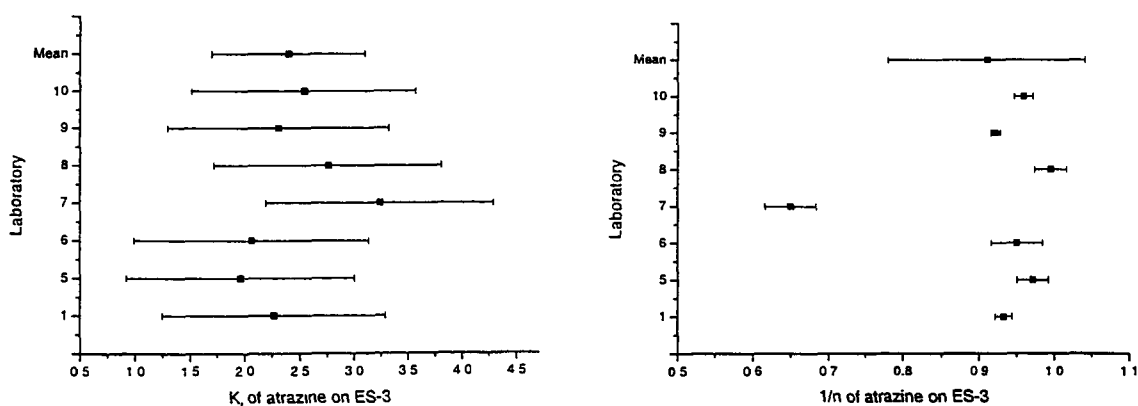


Figure 10 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for atrazine on EUROSIL 3 and the certified value ($\pm U_{CRM}$).

Table 40 - Individual results of Freundlich isotherm determinations of atrazine on EUROSOIL 4 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
1	484	0.7253	1.0214	0.8886	0.0109	0.9991
	566	0.7034	1.0532	0.9097	0.0269	0.9948
5	391	0.2583	1.0967	0.8865	0.0495	0.9817
	637	0.3114	1.1207	0.8861	0.0607	0.9726
6	249	0.4318	1.2936	0.9151	0.1308	0.8908
	453	0.7205	1.2325	1.1336	0.1086	0.9478
7	283					0.0000
	576	1.2841	1.0118	0.6675	0.0097	0.9987
8	461	0.6752	1.0676	0.7102	0.0344	0.9861
	631	0.9202	1.0541	0.9336	0.0283	0.9945
9	274	0.7048	1.0318	0.8769	0.0166	0.9979
	622	0.6962	1.0476	0.8540	0.0246	0.9951
10	317	0.8776	1.0228	0.9696	0.0118	0.9991
	515	0.8752	1.0344	0.9591	0.0177	0.9980

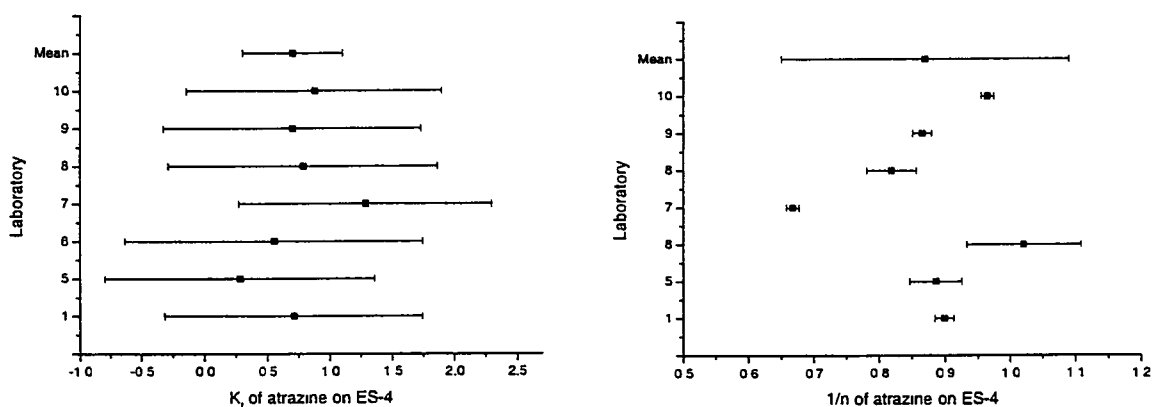


Figure 11 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for atrazine on EUROSOIL 4 and the certified value ($\pm U_{CRM}$).

Table 41 - Individual results of Freundlich isotherm determinations of atrazine on EUROSOIL 5 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
1	128	15.3444	1.0402	0.9361	0.0138	0.9987
	283	16.4855	1.0264	0.9498	0.0091	0.9994
2	70	10.7709	1.0917	0.8885	0.0323	0.9921
	193	10.5308	1.0668	0.8797	0.0238	0.9956
5	149	11.7971	1.0328	0.9446	0.0122	0.9990
	235	9.3115	1.1574	0.9420	0.0577	0.9780
6	170	14.8753	1.0522	0.9249	0.0176	0.9978
	363	16.2550	1.0520	0.9392	0.0174	0.9979
8	161	15.1171	1.0235	0.9045	0.0084	0.9995
	384	15.3642	1.0335	0.9171	0.0120	0.9990
9	39	12.3517	1.0340	0.9112	0.0123	0.9989
	396	13.6447	1.0292	0.9041	0.0104	0.9992
10	103	13.9864	1.0193	0.9387	0.0069	0.9997
	292	12.5580	1.0162	0.9120	0.0058	0.9998

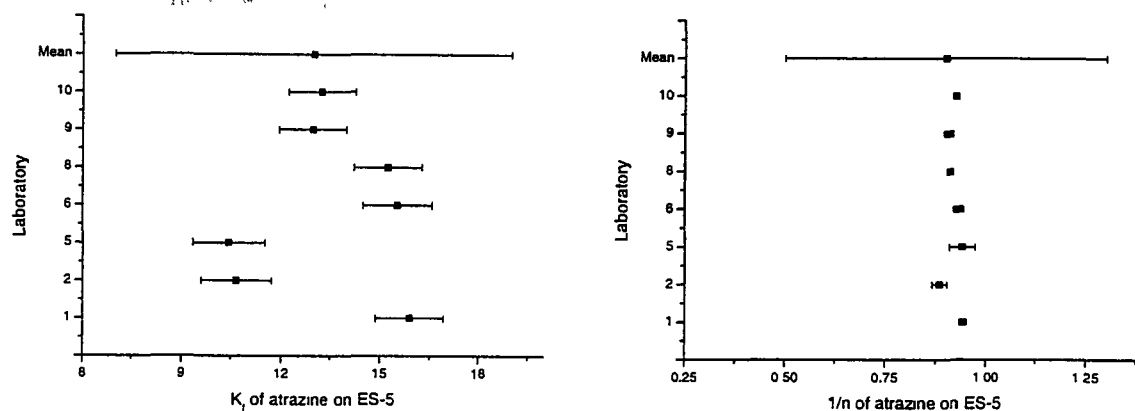


Figure 12 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for atrazine on EUROSOIL 5 and the certified value ($\pm U_{CRM}$).

Table 42 - Individual results of Freundlich isotherm determinations of atrazine on EUROSOIL 7 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
1	48	5.5928	1.6642	0.9428	0.0034	0.9999
	339	5.4710	1.4227	0.9289	0.0066	0.9998
5	105	3.2091	2.4975	0.9958	0.0279	0.9953
	472	2.9422	1.9472	0.9834	0.0167	0.9983
6	23	4.9467	1.4259	0.9352	0.0189	0.9976
	398	5.4293	4.0757	0.9436	0.0213	0.9969
7	63					
	384	4.4082	1.9738	0.7592	0.0658	0.9569
8	55	5.5340	1.3474	0.9206	0.0056	0.9998
	352	5.5021	1.5318	0.9345	0.0172	0.9980
9	71	5.3155	1.4592	0.9289	0.0033	0.9999
	451	5.0417	1.4135	0.9081	0.0087	0.9994
10	33	4.8274	1.2627	0.9602	0.0104	0.9993
	359	4.8163	1.2023	0.9576	0.0123	0.9990

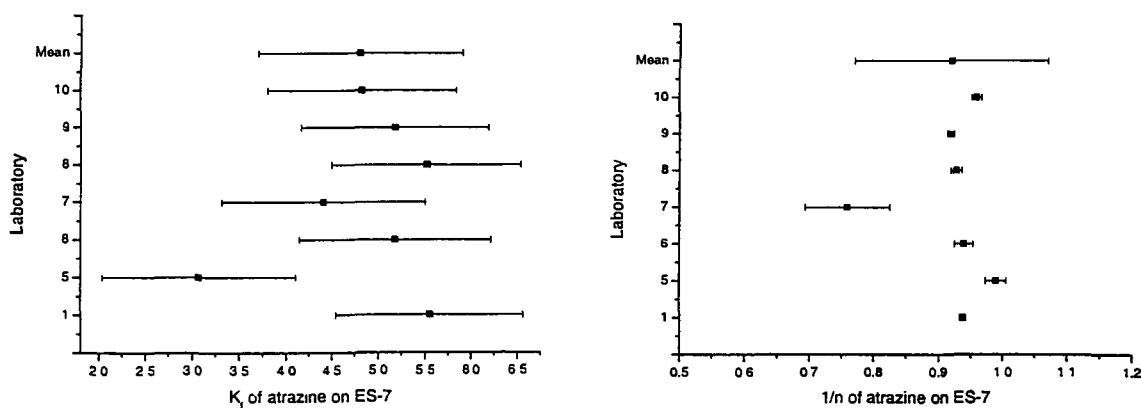


Figure 13 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for atrazine on EUROSOIL 7 and the certified value ($\pm U_{CRM}$).

Table 43 - Individual results of Freundlich isotherm determinations of 2,4-D on EUROSOIL 1 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
2	172	2.2805	1.1140	1.0445	0.0602	0.9837
	279	2.7585	1.0988	0.9648	0.0510	0.9862
5	269	2.5691	1.0294	0.9560	0.0163	0.9983
	393	2.6448	1.0268	0.9381	0.0148	0.9985
6	235	2.7539	1.0313	0.7818	0.0157	0.9976
	329	2.5512	1.0397	0.8529	0.0205	0.9965
7	345	2.3675	1.1321	1.0461	0.0754	0.9698
	289	2.4590	1.0980	1.0641	0.0777	0.9791
8	12	2.5974	1.0257	0.8424	0.0138	0.9984
	215	2.5249	1.0469	0.8630	0.0251	0.9950
9	2	2.5095	1.0259	0.8670	0.0137	0.9985
	183	2.4952	1.0351	0.8756	0.0187	0.9973
10	24	2.0914	1.0290	0.9095	0.0160	0.9981
	311	2.1488	1.0354	0.8769	0.0192	0.9971

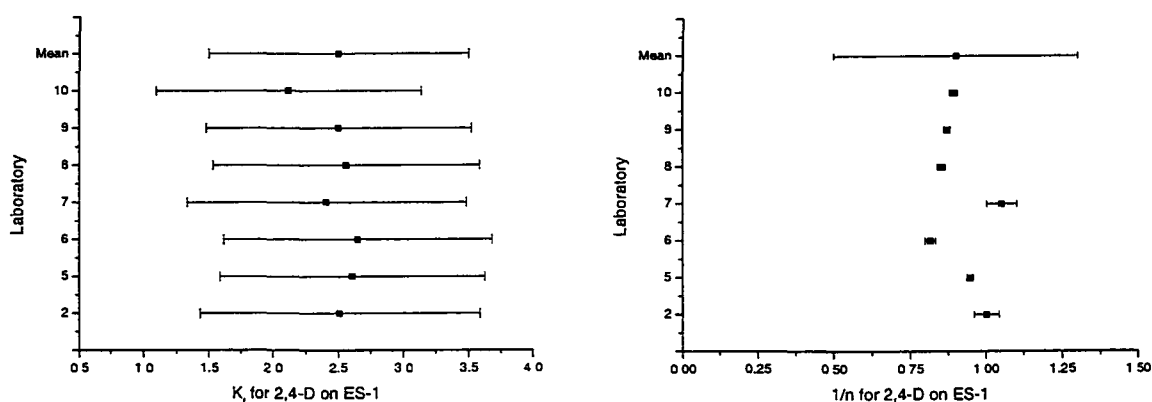


Figure 14 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for 2,4-D on EUROSOIL 1 and the certified value ($\pm U_{CRM}$).

Table 44 - Individual results of Freundlich isotherm determinations of 2,4-D on EUROSOIL 2 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
2	11	0.5907	1.3403	1.0944	0.2137	0.8398
	131	0.6870	1.2385	1.0794	0.1267	0.9478
5	3	1.5453	1.0450	1.0081	0.0256	0.9961
	294	1.4808	1.0445	0.9462	0.0250	0.9958
6	195	0.6271	1.0320	1.0747	0.0230	0.9982
	301	0.6475	1.0162	1.0823	0.0118	0.9995
7	274	1.1837	1.0884	0.8685	0.0540	0.9773
	62	0.9996	1.1695	0.9957	0.0865	0.9745
8	223	1.1987	1.0238	0.8051	0.0132	0.9984
	73	1.0071	1.0857	0.8505	0.0468	0.9821
9	42	1.0570	1.0479	0.8681	0.0264	0.9945
	89	1.0782	1.0479	0.8966	0.0265	0.9948
10	162	0.9081	1.0537	0.9806	0.0304	0.9943
	266	0.9066	1.1010	0.9472	0.0558	0.9796

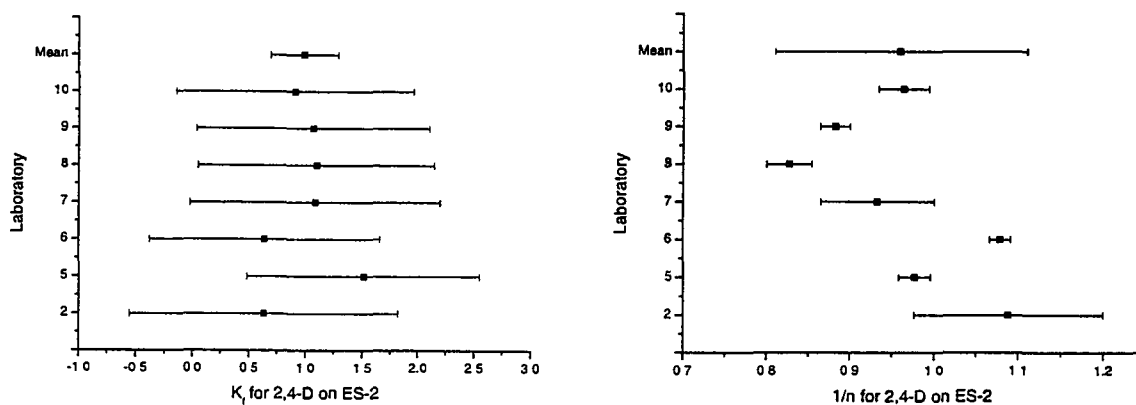


Figure 15 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for 2,4-D on EUROSOIL 2 and the certified value ($\pm U_{CRM}$).

Table 45 - Individual results of Freundlich isotherm determinations of 2,4-D on EUROSOIL 3 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
2	16	1.2909	1.1901	1.2578	0.1057	0.9593
	163	1.1397	1.1482	1.1786	0.0832	0.9710
5	67	1.7686	1.0515	0.9105	0.0283	0.9942
	275	1.8937	1.0469	0.9275	0.0260	0.9953
6	7	1.1680	1.0093	0.8892	0.0051	0.9998
	352	1.1815	1.0130	0.8278	0.0071	0.9996
7	13	0.9814	1.0862	0.8219	0.0524	0.9762
	291	1.2245	1.0644	0.9787	0.0396	0.9903
8	103	1.3611	1.0385	0.8297	0.0212	0.9961
	378	1.4222	1.0797	0.8798	0.0434	0.9856
9	27	1.2828	1.0392	0.8870	0.0217	0.9964
	142	1.3363	1.0378	0.8901	0.0208	0.9967
10	202	1.0863	1.0919	0.8997	0.0506	0.9814
	337	1.2806	1.0242	0.9056	0.0137	0.9986

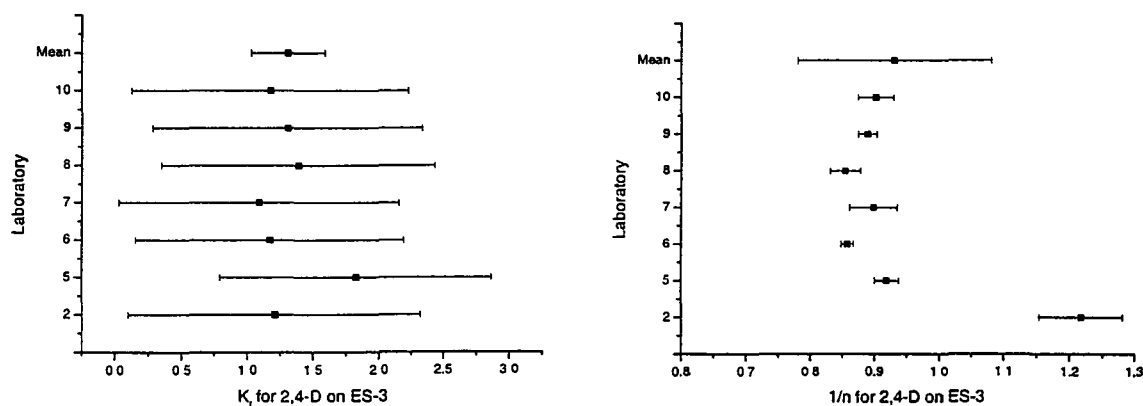


Figure 16 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for 2,4-D on EUROSOIL 3 and the certified value ($\pm U_{CRM}$).

Table 46 - Individual results of Freundlich isotherm determinations of 2,4-D on EUROSOIL 4 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
5	391	0.6974	1.0578	0.8639	0.0324	0.9916
	637	0.6170	1.0723	0.8356	0.0401	0.9864
6	249	0.2120	1.1130	0.9394	0.0619	0.9746
	453	0.1582	1.2788	1.1147	0.1415	0.9118
7	576	0.3424	1.2148	0.9498	0.1331	0.8946
	283	0.3396	1.2414	0.5723	0.1449	0.7221
8	461	0.5134	1.0889	0.7040	0.0484	0.9724
	631	0.2773	1.6140	0.8360	0.2770	0.6028
9	274	0.3817	1.1379	0.8570	0.0744	0.9567
	622	0.4270	1.0772	0.7292	0.0423	0.9802
10	317	0.4147	1.0654	0.8792	0.0368	0.9896
	515	0.3383	1.0767	1.0342	0.0436	0.9895

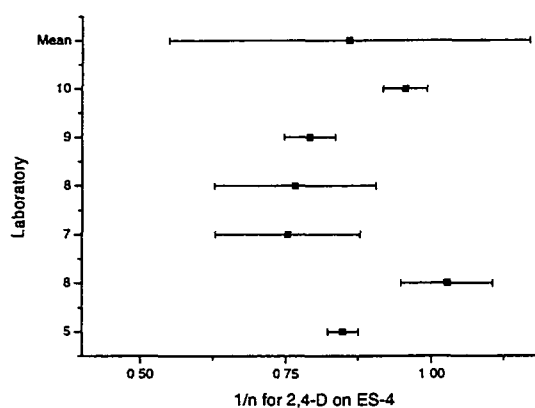
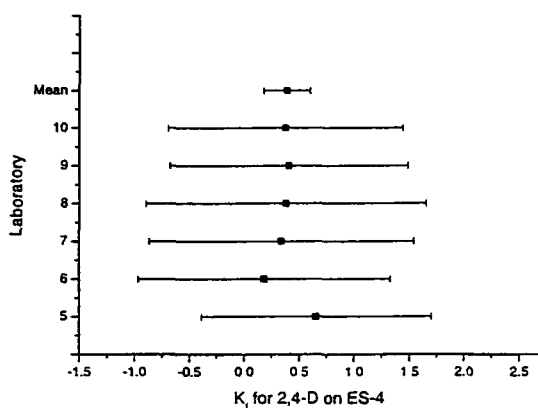


Figure 17 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for 2,4-D on EUROSOIL 4 and the certified value ($\pm U_{CRM}$).

Table 47 - Individual results of Freundlich isotherm determinations of 2,4-D on EUROSOIL 5 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
2	70	15.7541	1.1363	1.0671	0.0608	0.9809
	193	15.6394	1.0730	0.9862	0.0316	0.9939
5	149	19.0172	1.0508	0.9175	0.0200	0.9972
	235	17.7096	1.0686	0.8995	0.0268	0.9947
6	170	17.9553	1.0342	0.9289	0.0136	0.9987
	363	18.9706	1.0224	0.8528	0.0081	0.9995
7	374	15.6880	1.3192	0.8107	0.0864	0.9363
	121	16.3269	1.2485	0.7905	0.0845	0.9563
8	161	18.3965	1.0177	0.8452	0.0068	0.9996
	384	19.5971	1.0174	0.9097	0.0070	0.9996
9	39	15.7795	1.0691	0.8803	0.0268	0.9945
	396	17.6488	1.0600	0.8725	0.0225	0.9960
10	103	21.0221	1.0245	0.8894	0.0093	0.9993
	292	19.7943	1.0198	0.8638	0.0075	0.9996

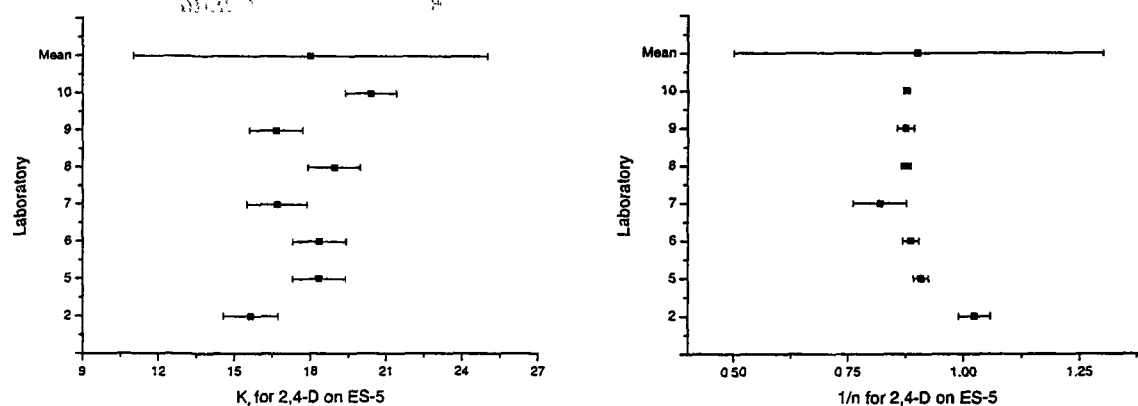


Figure 18 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for 2,4-D on EUROSOIL 5 and the certified value ($\pm U_{CRM}$).

Table 48 - Individual results of Freundlich isotherm determinations of 2,4-D on EUROSOIL 7 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
2	27	7.0774	1.0666	0.9796	0.0334	0.9931
	202	7.3572	1.0524	1.0143	0.0268	0.9958
5	105	8.1760	1.0814	0.8840	0.0371	0.9895
	472	6.8690	1.0378	0.8785	0.0180	0.9975
6	23	9.5154	1.0440	0.8927	0.0226	0.9968
	398	9.2417	1.0226	0.8549	0.0096	0.9994
7	384	7.2836	1.0832	0.7535	0.0304	0.9903
	63	6.9713	1.4942	0.8290	0.1648	0.8084
8	55	8.8308	1.0238	0.8599	0.0108	0.9990
	352	9.0448	1.0172	0.8702	0.0079	0.9995
9	71	9.7325	1.0242	0.8721	0.0106	0.9991
	451	9.3814	1.0309	0.8660	0.0132	0.9986
10	33	7.6754	1.3797	0.9259	0.1769	0.8204
	359	8.7330	1.0198	0.8783	0.0091	0.9994

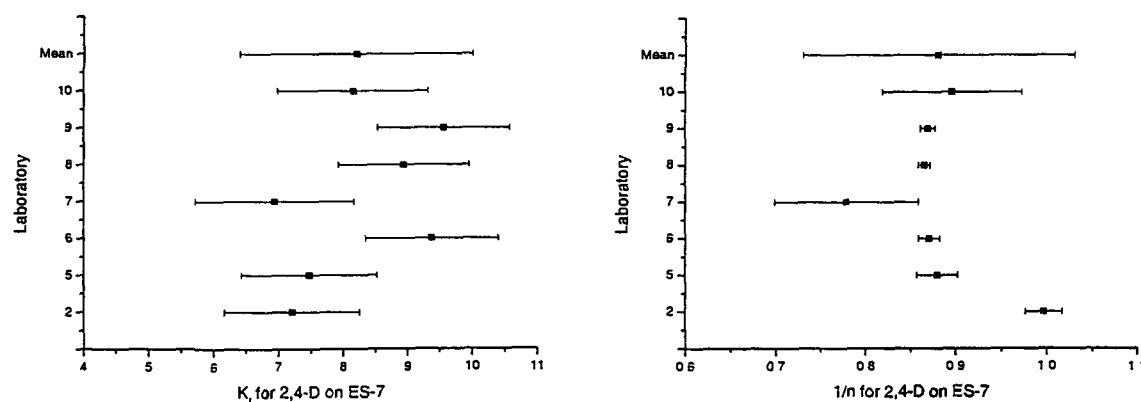


Figure 19 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for 2,4-D on EUROSOIL 7 and the certified value ($\pm U_{CRM}$).

Table 49 - Individual results of Freundlich isotherm determinations of lindane (γ -HCH) on EUROSOIL 1 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
1	206	80.9565	1.0637	0.9603	0.0124	0.9990
	400	116.5770	1.9226	1.0831	0.1395	0.9095
2	172	96.8986	1.6432	1.0498	0.1150	0.9434
	279	89.9321	1.5915	1.0631	0.1105	0.9487
5	296	56.6988	1.1402	0.9110	0.0270	0.9948
	393	62.9403	1.0409	0.9507	0.0084	0.9995
6	112	33.5618	1.1249	0.7736	0.0202	0.9932
	329	93.4934	2.2387	0.9835	0.1246	0.9689
8	12	62.8161	1.0839	0.8941	0.0165	0.9980
	215	44.9148	1.2198	0.7862	0.0384	0.9859

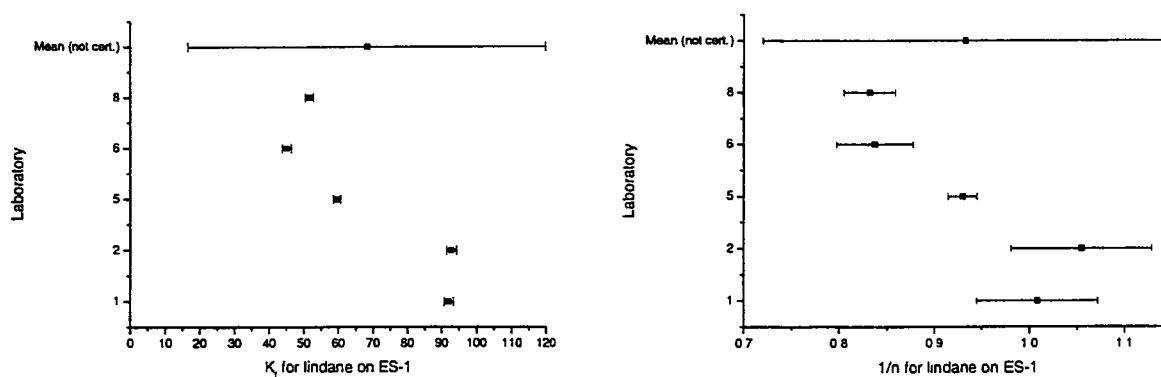


Figure 20 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for lindane (γ -HCH) on EUROSOIL 1 and the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 50 - Individual results of Freundlich isotherm determinations of lindane (γ -HCH) on EUROSOIL 2 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
1	289	50.6191	1.0247	0.9856	0.0055	0.9998
	111	55.7036	1.0737	1.0245	0.0164	0.9985
2	11	67.2756	1.7014	1.1131	0.1210	0.9442
	131	41.8972	1.7494	0.9459	0.1375	0.8875
5	3	41.5169	1.0681	0.9410	0.0148	0.9985
	294	45.8061	1.0409	0.9633	0.0091	0.9995
6	101	43.9268	1.1749	0.9266	0.0299	0.9918
8	73	42.5254	1.0491	0.9692	0.0114	0.9992
	223	47.2394	1.1771	0.9986	0.0388	0.9910

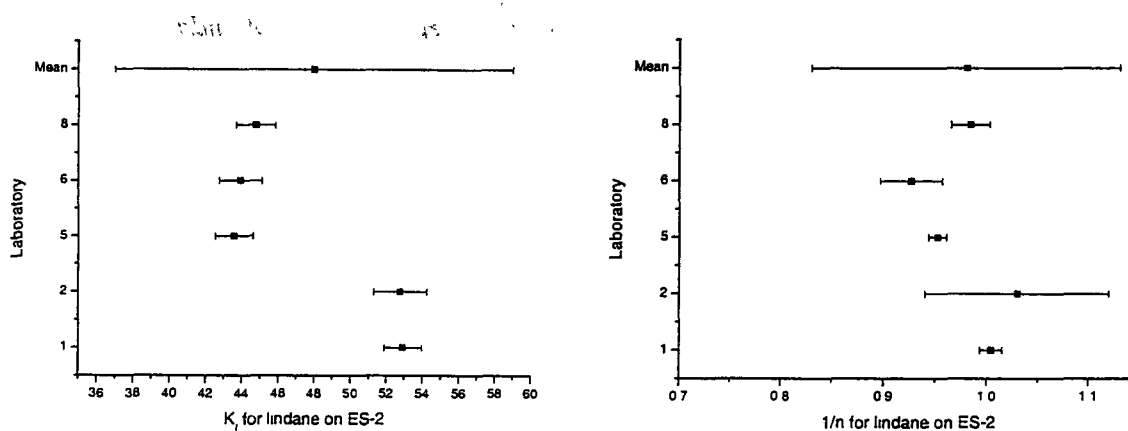


Figure 21 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for lindane (γ -HCH) on EUROSOIL 2 and the certified value ($\pm U_{CRM}$).

Table 51 - Individual results of Freundlich isotherm determinations of lindane (γ -HCH) on EUROSOIL 3 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
1	269	48.6686	1.1301	0.9991	0.0282	0.9952
	88	37.8910	1.0698	0.9643	0.0159	0.9984
2	16	36.5740	1.5177	0.9793	0.0948	0.9653
	163	42.8412	1.2776	1.0186	0.0647	0.9802
5	61	36.5156	1.0809	0.9846	0.0187	0.9978
	275	29.8417	1.0498	0.9684	0.0120	0.9991
6	7	38.0210	1.1822	0.9521	0.0341	0.9874
	49	89.7847	2.2167	1.0191	0.1278	0.9695
8	103	34.5519	1.0683	0.9596	0.0152	0.9987
	378	28.1445	1.0780	0.8826	0.0177	0.9976

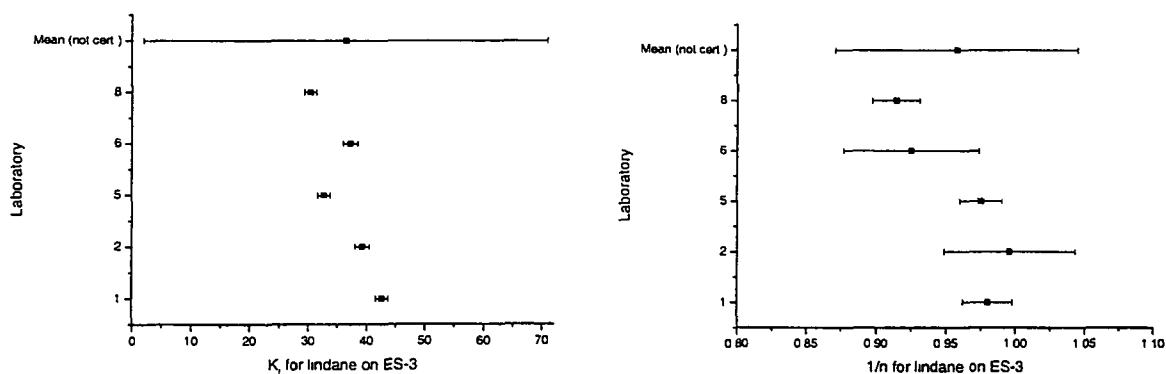


Figure 22 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for lindane (γ -HCH) on EUROSOIL 3 and the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 52 - Individual results of Freundlich isotherm determinations of lindane (γ -HCH) on EUROSOIL 4 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
1	484	9.7929	1.0430	0.9523	0.0128	0.9989
	566	10.7097	1.1038	0.9807	0.0301	0.9944
2	85	10.6573	1.0952	0.9267	0.0250	0.9949
	429	10.0561	1.1166	0.9687	0.0317	0.9942
5	391	7.2457	1.0390	0.8757	0.0116	0.9989
	637	6.7297	1.0770	0.8904	0.0231	0.9960
6	453	4.2713	1.0678	0.6932	0.0162	0.9946
8	461	8.4892	1.0602	0.9237	0.0185	0.9976
	631	8.1989	1.0597	0.9157	0.0183	0.9976

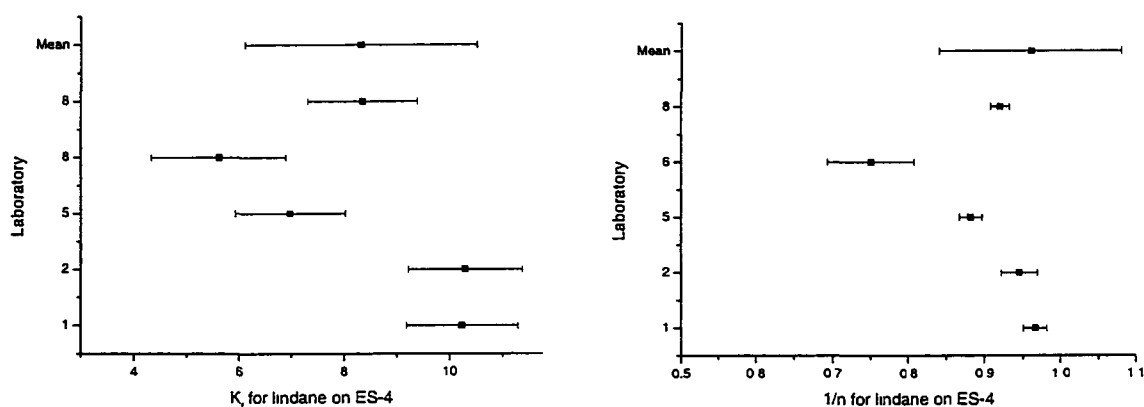


Figure 23 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for lindane (γ -HCH) on EUROSOIL 4 and the certified value ($\pm U_{CRM}$).

Table 53 - Individual results of Freundlich isotherm determinations of lindane (γ -HCH) on EUROSOIL 5 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
1	283	80.6449	1.1189	0.9553	0.0226	0.9967
	128	131.1463	1.3186	1.0109	0.0536	0.9834
2	70	136.3747	2.1057	0.9866	0.1443	0.9239
	193	125.5538	1.8038	0.9477	0.1314	0.9286
5	149	129.6132	1.0718	0.9821	0.0131	0.9989
	235	96.1454	1.2639	0.9616	0.0459	0.9865
6	170	43.7242	1.6170	0.7958	0.0789	0.9105
	264	59.3599	3.3799	0.8867	0.1826	0.9218
8	161	81.8644	1.0708	0.8994	0.0132	0.9987
	384	123.5629	1.1655	1.0018	0.0304	0.9945

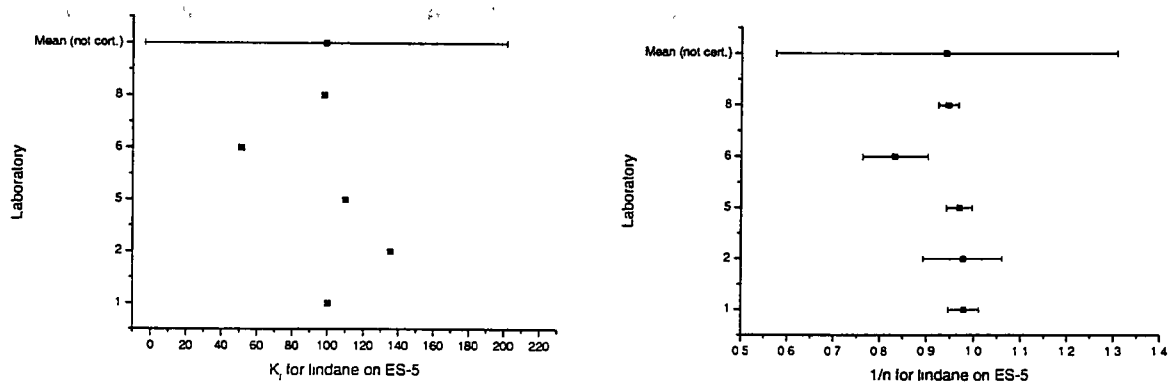


Figure 24 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for lindane (γ -HCH) on EUROSOIL 5 and the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 54 - Individual results of Freundlich isotherm determinations of lindane (γ -HCH) on EUROSOIL 7 and their statistical evaluation by ANOVA

Lab-Code	Bottle	K_f	($\pm Se(K_f)$)	$1/n$	($\pm Se(1/n)$)	r^2
1	48	50.5591	2.1577	0.7936	0.1554	0.8129
	339	72.9386	1.0646	0.9710	0.0130	0.9989
2	27	77.7426	1.3409	0.9568	0.0645	0.9778
	202	32.8163	1.8604	0.6893	0.1054	0.9181
5	105	68.1167	1.0932	0.9925	0.0192	0.9978
	472	84.1543	1.3372	0.9969	0.0604	0.9785
6	15	42.3855	1.1781	0.7915	0.0275	0.9881
8	55	78.0185	1.0619	1.0075	0.0131	0.9990
	352	61.6111	1.1937	0.9325	0.0374	0.9904

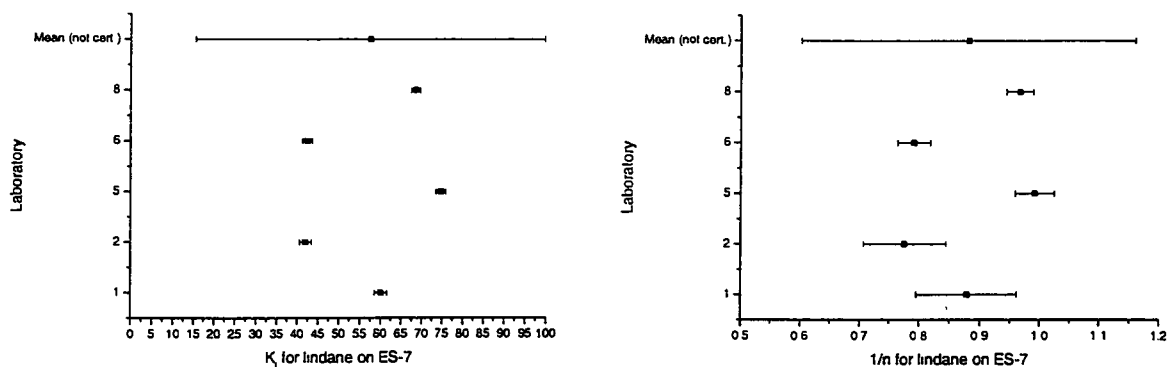


Figure 25 - Graphical comparison between individual adsorption coefficients K_f and $1/n$ for lindane (γ -HCH) on EUROSOIL 7 and the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

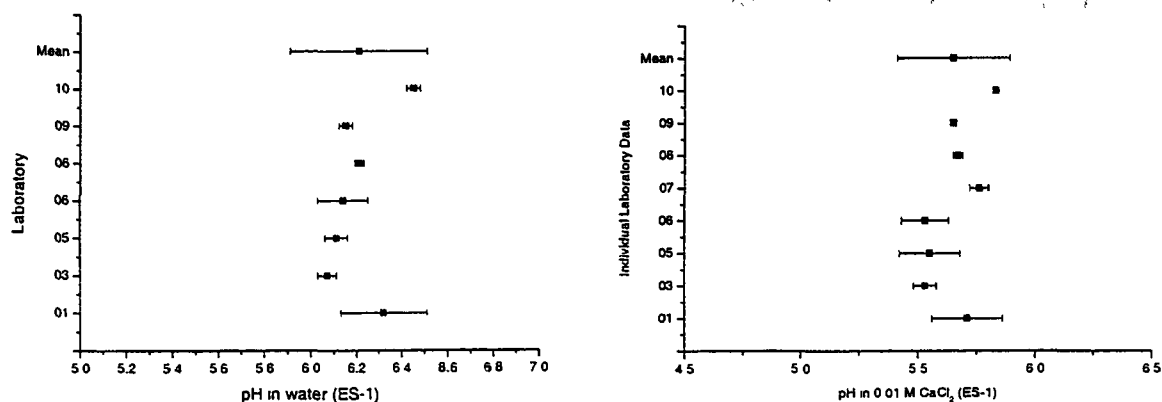


Figure 26 - Graphical comparison between laboratory means for pH in suspensions of water and 0.01M CaCl₂ for EUROSOIL 1 and the certified value ($\pm U_{CRM}$).

Table 22b - Individual laboratory data for pH in suspension of water for EUROSOIL 1

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean	SD
1	400	6.47	6.42	6.48			6.46	0.03
	206	6.12	6.11				6.12	0.01
3	93	6.06	6.03	6.02	6.08	6.03	6.04	0.03
	251	6.06	6.05	6.13	6.11	6.12	6.09	0.04
	337	6.13	6.11	6.09	6.1	6.12	6.11	0.02
5	269	6.11	6.16				6.14	0.04
	393	6.03	6.12	6.15			6.10	0.06
6	112	6.26	6.2	6.19			6.22	0.04
	235	5.97	6.1				6.04	0.09
8	12	6.15	6.2	6.21	6.21	6.24	6.20	0.03
	215	6.23	6.21	6.21	6.22	6.22	6.22	0.01
9	2	6.12	6.13				6.13	0.01
	183	6.18	6.17	6.17			6.17	0.01
10	24	6.47	6.43	6.43	6.43	6.4	6.43	0.02
	311	6.5	6.44	6.43	6.44	6.48	6.46	0.03

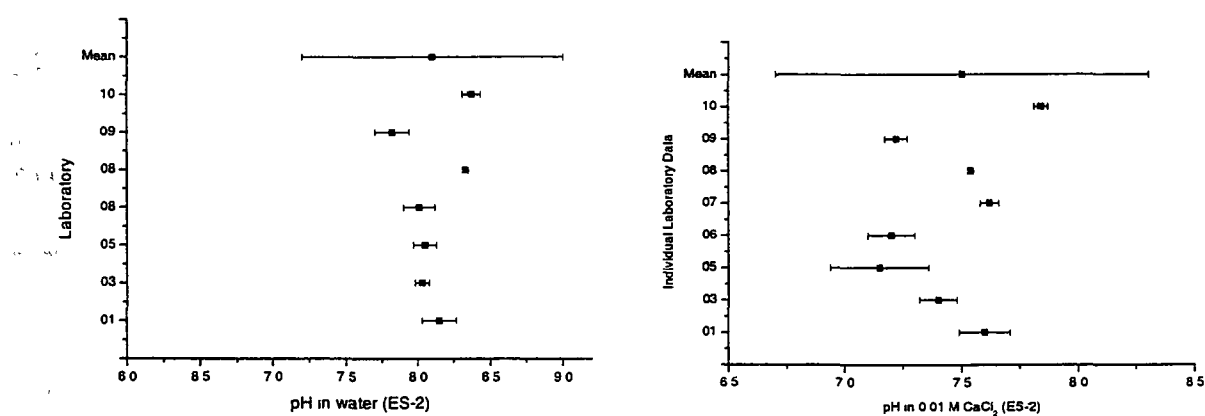


Figure 27 - Graphical comparison between laboratory means for pH in suspensions of water and 0.01M CaCl₂ for EUROSOIL 2 and the certified value ($\pm U_{CRM}$).

Table 22c - Individual laboratory data for pH in suspension of 0.01M CaCl₂ for EUROSIL 1

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean	SD
1	400	5.54	5.54	5.81			5.63	0.16
	206	5.85	5.8				5.83	0.04
3	93	5.49	5.52	5.47	5.52	5.44	5.49	0.03
	251	5.57	5.59	5.61	5.53	5.54	5.57	0.03
	337	5.55	5.47	5.6	5.54	5.53	5.54	0.05
5	269	5.51	5.37				5.44	0.10
	393	5.53	5.61	5.71			5.62	0.09
6	112	5.46	5.53	5.68			5.56	0.11
	235	5.42	5.54				5.48	0.08
7	345	5.75	5.76	5.77	5.77	5.77	5.76	0.01
	289	5.73	5.71	5.71	5.78	5.84	5.75	0.06
8	12	5.66	5.67	5.67	5.72	5.66	5.68	0.03
	215	5.67	5.64	5.67	5.66	5.67	5.66	0.01
9	2	5.64	5.64				5.64	0.00
	183	5.66	5.65	5.64			5.65	0.01
10	24	5.83	5.82	5.83	5.84	5.82	5.83	0.01
	311	5.83	5.84	5.84	5.84	5.84	5.84	0.00

Table 23b - Individual laboratory data for pH in suspension of water for EUROSIL 2

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean	SD
1	111	8.22	8.25	8.25			8.24	0.02
	289	8.02	8.03				8.03	0.01
3	18	8.04	8.07	7.97	8.09	8.06	8.05	0.05
	143	8.04	8.03	7.93	8.02	8.04	8.01	0.05
	247	8.1	8.09	8.13	8.08	8.11	8.10	0.02
5	3	8.02	7.98				8.00	0.03
	294	7.99	8.14	8.14			8.09	0.09
6	101	8.05	8.07	8.07			8.06	0.01
	195	7.82	8.03				7.93	0.15
8	73	8.33	8.33	8.35	8.33	8.32	8.33	0.01
	223	8.28	8.33	8.32	8.35	8.33	8.32	0.03
9	42	7.61	7.84				7.73	0.16
	89	7.86	7.89	7.92			7.89	0.03
10	162	8.43	8.46				8.45	0.02
	266	8.31	8.32	8.38	8.38	8.29	8.34	0.04

Table 23c - Individual laboratory data for pH in suspension of 0.01M CaCl₂ for EUROSIL 2

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean	SD
1	111	7.43	7.57	7.64			7.55	0.11
	289	7.72	7.63				7.68	0.06
3	18	7.37	7.41	7.43	7.39	7.36	7.39	0.03
	143	7.27	7.31	7.34	7.29	7.33	7.31	0.03
	247	7.48	7.47	7.51	7.5	7.52	7.50	0.02
5	3	7.21	7.39				7.30	0.13
	294	7.16	6.81	7.19			7.05	0.21
6	101	7.11	7.17	7.29			7.19	0.09
	195	7.12	7.32				7.22	0.14
7	274	7.65	7.6	7.67	7.64	7.67	7.65	0.03
	62	7.62	7.58	7.63	7.61	7.56	7.60	0.03
8	73	7.54	7.55	7.54	7.54	7.54	7.54	0.00
	223	7.52	7.54	7.54	7.55	7.54	7.54	0.01
9	42	7.17	7.29				7.23	0.08
	89	7.16	7.21	7.25			7.21	0.05
10	162	7.88	7.88				7.88	0.00
	266	7.83	7.83	7.83	7.83	7.82	7.83	0.00

Table 24b - Individual laboratory data for pH in suspension of water for EUROSIL 3

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean	SD
1	88	5.94	5.92				5.93	0.01
	269	6.17	6.25	6.27			6.23	0.05
3	3	5.96	6.04	6.01	6.04	6	6.01	0.03
	123	6	5.91	5.89	5.93	5.88	5.92	0.05
	403	5.88	5.92	5.97	5.91	5.92	5.92	0.03
5	61	6.48	6.38	6.31			6.39	0.09
	275	6.61	6.31				6.46	0.21
6	49	5.96	6.16	6.07			6.06	0.10
	352	6.52	6.46				6.49	0.04
8	103	6.12	6.16	6.13	6.11	6.13	6.13	0.02
	378	6.35	6.2	6.4	6.14	6.13	6.24	0.12
9	27	6.17	6.15	6.12			6.15	0.03
	142	6.36	6.16				6.26	0.14
10	202	6.29	6.25	6.26	6.26	6.27	6.27	0.02
	337	6.2	6.22	6.23	6.24	6.23	6.22	0.02

Table 24c - Individual laboratory data for pH in suspension of 0.01M CaCl₂ for EUROSOIL 3

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean	SD
1	88	5.58	5.62				5.60	0.03
	269	5.5	5.4	5.38			5.43	0.06
3	3	5.36	5.33	5.34	5.3	5.31	5.33	0.02
	123	5.31	5.33	5.29	5.3	5.28	5.30	0.02
	403	5.3	5.32	5.29	5.25	5.27	5.29	0.03
5	61	5.8	5.41	5.61			5.61	0.20
	275	5.81	5.63				5.72	0.13
6	49	5.76	5.54	5.46			5.59	0.16
	352	6.31	6.07				6.19	0.17
7	13	5.77	5.52	5.53	5.47	5.49	5.56	0.12
	291	5.56	5.45	5.42	5.47	5.45	5.47	0.05
8	103	5.39	5.38	5.38	5.37	5.38	5.38	0.01
	378	5.65	5.49	5.43	5.42	5.4	5.48	0.10
9	27	5.66	5.55	5.48			5.56	0.09
	142	5.67	5.55				5.61	0.08
10	202	5.54	5.55	5.54	5.54	5.54	5.54	0.00
	337	5.51	5.51	5.51	5.51	5.51	5.51	0.00

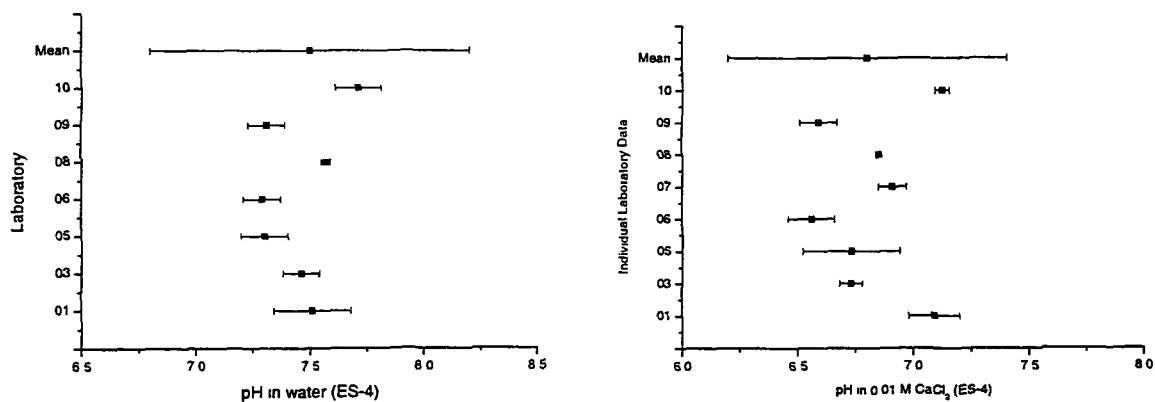


Figure 28 - Graphical comparison between laboratory means for pH in suspensions of water and 0.01M CaCl₂ for EUROSOIL 4 and the certified value ($\pm U_{CRM}$).

Table 25b - Individual laboratory data for pH in suspension of water for EUROSIL 4

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean	SD
1	484	7.35	7.3				7.33	0.04
	566	7.61	7.66	7.63			7.63	0.03
3	261	7.56	7.54	7.5	7.53	7.52	7.53	0.02
	473	7.38	7.36	7.41	7.39	7.42	7.39	0.02
	612	7.32	7.39	7.38	7.32	7.27	7.34	0.05
5	391	7.16	7.31				7.24	0.11
	637	7.25	7.38	7.4			7.34	0.08
6	249	7.26	7.29				7.28	0.02
	583	7.17	7.35	7.39			7.30	0.12
8	461	7.6	7.59	7.58	7.57	7.59	7.59	0.01
	631	7.53	7.53	7.58	7.58	7.57	7.56	0.03
9	274	7.36	7.37	7.37			7.37	0.01
	622	7.2	7.26				7.23	0.04
10	317	7.59	7.63	7.61	7.63	7.62	7.62	0.02
	515	7.79	7.8	7.82	7.82	7.83	7.81	0.02

Table 25c - Individual laboratory data for pH in suspension of 0.01M CaCl₂ for EUROSIL 4

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean	SD
1	484	6.98	7.03				7.01	0.04
	566	7.07	7.12	7.27			7.15	0.10
3	261	6.77	6.78	6.82	6.8	6.83	6.80	0.03
	473	6.68	6.71	6.73	6.7	6.71	6.71	0.02
	612	6.7	6.72	6.71	6.64	6.7	6.69	0.03
5	391	6.41	6.84				6.63	0.30
	637	6.61	6.86	6.91			6.79	0.16
6	249	6.58	6.68				6.63	0.07
	583	6.39	6.58	6.56			6.51	0.10
7	576	6.9	6.94	6.97	6.97	6.93	6.94	0.03
	283	6.84	6.95	6.96	6.83	6.84	6.88	0.07
8	461	6.86	6.85	6.82	6.83	6.84	6.84	0.02
	631	6.84	6.85	6.85	6.86	6.85	6.85	0.01
9	274	6.61	6.64	6.67			6.64	0.03
	622	6.48	6.54				6.51	0.04
10	317	7.08	7.09	7.09	7.09	7.09	7.09	0.00
	515	7.16	7.16	7.15	7.14	7.13	7.15	0.01

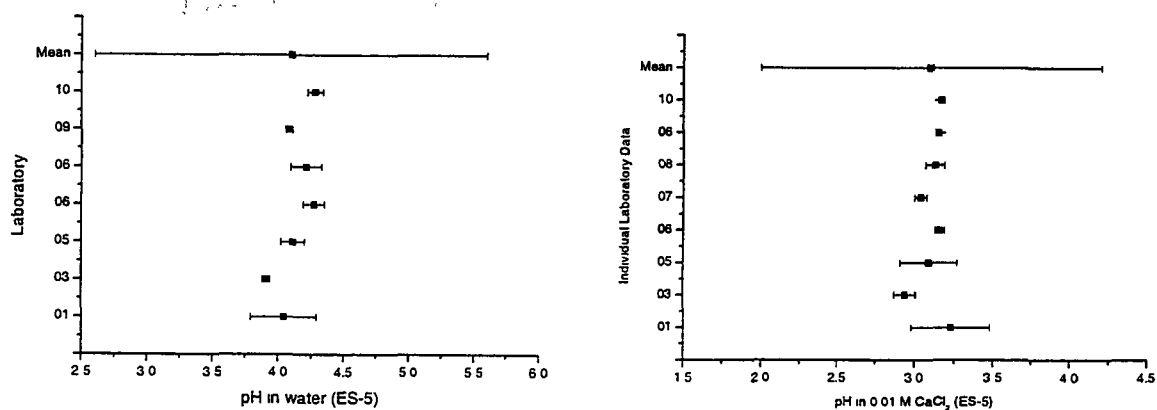


Figure 29 - Graphical comparison between laboratory means for pH in suspensions of water and 0.01M CaCl₂ for EUROSOIL 5 and the certified value ($\pm U_{CRM}$).

Table 26b - Individual laboratory data for pH in suspension of water for EUROSOIL 5

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean	SD
1	128	4.16	4.25	4.26			4.22	0.06
	283	3.75	3.79				3.77	0.03
3	48	3.91	3.9	3.93	3.89	3.88	3.90	0.02
	270	3.92	3.9	3.98	3.91	3.92	3.93	0.03
	417	3.93	3.97	3.98	3.92	3.9	3.94	0.03
5	149	4.21	4.01				4.11	0.14
	235	4.1	4.04	4.18			4.11	0.07
6	264	4.39	4.24	4.2			4.28	0.10
	363	4.3	4.23				4.27	0.05
8	161	4.29	4.36	4.29	4.04	4.31	4.26	0.13
	384	3.96	4.2	4.22	4.21	4.2	4.16	0.11
9	39	4.12	4.09				4.11	0.02
	396	4.08	4.05	4.04			4.06	0.02
10	103	4.22	4.26	4.24	4.22	4.21	4.23	0.02
	292	4.36	4.33	4.34	4.3	4.3	4.33	0.03

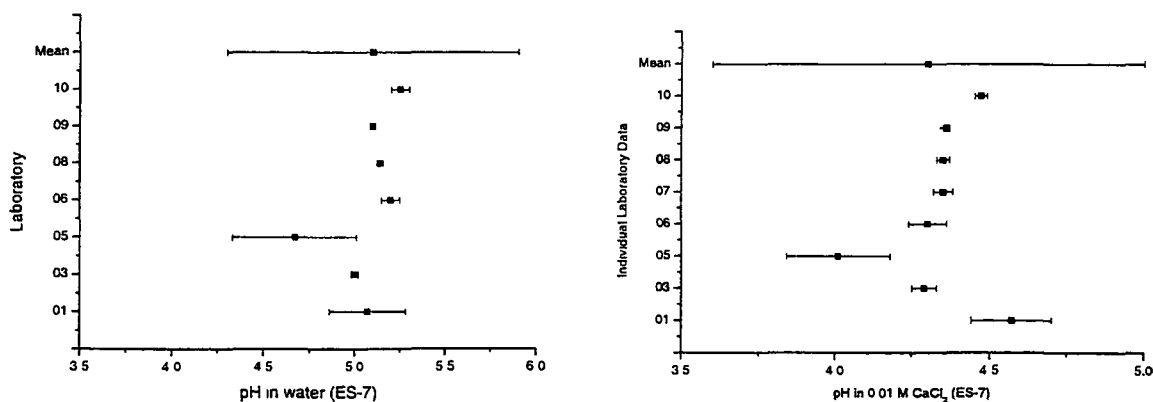


Figure 30 - Graphical comparison between laboratory means for pH in suspensions of water and 0.01M CaCl₂ for EUROSOIL 7 and the certified value ($\pm U_{CRM}$).

Table 26c - Individual laboratory data for pH in suspension of 0.01M CaCl₂ for EUROSIL 5

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean	SD
1	128	3.05	3.5	3.5			3.35	0.26
	283	3.02	3.06				3.04	0.03
3	48	2.88	2.86	2.91	2.9	2.83	2.88	0.03
	270	2.88	3.03	2.92	2.9	3.01	2.95	0.07
	417	3.03	3	3.01	2.99	3	3.01	0.02
5	149	3.38	3.11				3.25	0.19
	235	2.91	2.97	3.06			2.98	0.08
6	264	3.17	3.14	3.13			3.15	0.02
	363	3.19	3.18				3.19	0.01
7	374	3.03	3	3.03	3.02	3	3.02	0.02
	121	3.13	3.02	3.06	3.05	3.05	3.06	0.04
8	161	3.2	3.08	3.18	3.06	3.2	3.14	0.07
	384	3.13	3.07	3.17	3.06	3.15	3.12	0.05
9	39	3.17	3.16				3.17	0.01
	396	3.14	3.13	3.14			3.14	0.01
10	103	3.16	3.17	3.16	3.14	3.16	3.16	0.01
	292	3.2	3.19	3.16	3.17	3.17	3.18	0.02

Table 27b - Individual laboratory data for pH in suspension of water for EUROSIL 7

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean	SD
1	339	4.87	4.81				4.84	0.04
	48	5.16	5.24	5.27			5.22	0.06
3	95	5.01	4.98	5.03	5.01	4.97	5.00	0.02
	277	5	5.02	5.04	4.99	4.97	5.00	0.03
	418	4.99	4.98	5	5.01	4.98	4.99	0.01
5	82	4.44	4.36	4.81			4.54	0.24
	472	4.54	5.19				4.87	0.46
6	15	5.17	5.18	5.2			5.18	0.02
	398	5.17	5.28				5.23	0.08
8	55	5.15	5.14	5.13	5.17	5.16	5.15	0.02
	352	5.15	5.13	5.14	5.13	5.13	5.14	0.01
9	71	5.11	5.08				5.10	0.02
	451	5.12	5.1	5.1			5.11	0.01
10	33	5.16	5.21				5.19	0.04
	359	5.28	5.27	5.25	5.27	5.28	5.27	0.01

Table 27c - Individual laboratory data for pH in suspension of 0.01M CaCl₂ for EUROSOIL 7

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean	SD
1	339	4.54	4.54				4.54	0.00
	48	4.4	4.61	4.75			4.59	0.18
3	95	4.22	4.26	4.21	4.26	4.28	4.25	0.03
	277	4.31	4.32	4.29	4.3	4.28	4.30	0.02
	418	4.33	4.31	4.32	4.31	4.29	4.31	0.01
5	82	3.81	3.87	3.99			3.89	0.09
	472	4.17	4.19				4.18	0.01
6	15	4.22	4.29	4.34			4.28	0.06
	398	4.29	4.37				4.33	0.06
7	384	4.35	4.33	4.39	4.4	4.37	4.37	0.03
	63	4.34	4.33	4.34	4.33	4.33	4.33	0.01
8	55	4.33	4.34	4.34	4.35	4.35	4.34	0.01
	352	4.34	4.35	4.39	4.36	4.36	4.36	0.02
9	71	4.36	4.37				4.37	0.01
	451	4.35	4.36	4.37			4.36	0.01
10	33	4.46	4.44				4.45	0.01
	359	4.47	4.48	4.48	4.49	4.49	4.48	0.01

Table 55a – Individual data for the determination of total carbon content in EUROSOIL 1

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	206	34.63	33.24	32.85		33.57	0.94
	400	35.69	34.58	34.37		34.88	0.71
3	93	33.5	33.1	32.5	33.4	33.13	0.45
	241	37.2	34.3	35.6	36	35.78	1.20
	337	35.4	35.3	36	35.1	35.45	0.39
6	112	32.45	32.75	32.53	32.45	32.55	0.14

Table 28b - – Individual data for the determination of organic carbon content in EUROSOIL 1

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	206	25.9	27.2	27.5		26.87	0.85
	400	25.9	27.9	30.4		28.07	2.25
3a	93	33.4	33.1	32.9	33	33.10	0.22
	251	34.4	37.1	36.3	35.8	35.90	1.13
	337	35.4	35.9	35.2	35.7	35.55	0.31
3b	93	33.1	32.4	33.5	33.3	33.08	0.48
	251	34.5	36.9	36.1	35.6	35.78	1.00
	337	35.6	36	35.5	35.4	35.63	0.26
6	112	32.07	32.13	32.56	37.34	33.53	2.55

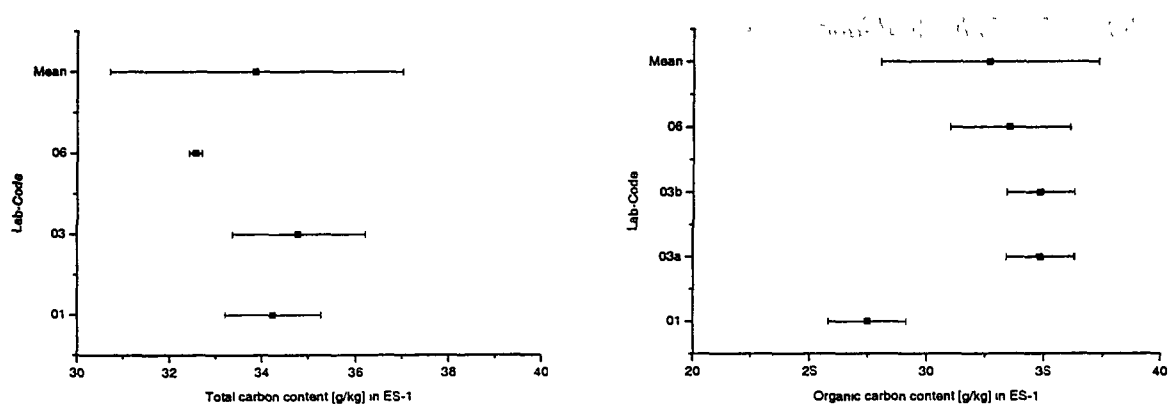


Figure 31 - Graphical comparison between laboratory means for C_{tot} and C_{org} for EUROSOIL 1 and the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 56 a – Individual data for the determination of total carbon content in EUROSOIL 2

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	111	114.97	114.42	115.25		114.88	0.42
	289	114.57	114.26	113.85		114.23	0.36
3	18	107.9	110.2	106	110.5	108.65	2.11
	143	107.4	107.6	107.2	108.5	107.68	0.57
	106.7	109.4	109.1	106.2		108.23	1.77
6	101	101.07	101.67	101.4	101.46	101.40	0.25

Table 29b - - Individual data for the determination of organic carbon content in EUROSOIL 2

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	111	33.2	36.3	42.6		37.37	4.79
	289	32.6	34.7	37.7		35.00	2.56
3a	18	33.7	34.2	34.3	32.9	33.78	0.64
	143	32.9	34	33.6	32.8	33.33	0.57
	247	32.9	32.2	33.2	32.6	32.73	0.43
	18	44.5	39.2	39.1	43.9	41.68	2.93
3b	143	39.7	38.3	40.1	38.8	39.23	0.82
	247	39.3	40.3	39	39.5	39.53	0.56
6	101	38.43	42.36	38.47	38.16	39.36	2.01

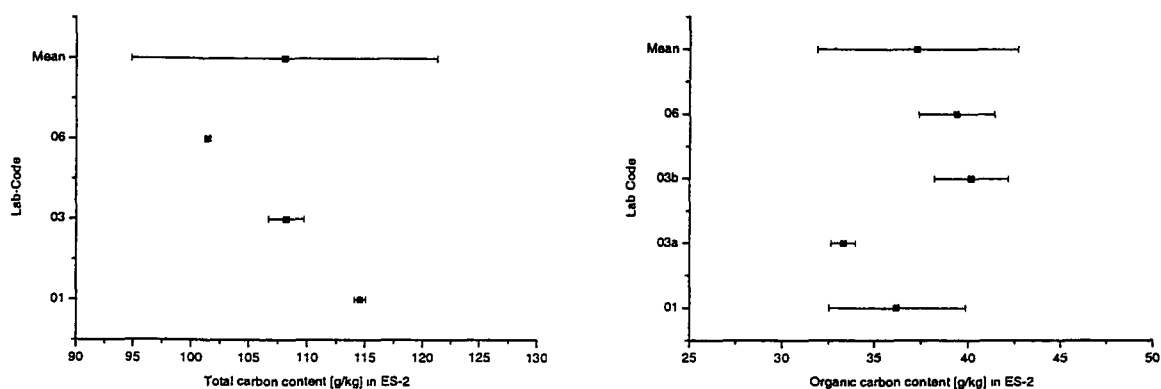


Figure 32 - Graphical comparison between laboratory means for C_{tot} and C_{org} for EUROSOIL 2 and the the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 57 a – Individual data for the determination of total carbon content in EUROSOIL 3

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	88	35.56	35.42	35.24		35.41	0.16
	269	33.18	32.7	32.02		32.63	0.58
3	3	29.8	30.4	29	30.2	29.85	0.62
	123	32.6	33.2	34.8	34.8	33.85	1.12
	403	29.6	27.9	28.6	27.1	28.30	1.06
6	49	32.51	32.34	32.89	32.89	32.66	0.28

Table 30b - - Individual data for the determination of organic carbon content in EUROSOIL 3

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	88	27.2	27.8	28.2		27.73	0.50
	269	27	26.8	25.4		26.40	0.87
3a	3	30.3	29.9	30.1	29	29.83	0.57
	123	34.7	33.5	33.6	33.9	33.93	0.54
	403	27.2	28.5	27.5	28.9	28.03	0.81
3b	3	29.9	30.3	30	29.8	30.00	0.22
	123	33.7	34.6	33.6	32.9	33.70	0.70
	403	28.3	27.5	27.9	28.9	28.15	0.60
6	49	32.43	32.07	32.11		32.20	0.20

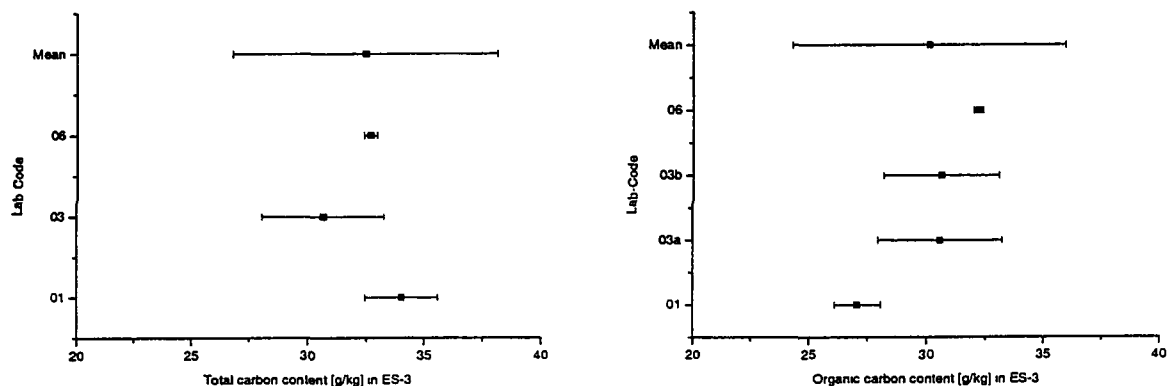


Figure 33 - Graphical comparison between laboratory means for C_{tot} and C_{org} for EUROSOIL 3 and the the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 58 a -- Individual data for the determination of total carbon content in EUROSOIL 4

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	484	15.42	15.46	15.23		15.37	0.12
	566	15.21	15.44	15.62		15.42	0.21
3	261	14.1	13.7	13.8	13.9	13.88	0.17
	473	14.1	13.6	14.4	13.6	13.93	0.39
	612	14.3	14.5	13.8	13.2	13.95	0.58
6	583	14.29	14.11	14.08	14.07	14.14	0.10

Table 31b -- Individual data for the determination of organic carbon content in EUROSOIL 4

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	484	11.8	12	11.9		11.90	0.10
	566	9.8	10.2	10.3		10.10	0.26
3a	261	13.6	13.9	14	13.9	13.85	0.17
	473	13.7	14.2	14.1	13.6	13.90	0.29
	612	13.7	14.4	14.2	13.9	14.05	0.31
3b	261	13.9	14	13.8	13.7	13.85	0.13
	473	13.8	14.1	13.7	14.2	13.95	0.24
	612	14.2	13.8	13.9	14.1	14.00	0.18
6	583	13.36	13.49	13.38	13.22	13.36	0.11

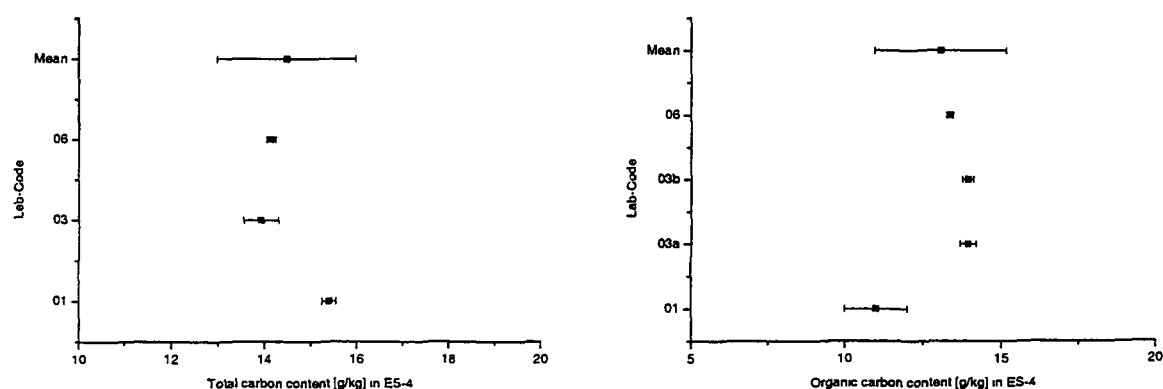


Figure 34 - Graphical comparison between laboratory means for C_{tot} and C_{org} for EUROSOIL 4 and the the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 59 a – Individual data for the determination of total carbon content in EUROSOIL 5

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	128	67.47	72.13	89.1		76.23	11.38
	283	71.15	79.26	63.54		71.32	7.86
3	48	65	63.2	62.1	68.2	64.63	2.67
	270	48.2	48.9	49.3	48.9	48.83	0.46
	417	68.1	69.1	66.2	66.9	67.58	1.28
6	264	60.68	59.53	57.6	56.8	58.65	1.77

Table 32b - - Individual data for the determination of organic carbon content in EUROSOIL 5

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	128	56.7	58.9	61.3		58.97	2.30
	283	64.3	57.1	65		62.13	4.37
3a	48	62.5	64.8	63.6	67	64.48	1.93
	270	48.8	48.4	49	48.9	48.78	0.26
	417	66.9	68.2	68.3	67.8	67.80	0.64
3b	48	64.2	64.8	64.5	65.2	64.68	0.43
	270	48.9	49.1	48.7	48.5	48.80	0.26
	417	68.3	67.4	68.4	67.5	67.90	0.52
6	264	59.68	58.15	55.07	55.75	57.16	2.14

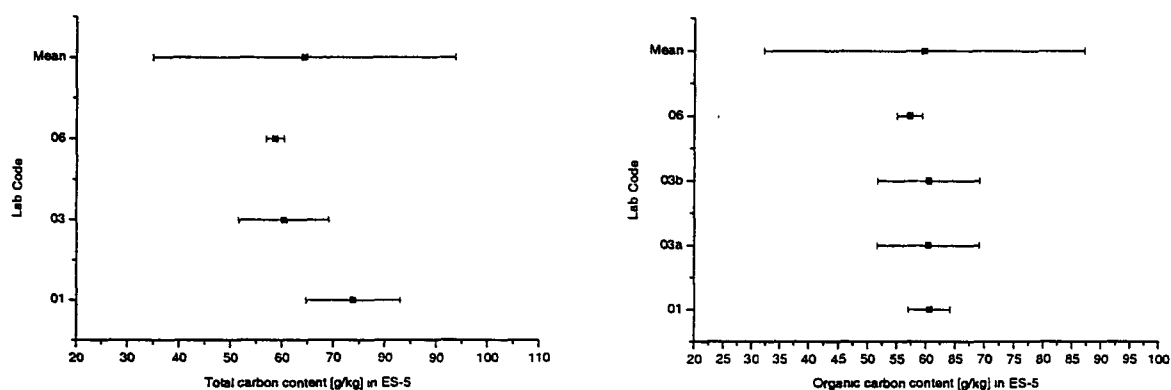


Figure 35 - Graphical comparison between laboratory means for C_{tot} and C_{org} for EUROSOIL 5 and the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 60 a – Individual data for the determination of total carbon content in EUROSOIL 7

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	339	54.52	55.22	54.52		54.75	0.40
	48	61.48	56.69	55.22		57.80	3.27
3	95	69.3	71.1	69.8	69.1	69.83	0.90
	277	65	65	65.2	65.6	65.20	0.28
	418	65.8	67.9	68	65.3	66.75	1.40
6	15	52.4	52.61	52.78	52.65	52.61	0.16

Table 33b - - Individual data for the determination of organic carbon content in EUROSOIL 7

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	339	41.7	40.4	43.5		41.87	1.56
	48	46	43.9	45.9		45.27	1.18
3a	95	66.6	66.5	66.7	66.6	66.60	0.08
	277	62.6	61.4	63.9	64.3	63.05	1.32
	418	62.4	62	61.8	61.4	61.90	0.42
3b	95	70.6	69.2	68.9	69.5	69.55	0.74
	277	65.2	65	64.6	65.1	64.98	0.26
	418	66.1	66.5	67.9	65.9	66.60	0.90
6	15	49.99	49.93	50.73	50.52	50.29	0.39

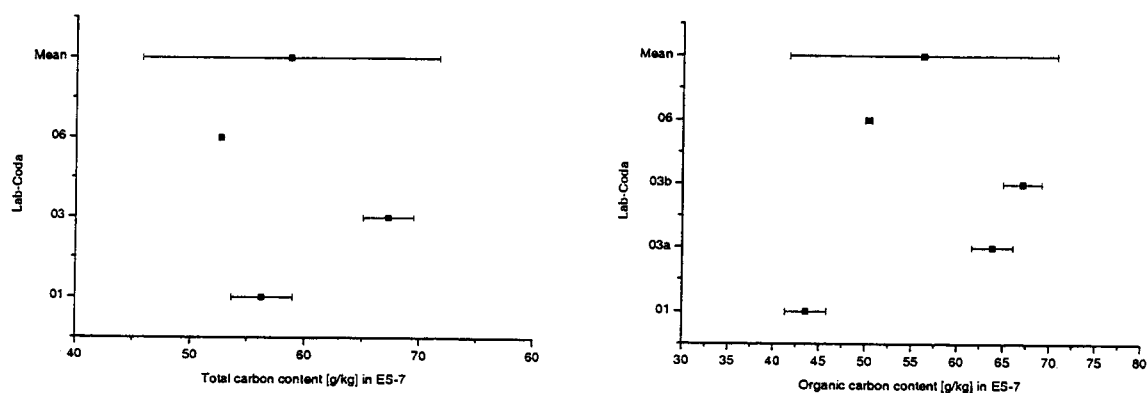


Figure 36 - Graphical comparison between laboratory means for C_{tot} and C_{org} for EUROSOIL 7 and the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 61 – Individual data for the determination of total nitrogen content (N_{tot}) of EUROSOIL 1

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	206	3.85	3.36	3.48		3.56	0.26
	400	3.62	3.62	3.6		3.61	0.01
3	93	3.4	3.3	3.5	3.7	3.48	0.17
	251	2.9	2.6	2.5	3	2.75	0.24
	337	2.5	2.4	2.8	2.9	2.65	0.24
6	112	3.61	3.66	3.64	3.63	3.64	0.02

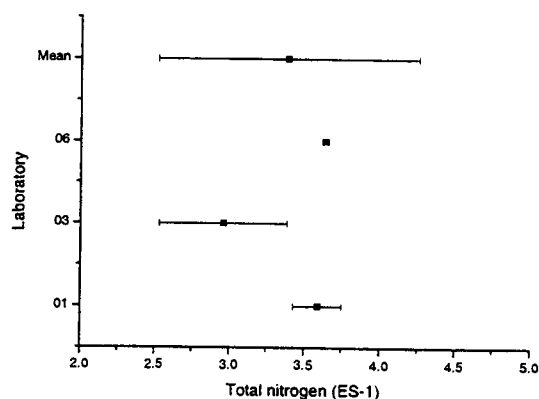


Figure 37 - Graphical comparison between laboratory means for N_{tot} for EUROSOIL 1 and the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 62 - Individual data for the determination of total nitrogen content (N_{tot}) of EUROSOIL 2

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	111	2.82	2.99	3.03		2.95	0.11
	289	2.94	2.92	2.98		2.95	0.03
3	18	2.4	2.5	2.3	2.4	2.40	0.08
	143	1.8	1.9	1.7	2	1.85	0.13
	247	1.7	2	1.6	1.8	1.78	0.17
6	101	2.5	2.54	2.53	2.54	2.53	0.02

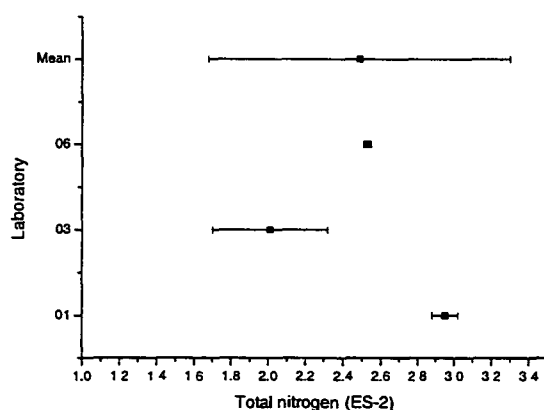


Figure 38 - Graphical comparison between laboratory means for N_{tot} for EUROSOIL 2 and the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 63 - Individual data for the determination of total nitrogen content (N_{tot}) of EUROSOIL 3

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	88	3.69	3.58	3.57		3.61	0.07
	269	3.4	3.33	3.28		3.34	0.06
3	3	2.3	2.4	2.4	2.2	2.33	0.10
	123	2.4	2.2	2.7	2.7	2.50	0.24
	403	2.3	2.2	2.6	2.1	2.30	0.22
6	49	3.28	3.31	3.29	3.29	3.29	0.01

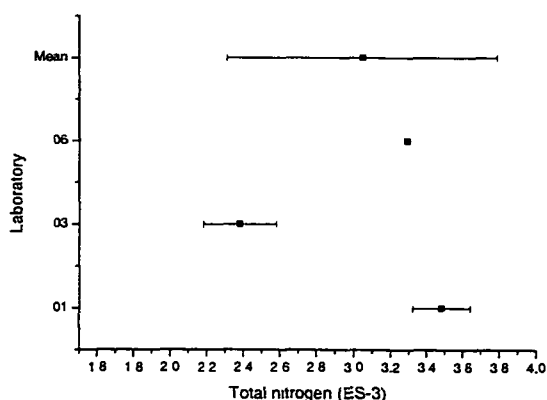


Figure 39 - Graphical comparison between laboratory means for N_{tot} for EUROSOIL 3 and the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 64 - Individual data for the determination of total nitrogen content (N_{tot}) of EUROSOIL 4

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	484	1.86	1.83	1.81		1.83	0.03
	566	1.87	1.82	1.8		1.83	0.04
3	261	1	1.1	1	1.2	1.08	0.10
	473	1.2	1.2	1.4	1.2	1.25	0.10
	612	1.1	1.1	1.1	1	1.08	0.05
6	583	1.67	1.71	1.65	1.72	1.69	0.03

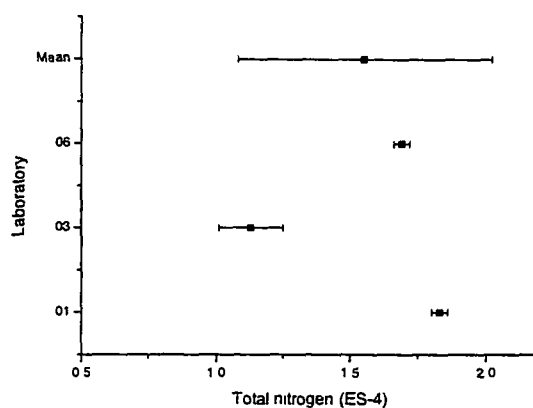


Figure 40 - Graphical comparison between laboratory means for N_{tot} for EUROSOIL 4 the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 65 - Individual data for the determination of total nitrogen content (N_{tot}) of EUROSOIL 5

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	128	3.09	3.07	3.96		3.37	0.51
	283	3.06	3.32	3.02		3.13	0.16
3	48	1.7	1.5	1.6	1.8	1.65	0.13
	270	1.5	1.3	1.5	1.4	1.43	0.10
	417	1.6	1.6	1.6	1.7	1.63	0.05
6	264	2.25	2.19	2.15	2.19	2.20	0.04

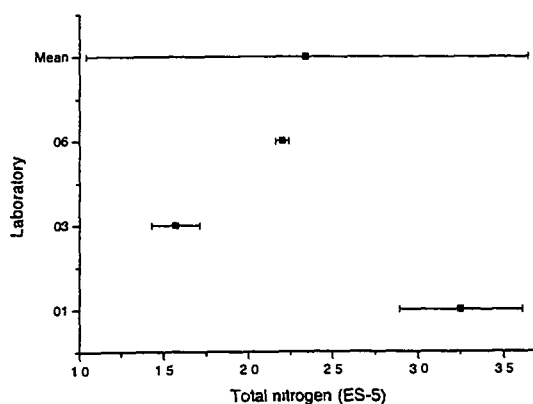


Figure 41 - Graphical comparison between laboratory means for N_{tot} for EUROSOIL 5 and the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

Table 66 - Individual data for the determination of total nitrogen content (N_{tot}) of EUROSOIL 7

Lab-Code	Bottle	Trial 1	Trial 2	Trial 3	Trial 4	Mean	SD
1	48	5.47	4.92	4.85		5.08	0.34
	339	4.9	4.92	5		4.94	0.05
3	95	4.7	5	5.1	4.8	4.90	0.18
	277	4.7	4.3	5	4.9	4.73	0.31
	418	4.3	4.5	4.6	4.7	4.53	0.17
6	15	4.4	4.61	4.62	4.66	4.57	0.12

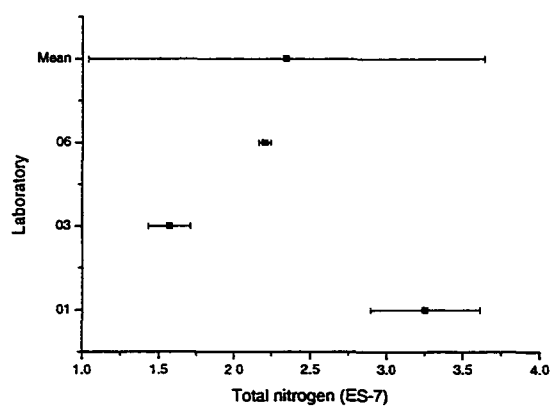


Figure 42 - Graphical comparison between laboratory means for N_{tot} for EUROSOIL 7 and the uncertified mean value ($\pm$ expanded uncertainty $k=2$).

13. ANNEX III – TABLES OF METHODS

Table 67 – Table of methods for adsorption experiments with atrazine

<i>Laboratory</i>	<i>Experimental</i>	<i>Analytical method</i>
Lab1	2g of soil, 10 mL of solution added, glass vessels, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Origin of Standard not stated.
Lab 2	2g of soil, 10 mL of solution added, glass vessels, indirect approach with unlabelled compound	Extraction by SPE (Endcapped C-18 columns), Internal standard was 10µg/mL simazine. Detection by LC/MS/MS
Lab 4	5g of soil, 25 mL of solution added, glass vessels, indirect approach with unlabelled compound	GC-NPD-Detection, column not specified, Standards provided by IRMM was used (> 99%).
Lab 5	4g of soil, 20 mL of solution added, glass vessels, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Standard provided by supplier of instrument was used.
Lab 6	10g of soil, 50 mL of solution added, glass vessels with ground-in stopper (80 mL), indirect approach with unlabelled compound	Dilution of sample with analytical-grade methanol, SPE (C18), HPLC-DAD with isocratic elution (35% H ₂ O with 65% MeOH, Column OPTILAB Hypersil MOS - C8, 250 x 4.6 mm), detection at 221 nm, standard from Riedel-de-Haen PESTANAL® (>99%)
Lab 7	4g of soil, 20 mL of solution added, glass vessels, indirect approach with unlabelled compound	HPLC-DAD with isocratic elution (45% H ₂ O with 55% Acetonitrile, Pre-column C8 (20 x 2.1 mm) and Column C8 (100 x 2.1 mm), detection at 221 and 228 nm, standard provided by IRMM was used (> 99%)
Lab 8	5g of soil, 25 mL of solution added, PTFE centrifuge tubes with screw cap, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Standard provided by Institute of Isotopes Co (Budapest) (> 95%).
Lab 9	5g of soil, 25 mL of solution added, glass vessel with PE-cap, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Standard provided by SIGMA-ALDRICH (Saint-Louis, USA) (98.1%). Stability and identity of test-substance were checked by HPLC-Radio/UV detection
Lab 10	5g of soil, 25 mL of solution added, PP-copolymer vessels with screw-cap, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Standard provided by SIGMA-ALDRICH (Saint-Louis, USA) (98.88 %). Quench correction curves generated by counting quenched standards from Packard Biosciences Berkshire, England.

Table 68 - Table of methods for adsorption experiments with 2,4-D

<i>Laboratory</i>	<i>Experimental</i>	<i>Detection</i>
Lab1	2g of soil, 10 mL of solution added, glass vessels, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Origin of Standard not stated.
Lab 2	2g of soil, 10 mL of solution added, glass vessels, indirect approach with unlabelled compound	Extraction by SPE (Endcapped C-18 columns), Internal standard was 10µg/mL MCPA. Detection by LC/MS/MS
Lab 4	5g of soil, 25 mL of solution added, glass vessels, indirect approach with unlabelled compound	HPLC-UV, column not specified, Standards provided by IRMM was used (>99%).
Lab 5	4g of soil, 20 mL of solution added, glass vessels, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Standard provided by supplier of instrument was used.

Laboratory	Experimental	Detection
Lab 6	10g of soil, 50 mL of solution added, glass vessels with ground-in stopper (80 mL), indirect approach with unlabelled compound	Dilution of sample with analytical-grade methanol, SPE (Bakerbond C18) for low concentrations, HPLC-DAD with gradient elution (0.05M H ₃ PO ₄ and Acetonitrile, Column OPTILAB Hypersil MOS - C8, 250 x 4.6 mm), detection at 208 nm, standard from ACROS Organics (99+ %)
Lab 7	4g of soil, 20 mL of solution added, glass vessels, indirect approach with unlabelled compound	HPLC-DAD with isocratic elution (50% 0.05M H ₃ PO ₄ with 50% Acetonitrile, Column SymmetryShield™ TP-8 of 5μm (150 x 2.1 mm), detection at 205 and 229 nm, standard provided by IRMM was used (>99 %)
Lab 8	5g of soil, 25 mL of solution added, PTFE centrifuge tubes with screw cap, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Standard provided by Institute of Isotopes Co (Budapest) (> 95%).
Lab 9	5g of soil, 25 mL of solution added, glass vessel with PE-cap, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Standard provided by SIGMA-ALDRICH (Saint-Louis, USA) (99.0%). Stability and identity of test-substance were checked by HPLC-Radio/UV detection
Lab 10	5g of soil, 25 mL of solution added, PP-copolymer vessels with screw-cap, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Standard provided by SIGMA-ALDRICH (Saint-Louis, USA) (≥ 98 %). Quench correction curves generated by counting quenched standards from Packard Biosciences Berkshire, England.

Table 69- Table of methods for adsorption experiments with lindane

Laboratory	Experimental	Detection
Lab1	2g of soil, 10 mL of solution added, glass vessels, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Origin of Standard not stated.
Lab 2	2g of soil, 10 mL of solution added, glass vessels, indirect approach with unlabelled compound	Liquid-Liquid-Extraction with 1mL n-hexane, Internal standard was δ-HCH (0.1 ng/μL). Detection by GC/MS in SIM-Mode
Lab 5	4g of soil, 20 mL of solution added, glass vessels, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Standard provided by supplier of instrument was used.
Lab 6	10g of soil, 50 mL of solution added, glass vessels with ground-in stopper (80 mL), indirect approach with unlabelled compound	Liquid-Liquid-Extraction with 1-5 mL n-hexane, Internal standard was hexachlorobenzene (0.5 ng/μL). Detection by GC/ECD (splitless injection)
Lab 8	5g of soil, 25 mL of solution added, PTFE centrifuge tubes with screw cap, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Standard provided by Institute of Isotopes Co (Budapest) (> 95%).
Lab 10	5g of soil, 25 mL of solution added, PP-copolymer vessels with screw-cap, indirect approach with radio-labelled compound	Liquid Scintillation Counting (LSC); Standard provided by SIGMA-ALDRICH (Saint-Louis, USA) (98.88 %). Quench correction curves generated by counting quenched standards from Packard Biosciences Berkshire, England.

Table 70 – Table of methods for pH-determinations

Laboratory	Instrument
Lab1	pH-meter HI 9321 (HANNA Instruments) Microprocessor, two point calibration (4.00 and 7.00)
Lab 3	pH-meter WTW 196 with an WTW SENTIX HW Electrode; two point calibration (4.00 and 7.00)

<i>Laboratory</i>	<i>Instrument</i>
Lab 5	Benchtop pH/ISE Meters, Model 710A from ORION with ROSS Combination Glass pH electrode; two point calibration (standards from ORION) at 4.01 and 7.00 or 7.00 and 10.01
Lab 6	WTW Microprocessor pH/ION Meter pMX 300 with WTW pH-Electrode SENTIX 61 combined with automatic temperature control WTW TFK 150; two point calibration (4.00 and 7.00 with MERCK pH-Set (buffer capsules)
Lab 7	pH-Meter CRISON micropH 2001 with respective electrode; two point calibration with instrument supplier provided standards at 7.02 and 4.00
Lab 8	pH-Meter Model 720 from ORION with ROSS Combination Glass pH electrode; two point calibration (standards from ORION) at 4.01 and 7.00
Lab 9	pH-Meter Schott Field Lab with a Schott Blue Line 24 Electrode; two point calibration (4.00 and 7.00) with Schott pH cal standards
Lab 10	WTW pH-Meter pH191 with WTW pH-Electrode SENTIX 8I; three point calibration (4.00, 7.00 and 9.20) with buffers supplied by Fisher Scientific

Table 71 - Table of methods for C_{lob} , C_{org} and N_{tot} -determinations

<i>Laboratory</i>	<i>C_{tot}</i>	<i>C_{org}</i>	<i>N_{tot}</i>
Lab1	Determination with CHN 1108 Carlo Erba at 1020°C calibration with 7-cyclohexanone-2,4-dinitrophenylhydrazone and hydroxy-8-quinolin	Device used was Carmograph 12 WOSTOFF operated at 950°C under oxygen; Removal of carbonates by adding HCl to the sample; calibration with precipitated calcium carbonate (12%)	Determination with CHN 1108 Carlo Erba at 1020°C calibration with 7-cyclohexanone-2,4-dinitrophenylhydrazone and hydroxy-8-quinolin
Lab 3	Device was Ströhlein C-MAT 550. Digestion by heating the sample in an oxygen atmosphere at 900C and determination of the released CO ₂ using IR-absorption; calibration with calcium carbonate (MERCK)	Device was Strohlein C-MAT 550. Removal of carbonates by adding HCl to the sample. Digestion by heating the sample in an oxygen atmosphere at 900C and determination of the released CO ₂ using IR-absorption; calibration with calcium carbonate (MERCK)	Device used was Büchi 430 Digestor with Büchi 321 Digestion Unit. Calibration was with sulfanic acid from FLUKA (> 98%) for digestion and ammonium sulphate from MERCK (>99.5%) for distillation. MERCK Kjeldahl tablets for Wieninger method were used.
Lab 6			

14. ANNEX IV – ADDITIONAL DATA

The following analyses were performed by the National Institute for Radiobiology and Radiohygiene, Budapest (HUN) and complete already large amount of information available on the EUROSOLS. In some cases, these data may be useful to understand the outcome of sorption experiments or pH-Measurements.

Table 72 - Effective CEC and exchangeable metal content of EUROSOLS measured according to ISO 11260. The analyses were performed on one randomly selected unit of each soil in three replicates.

IRMM-443	CEC		K_{ex}		Na_{ex}		Ca_{ex}		Mg_{ex}	
	(mmol/kg)		(mmol/kg)		(mmol/kg)		(mmol/kg)		(mmol/kg)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	283.2	3.0	15.5	0.2	13.6	3.9	165.1	3.2	73.9	5.9
2	286.8	5.1	3.7	0.3	2.6	0.3	342.9	8.1	9.9	0.2
3	90.3	14.9	6.7	0.3	2.1	1.0	59.1	3.2	16.0	1.4
4	159.0	5.8	4.7	0.5	1.9	0.6	154.7	0.7	6.1	0.3
5	61.2	5.1	u.d.		2.0	0.2	2.9	0.2	2.6	0.4
7	56.7	23.7	1.6	0.1	4.2	1.6	18.6	0.1	6.3	0.8

u.d. under detection limit

EUR 20152 EN –Certification of soil-pH (suspensions of water and CaCl₂) and adsorption coefficients for atrazine, 2,4-D and lindane in six different reference soils (EUROSOILS) IRMM-443

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Abstract

The Institute for Reference Materials and Measurements has characterised and certified a set of six European reference soils, the so-called EUROSOILS - under the number IRMM-443. This unique set reference soils has been originally designed by the former JRC Environment Institute (now Institute for Environment and Sustainability – IES). After a successful validation and trial period it was decided to transfer the project to IRMM in order to produce a new type of certified reference materials.

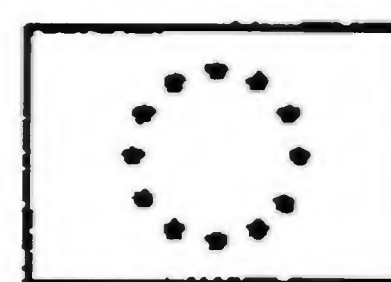
This report describes the certification of pH in suspensions of pure water and 0.01 M CaCl₂ as well as of the adsorption coefficients for atrazine, 2,4-D and lindane in these soils. Additionally, indicative values for the pedological parameters C_{tot} , C_{org} and N_{tot} are given. The adsorption coefficients were obtained according to the prescriptions made in the OECD Testguideline 106 whereas for the pedological parameters the respective ISO Standards were followed.

The certified values ($\pm$ expanded uncertainty U_{CRM} with a coverage factor $k=2$) are:

<i>Parameter</i>	<i>EUROSOIL 1</i>	<i>EUROSOIL 2</i>	<i>EUROSOIL 3</i>	<i>EUROSOIL 4</i>	<i>EUROSOIL 5</i>	<i>EUROSOIL 7</i>
K_f of atrazine	7.0 ± 1.5	2.7 ± 0.7	2.4 ± 0.7	0.7 ± 0.4	13 ± 6	4.8 ± 1.1
1/n of atrazine	0.91 ± 0.10	0.93 ± 0.12	0.91 ± 0.13	0.87 ± 0.22	0.9 ± 0.4	0.92 ± 0.15
K_f of 2,4-D	2.5 ± 1.0	0.99 ± 0.30	1.31 ± 0.28	0.39 ± 0.21	18 ± 7	8.2 ± 1.8
1/n of 2,4-D	0.9 ± 0.4	0.96 ± 0.15	0.93 ± 0.15	0.86 ± 0.31	0.9 ± 0.4	0.88 ± 0.15
K_f of lindane	*	48 ± 11	*	8.3 ± 2.2	*	*
1/n of lindane	*	0.98 ± 0.15	*	0.96 ± 0.12	*	*
pH in water	6.21 ± 0.30	8.1 ± 0.9	6.2 ± 0.4	7.5 ± 0.7	4.1 ± 1.5	5.1 ± 0.8
pH in 0.01 M CaCl ₂	5.65 ± 0.24	7.5 ± 0.8	5.5 ± 0.4	6.8 ± 0.6	3.1 ± 1.1	4.3 ± 0.7

The reference materials are intended to control and optimise the performance of adsorption testing, as well as to improve the measurement quality and comparability of pedological parameter measurements, especially in relations to the respective European legislation.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.



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